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Exploitation, Technology and Function of Plant Resin in Oceania:

Molecular Analysis of Ethnographic Museum Artefacts and the Implications for Archaeological Resin Analysis



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Abstract

Research Laboratory for Archaeology and the History of Art (RLAHA)
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by Fiona Bradshaw

Oceania has an extremely diverse and unique flora that includes many endemic species of restricted geographic range. This flora comprises coniferous, deciduous, and monocot plants and trees that include many resin-producing species. Plant resins have a long ethnobotanical history in Indigenous Oceania, as is recognised by some rare archaeological finds as well as a rich ethnographic record. In this study, gas chromatography-mass spectrometry (GC-MS) has been employed to chemically investigate resins of ethnobotanical importance in Oceania including Australia. A total of 173 samples of resinous material from ethnographic artefacts, currently held in museums, was analysed alongside botanically identified reference materials from in and aound the area. The aim was to both contribute to our understanding of the role of resins in Indigenous Oceania, and provide a framework for efficiently and effectively analysing valuable resinous archaeological finds from the region.

Four main types of resin were found to be regularly used in various regions of Oceania, namely conifer-type diterpenoid, non-conifer-type diterpenoid, triterpenoid and phenolic resins. A number of samples have been identified to source family, genus and in some cases species by comparison with authenticated resin samples collected from botanic gardens and herbariums. The results show that a much wider range of plant resins have been exploited in Oceania than has been generally recognised, particularly in reference to the descriptions of resin use in the ethnographic literature. The chemical characterisation of a range of resins including samples from three species that were previously unpublished has been presented. Also presented are the chromatographic profiles of ethnographically collected putative spinifex (*Triodia*) and northern ironwood (*Erythrophleum chlorostachys*) resins. The range of functions served by plant resins in Indigenous Oceania is discussed with an emphasis on both hafting and non-hafting uses.

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Abbreviations

WA	Western Australia
NT	Northern Territory, Australia
FN Qld	Far North Queensland, Australia
Qld	Queensland, Australia
NSW	New South Wales, Australia
Vic	Victoria, Australia
Tas	Tasmania
PNG	Papua New Guinea
RBG	Royal Botanic Garden(s)
BMBG	Blue Mountain Botanic Garden
ABG	Australian Botanic Garden
Kew EBC	Economic Botany Collection at RBG Kew
AM EB	Australian Museum Ethnobotany Collection
AM / AustMus	Australian Museum, Sydney, Australia
PBH	Peabody Museum of Archaeology and Ethnology at Harvard University, MA, USA
PRM	Pitt Rivers Museum, Oxford, UK
TRI	Timber Research Institute at Kuching, Sarawak, Malaysia (Borneo)
GC-MS	Gas chromatography-mass spectrometry
FTIR	Fourier transform infra-red spectroscopy
NIST	National Institute of Standards and Technology
ALA	Atlas of Living Australia
GBIF	Global Bioderversity Information Facility

Chapter 1

Introduction

1.1 Introduction

Resin is produced naturally by numerous species scattered throughout the plant kingdom (Langenheim; 2003). Plant exudates containing resin have properties that make them particularly useful materials, foremost, having thermoplastic, water-resistant and adhesive qualities as well as a pleasant aroma. Natural resins vary in fluidity from oleoresins through to hard copals, in colour from blacks, browns and reds through to yellows and almost white, and they present a multitude of characteristics in various amounts and combinations. Because of these properties, resins have been exploited for a number of purposes all over the world, and throughout the past. In some cases, resin production has been managed and increased through 'tapping' the trees, often for the resin to be sold commercially. Resin can be heated, separated and/or mixed with other components to form tars, pitches, rosin, paints and varnishes.

1.1.1 The significance of plant resin for archaeological investigation

Plant resin is an organic material exuded from a variety of certain trees and plants. Organic materials in general are relatively scarce in the archaeological record, however, plant resin has been recovered and identified in a number of archeological contexts. It is notable that resinous residues survive in a recognisable form in some particular situations, even when other organic materials do not. This preservation is due to the complex structure of resin, which includes large, non-volatile molecules, as well as an ability to fossilise, and in some cases, polymerise, along with anti-microbial properties and insolubility in water.

Plant resin is relevant to many archaeological questions. The development of the relationship between people and their environment, the development and spread of hafting technologies and also trade routes of commodoties such as wine, incense and weapons, for example, all benefit from the study of resin. Resins are highly versatile, easily preserved and travel well, thus they have accordingly been traded long-distance for at least 3,000, possibly 5,000 years (Michie and Cooper; 1991, p. 603). Trade and exchange on a more local level in indigenous communities is likely to have a much longer history. As the types of resin produced in different parts of the world vary, it is often possible to deduce archaeologically whether resins had been trade items or were locally produced, by identifying the botanical source of the resin (e.g. Burger et al.; 2010; Regert et al.; 2008). Resin is also associated with other interesting uses connected with religion, sorcery and ceremony, including mummification.

When found in an archaeological context, usually either as a visible amorphous mass or absorbed into an inorganic matrix, resinous remnants offer a substantial amount of chemical information. Chemical resin analysis is an important tool for investigating exploitation, technology and function of the organic material. It can provide information about the

resin including botanical origin, state of maturation and any diagenetic and anthropogenic alterations. This information can then be interpreted to provide insight to the context in which the resin was recovered.

Archaeological resinous finds are few and far between and there needs to be a strong justification for performing destructive chemical analysis on rare materials. The use of ethnographic analogy for aiding the study and interpretation of archaeological resin is problematic but vital for progressing the very promising field of resin analysis for archaeology.

1.1.2 The problem

Chemical resin analysis has been importantly and successfully applied to several archaeological investigations in Western Europe and the Middle East. Several different resins and organic materials have been identified with the majority of resin coming from the Pinaceae family and *Pistacia* genus, as well as birch bark tar made from *Betula* resin (for example, Brettell et al.; 2015; Colombini, Modugno, Silvano and Onor; 2000; Colombini et al.; 2009; Giachi et al.; 2013; Helwig et al.; 2014; Hjulström et al.; 2006; Mathe et al.; 2009; Mazza et al.; 2006; Modugno et al.; 2006; Rageot et al.; 2016; Regert and Rolando; 2002; Regert; 2004; Regert et al.; 2008; Ribechini, Modugno, Colombini and Evershed; 2008; Ribechini, Modugno and Colombini; 2008; Stern et al.; 2003; Stern, Heron, Tellefsen and Serpico; 2008). However, the southern hemisphere offers its inhabitants a far greater range of resins than its northern counterpart, particularly in tropical regions.

Resinous materials have been recovered from archaeological contexts in Oceania (e.g. Maloney and O'Connor; 2014). However, in order to gain the maximum amount of information from those and future finds, more understanding of the types of resins exploited in which

areas, how those resins were likely to have been used, and how to recognise them in archaeological finds is needed. Archaeological resins are often highly degraded and found in very small quantities so it is important to have an analytical framework in place to be able to analyse them efficiently and in a targeted way.

Oceania is home to a substantial proportion of the resinous plants of the world, including many endemic species. Our academic knowledge of the resins from this region is largely restricted to those that were exported commercially for use in the varnish industry since European contact, such as kauri and Manila copal (e.g. Mills and White; 1994), and ambers that are thousands to millions of years old (e.g. Langenheim; 1990). Considering the vast range of resins occurring in this part of the world very little research has been carried out on them to date. If the resins used across different parts of Oceania are found to be clearly distinct, they have the potential to highlight differences in use between regions and possibly time periods, as well as the social aspects surrounding the use of plant resin.

We know from archaeological finds across the world that plant resin has been an important material throughout the past and almost universally across different socio-cultural groups. We also know from ethnographic fieldwork that plant resins have been used for a number of purposes, and are an extremely useful and important resource for indigenous communities in the tropics and sub-tropics where the majority of resinous plants thrive. However, the recorded ethnographic information on the specific types of resin used is very limited, particularly in Oceania.

The importance of plant resins to the people of the tropical and sub-tropical regions is demonstrated by Gianno (1986) in her work with the Semelai of Malaysia, describing the language and classification system used for different types of resin. The complexity of the Semelai naming system indicates considerable knowledge of the resins available to them,

and this is also likely to be true for the Indigenous[1] peoples of Oceania. Much of this information will likely have been lost in translation to European collectors, resulting in limited reports of the resin used on the artefacts that are now residing in museums across the world.

There are considerable quantities of ethnographic items from Oceania that were collected in the late 19th and early 20th centuries by ethnographers fascinated by the 'primitive' lifestyles of Indigenous communities in remote parts of Australia and the Oceanian islands. The study of these items currently held in museums has the potential to both enlighten our understanding of the role of resins in Indigenous Oceania, and provide a framework for analysing resinous archaeological finds, in terms of finding the most prolific way to analyse them chemically, and for understanding the context of the results.

1.1.3 The scope of this project

Resin analysis is a growing field of study within archaeology, with a range of techniques to analyse resinous materials that have been recovered through excavation. This project aims to use resin analysis to access a largely untapped information resource in the form of physical resin specimens on artefacts in museum collections that have already been gathered, mainly by the ethnographers of the late 19th and early 20th century, in order to review by chemical analysis the range of resins used in Indigenous Oceania. There has been excellent progress in resin analysis over the past few decades, and with an increase in accessibility and affordability of analytical instruments, chemical fingerprinting is now a standard and effective approach for the analysis of unknown organic materials (Pollard and

[1] The decision to capitalise the word 'Indigenous' when referring to First Nations people of Oceania, their customs, and their material culture within this thesis follows the precedent set by the Australian Museum and guidelines by Monash University (2020). Whilst acknowledging differing perspectives, for example those outlined by Stewart (2018), the intention is of respect to all past and present Aboriginal Australians, Torres Strait Islanders, and First Nations communities throughout Oceania.

Heron; 1996). Its application to samples of amorphous materials from museum artefacts can provide a simple, non-intrusive, and largely comprehensive chemical profile for each sample. This type of analysis then allows comparison of the composition and potentially the identification of the different organic materials, and specifically for this study, the resins, present.

The majority of museum items selected for this project were labelled as including "resin" or "gum", or perhaps for Australian samples "spinifex" as a material, but no further information was provided in most cases. The results from this analysis will highlight the range of different resins that are present on the artefacts, and the potential for identifying the botanical source of the resins when otherwise unknown. The implications of these finds for the future analysis of archaeological resins will be reflected upon. The main research questions to be addressed though the use of resin analysis fit into the following categories:

1) Exploitation - which plant resins have been exploited, and where were they found

2) Technology - how resins have been processed for use

3) Function - for which purposes resins have been used

These research topics all address questions around the choice of resin used: patterns of use, geographical restrictions, trade systems, use of specific resins for particular functions as well as the technological processes developed to enable use of locally sourced resins. This leads to bigger questions about how resin affects the development of associated technologies, and if different types of resins hold different functions, for example, physical, medicinal or spiritual. The collation of information from the ethnographic literature alongside the new chemical data will be used to address these questions.

The scope of this project is restricted to the study of museum artefacts from Oceania that were made available for analysis within a reasonable timeframe, and using a singular suitable analytical technique and preparation method, focussing on the resin component of the samples. This is also the case for the reference collection.

1.2 Background

1.2.1 Resin from plants

Some plants exude substances that collect on the outside of the plant, often forming an amorphous mass that serves as a protective barrier. Resin is one type of a range of natural exudates and is produced only by certain plant species. Resin is exuded spontaneously by a large number of trees and plants as a by-product of their metabolism (Mills and White; 1994). The ecological reason for the production of resin in plants is not wholly understood but it is thought to be principally a defence against disease and insect damage (Langenheim; 2003).

The definition of resin is complex yet vital for the study of it. Part of the confusion lies in the nature of plant exudates, some of which consist as pure materials, for example, pure resin, and some as mixtures, for example, gum-resins, and resin with latex. Plant resin is defined by Langenheim (2003, p. 24) as:

> [...]primarily a lipid-soluble mixture of volatile and non-volatile terpenoid and/or phenolic secondary compounds that are (1) usually secreted in specialised structures located either internally or on the surface of the plant and (2) of potential significance in ecological interactions.

Non-solubilty in water is a unifying factor of resins and is fundamental to both the usefulness and long-term survival of the material. Resin can be preserved for thousands of years and longer if it becomes fossilised.

There are many different types of plant resin. Historical categorisation and naming of resins is inconsistent and ambiguous due to a long history of use and trade of resin-like

materials, alongside continuous developments in botanical research. Resins are traditionally categorised by physical attributes for trading purposes, such as viscosity, colour and aroma rather than their botanical source, using terms such as 'oleo-resins', 'soft' and 'hard copals', and 'dammar' (Langenheim; 2003). This has caused much confusion in resin studies as there are multiple names for the same resin type, as well as names that include resins from a number of different sources. Additionally, the boundaries to these classifications often vary. In this thesis, resins are categorised by the taxonomic identity of the botanical source of the resin where possible.

1.2.1.1 History of resin use

Resin has long been a widely used and valued commodity and has therefore become a large part of social and economic activity in many regions. It has been used in so many cultures because of its abundance in a range of environments, and its many useful qualities, particularly the combination of adhesiveness and insolubility in water (Robertson; 2005, p. 66). Resin is a product that has been exploited throughout the past for a range of purposes from medicine to art and technology and continues to be used in the present (Barker et al.; 2002, p. 136) although the majority of resin used commercially is now synthetic.

Archaeologically, resin is known to have been used for lining pottery (e.g. Lampert; 2003), caulking boats (e.g. Burger et al.; 2010; Colombini et al.; 2003) and as incense (e.g. Modugno et al.; 2006) and torches (e.g. Barker et al.; 2002). There are also many archaeological examples of its use in hafting, waterproofing, as adhesives, and for embalming mummies (e.g. Buckley et al.; 1999; Font et al.; 2007; Modugno et al.; 2006; Regert and Rolando; 2002).

1.2.1.2 Archaeology and resin

Resin is an organic material that preserves relatively well in a number of conditions and is often found associated with archaeological artefacts, although it is not always easily recognisable (e.g. Evershed et al.; 1997; Lombard; 2005; Stacey et al.; 2006). Resins are sometimes archaeologically visible thanks to their chemical characteristics. Most resins have a tendency to harden over time, through loss of the volatile fraction, oxidation, polymerisation and cross-linking (Chaler and Grimalt; 2005). Resistance to microbial decay and water-insolubility (unlike water-soluble gums) aids the preservation of resin in archaeological contexts. Preservation is even more likely when resin is adhered to inorganic artefacts (stone tools, pottery etc.), where it may have been used as a material, for example for hafting, waterproofing or decorating. Preservation of resin is most likely to occur in anaerobic conditions such as waterlogged or arid environments, or under permafrost (Pollard and Heron; 1996, p. 246). Resin is therefore frequently found in an archaeological context, though usually in very small amounts, and sometimes as residue invisible to the naked eye (Pollard and Heron; 1996, p. 240).

Resin can occur in a number of situations archaeologically, and may be present, for example, as a residue or a pigment on the surface of stone tools (e.g. Lombard; 2005), walls, shells and bone (e.g. Pyatt et al.; 2005, p. 2010). It can occur on the surface of ceramics, or absorbed within a pottery matrix (e.g. Reber and Hart; 2008); or as a tar, glue or pitch within, or on the surface of an artefact (e.g. Font et al.; 2007). Resin can even form part, or the whole of an ornament or resource prepared for use (e.g. Modugno et al.; 2006) and can also be found in its raw or fossilized form (e.g. Pereira; 2011; Langenheim; 2003).

Resin can provide an unusual insight into past use of organic materials. Analysis of archaeological resin at a molecular level has limitations, however it is still possible to determine

the resin's botanical source to some extent, as well as identify certain alterations made to it and extrapolate the likely ways in which it was used. Identification of archaeological resins can therefore contribute information about a past culture's relationship with their surroundings and use of local natural materials. This could include insight into the knowledge that past cultures had of the various properties of resins and any technologies they developed to utilise such properties by altering the original form of a resin to something more functional. It may also include information about deliberate selection of certain types of resin and the effort involved in obtaining the desired resin, for example, travel to particular habitats and altitudes or reliance on trade. It might also include information about culture-based decisions versus practical-based decisions regarding material choice.

Management of plant resources is another area of Oceanian archaeology that can be assisted by the identification of regularly used plant resins, as an additional value to food resource plants, and may also be able to shed light on some of the debates around Lapita studies (Lilley; 2006).

Therefore, plant resins from an archaeological context can make a significant contribution to answering a number of archaeological questions regarding plant exploitation, trade, the technological proficiency of past communities and the relationships between past people, their environment and their material culture.

As an emerging area of research, resin analysis can be a valuable tool within archaeology and is increasingly being recognised as so amongst archaeologists (e.g. Regert et al.; 2008). There are many reasons for analysing the composition of resin-based archaeological materials, and many more for identifying the botanical source of the resin in question (Pollard and Heron; 1996, p. 246-264). The wealth of information on artefacts that we can gain from

the resin calls for the detailed and systematic analysis of archaeological resins wherever possible.

1.2.1.3 Ethnography and resin

Ethnographic information is also a valuable asset to archaeological investigation as it can often provide aspects of materiality invisible to the archaeologist and give an indication to how particular objects may have been made, used and what their social and cultural associations may have been. Alongside written accounts, detailed study of resin in museum collections can be a valuable tool for archaeological research. However, we must note the limitations of ethnographic analogy and apply data gained from ethnographic research with caution:

> The regional ethnohistoric record serves then as a source of territorial and economic modelling, rather than as an indicator of prehistoric behavioural patterns.
>
> Smith; 2011, p. 16-17

Ethnographic resins held in a museum context can contribute to archaeological research by providing organic material that is readily available and in a condition such that it can be reasonably easily analysed without being too invasive. Whilst ethnographic materials cannot be used as a substitute for archaeological materials, they are likely to have been similar to that used in the past and can assist in developing a framework for analysing and interpreting archaeological materials.

Collectors and ethnographers

Some of the most significant collectors of Oceanian artefacts also kept written accounts.

These accounts are useful ethnographic resources and in a few cases provide information on specific artefacts. The main collectors and ethnographic resources referred to in this thesis are summarised below.

Dr Emile Clement (1844-1928) was a collector and dealer of Aboriginal items from Western Australia, since his travels there in the late 19th century. He sold well over a thousand items to several museums in Britain, as well as numerous others to around thirty museums across the world, often with associated maps, sketches, and photographs, and some letters. A few of these items, from both the Pitt Rivers Museum and the Peabody Museum collections have been sampled in this project. Details of some of the objects he collected are in a publication by Clement in 1903, titled *Ethnographic notes on the Western-Australian Aborigines (with a descriptive catalogue of a collection of ethnographic objects from Western Australia by J. D. E. Schmeltz)* (Clement and Schmeltz; 1903).

Joseph Henry Maiden (1859-1925) was a botanist, collector and the first curator of the Technological Museum in Sydney (1881-1896). He was born in London and moved to New South Wales, Australia in 1880, and he established a herbarium at the museum in 1883. He collected specimens from all over Australia and published several papers. As noted by Clarke (2008), Maiden had an earlier interest in resin derived from soft spinifex grass (*Triodia pungens*), which led to an interest in resins in general. He then studied gums and resins for an appendix of a four-volume report of the Horn Expedition (Maiden; 1890, p. 197).

Beatrice Blackwood (1889-1975) was an ethnologist who worked at the Pitt Rivers Museum in Oxford, running it with curator Tom Penniman after the death of founder Henry Balfour, and was a graduate and lecturer at the University of Oxford. Her ethnographic fieldwork included an eighteen-month long excursion to New Guinea, where she studied local life on

the islands of Buka and Bougainville, and collected over 400 objects which she brought back to the Pitt Rivers Museum (Larson; 2005). Blackwood published *Both sides of Buka Passage* in 1935 (Blackwood; 1935). She continued to collect objects for the museum from further fieldwork in New Guinea and New Britain. One of the artefacts donated to the Pitt Rivers Museum by Blackwood has been sampled and included in this project (also initially analysed for the pilot study) as sample PRM23.

Norman B. Tindale (1900-1993) was an Australian ethnologist and collector of Aboriginal artefacts and multi-media documentary records of Aboriginal culture. He collected from all around Australia but particularly from northern and central Australia. He was a pioneering ethnographer and archaeologist, among the first to incorporate ecological and scientific techniques to these fields: skills which he transferred from the natural sciences as an entomologist (South Australian Museum; 2015b). He became a full-time ethnologist for the South Australian Museum, Adelaide, South Australia. He is best known for his maps of Aboriginal territories. He is also known for his eighteen-month field-trip around Australia and Tasmania in 1938, and continuing field-work, with Dr. Joseph Birdsell (South Australian Museum; 2017).

Dr Joseph B. Birdsell (1908-1994) was an American physical anthropologist with degrees from Harvard University and Massachusetts Institute of Technology, and held a tenured professorship at University of California, Los Angeles (UCLA) (South Australian Museum; 2015a). Together with Norman Tindale, Birdsell developed extensive databases from the Aboriginal populations of Australia, leading to groundbreaking research and many publications (South Australian Museum; 2015a). They continued to work together for several field seasons of the Australian Expedition, including the Peabody Museum and South Australian Museum Joint Australian Expedition, from which some of the artefacts from the Peabody Museum collection have been sampled in this project.

Other key ethnographic sources are:

- *Reports of the Cambridge Anthropological Expedition to Torres Straits* by Haddon and Rivers (1912)
- *Across Australia* by Spencer and Gillen (1912)
- *Spinifex resin* by Maiden (1890)

Bias in the ethnographic record

It is important to be aware of the bias in the ethnographic record, and recognise the limitations of the representation of sources such as museum collections, and ethnographic written records. These issues are discussed at length elsewhere (Pitman; 2010 and references within; Pitman and Wallis; 2012), and are simplistically summarised in the following sentence by Pitman (2010, p. 7) "These records are spatially and temporally restricted and reflect the European male bias of the discipline." This statement is equally applicable to this, and probably most similar projects.

1.2.1.4 Hafting material

Archaeology

One of the most significant areas that resin can provide insight into is the technological aspect of hafted composite stone tools (Parr; 2002, p. 260). The process of hafting was a crucial technological development in human evolution, and preserved resin residues offer a unique source of information, as well as potential direct dating (Maloney et al.; 2015). Archaeologically, resin is most likely to be preserved when adhered to the surface of a robust material such as ceramic, stone or bone, and in anaerobic conditions (Pollard and Heron; 1996, p. 246). Hafting resin is of notable value because it does tend to survive

archaeologically more often, and from older sites than resin used in most other contexts (Hiscock; 2008; Maloney et al.; 2015).

Hafting describes the construction of a composite tool by inserting or attaching a blade or stone tool to a handle usually made of wood, bone or antler (Robertson and Attenbrow; 2008, p. 33). There are three basic classifications of hafting: wedged, tied and mastic (Shaham et al.; 2010, p. 2010). Mastic[2] hafting uses a 'resin-like' material as a fixative to secure the haft (Shaham et al.; 2010, p. 2010). This style of hafting is particularly interesting as, theoretically, the cost of time, effort and materials required for hafting must be outweighed by advantages such as increased precision and efficiency in the use of the tool for hafting to be worthwhile (Robertson and Attenbrow; 2008, p. 33).

From the archaeological evidence it is clear that amorphous adhesive materials such as plant resin have been used for hafting composite tools in Oceania for a very long time. The recovery of certain axeheads imply hafting technologies appeared in the Pleistocene in parts of Australia more than 25,000 years ago,[3] and widespread hafting and associated technological changes occurring in the Holocene around 5,000 years ago (Hiscock; 2008, p. 111, 2016, p. 148). Tulas (backed and waisted stone tools) have also been found at archaeological sites in Australia, and are indicative of a hafting technology (Lilley; 2006).

It has been previously emphasised that the identification of resin to its source species in stratified archaeological deposits (e.g. on stone tools) would provide information on the hafting material used, specifically where it was obtained from, how it was processed, why it was chosen, and how the use of resins alonside tool manufacture has changed over time (Parr; 2002, p. 261). The ability to identify resins would be significant for the study of

[2]In some contexts, the term 'mastic' is used to describe a specific type of resin. True resin (although not necessarily mastic resin) is often used as hafting 'mastic', but in this context, mastic is a general technological term. According to ethnographic records, hafting mastic encompasses a wide range of adhesive materials, including gums and tars (Shaham et al.; 2010, p. 2010).

[3]Evidence of ground-edge axe production dated to 44-49K years BP (Hiscock et al.; 2016).

manufacture and function of hafted tools, the distribution and prestige of specific resins, and the trading of items. For example, mapping the distribution of the use of resins, comparing this to the natural distribution of the plants that produce the resins, as well as known exchange systems (particularly where they are already well documented, for example, in Australia (Berndt; 1954; Cribb and Cribb; 1981; Thomson; 1936; Parr; 2002) would be of great value to the topics previously mentioned, and beyond.

Ethnography

From the ethnographic literature it is evident that hafting occurs on a range of artefact types, and has been employed throughout Oceania. Hafting resins are recorded ethnographically as being reinforced with other materials such as burnt mussel shells, powdered charcoal, fine sand, dry grass, dust, blood, hair, kangaroo dung, stingray fat and beeswax to improve their hafting capabilities or, possibly, to increase their volume for trading purposes (Cribb and Cribb; 1981; Dickson; 1981; Robertson; 2005, p. 68). Ochre has been known to be added to hafting resin, possibly as a colouring pigment for decoration, but it also has a practical application in reducing the brittle character of the resin and may have been added as a filler (Wadley; 2005, p. 670).

Ethnographic research into the use of resin for hafting is important as it can provide a context for similar archaeological finds, and offer insight into potential ways the artefacts came into existence, what they may have looked like complete, and what they may have been used for. Chemical research can provide specific detail regarding the exploitation and technology of hafting resins by detecting chemical markers that can be used to identify the botanical source of the resin, and highlight any chemical alterations to the resin. The chemical analysis of hafting resins on ethnographic artefacts can provide an extra layer

of information to really develop our knowledge and understanding of the technological processes of hafting, and the employment of specific plant resins for this purpose.

In the museum collections studied for this project, there are some specimens of resin that were specifically collected for their ethnographic importance as a hafting cement. In some cases, further information surrounding these specimens has been located in the corresponding ethnographic literature (discussed in Chapter 8). These specimens are of particular importance as they can easily be analysed due to an abundance of material present, as opposed to a thin residue like on many artefacts, and can be directly compared to resinous materials on ethnographic artefacts due to their similar age and storage conditions (Chapters 4 to 6). They also represent material with the known intended use as hafting cement, often collected under the guidance of Indigenous locals, directly connecting them with the people who used those particular resins, and their names for them. This allows a direct connection between vernacular names of resins, and their chemistry, and potentially their botanical source if otherwise unknown.

1.2.2 Resin analysis

1.2.2.1 Molecular analysis of plant resin

Due to the versatility of resins, they can be difficult to recognise in archaeological and ethnographic contexts as they can occur in a variety of formats. Resin is often only part of the material being used, in either a naturally occurring or anthropogenic mixture, and can subsequently be difficult to analyse. When focussing on identifying the resin specifically, the resinous fraction of a mixed-material sample can be largely isolated by solvent-based lipid extraction, leaving behind any inorganic or fibrous inclusions, and any non-solvent soluble organic matter, thus improving the analytical visibility of the pure resin. This then allows

for clearer molecular analysis. Resin is itself a complex mixture of multiple compounds and the unique specific composition of each resin can potentially be characterised in order to identify its botanical source (Robertson; 2005, p. 66).

Resins vary widely in their physical characteristics owing to their different mixes of volatile and non-volatile terpenoid and/or phenolic compounds (Langenheim; 2003, p. 24). The resin is more fluid if the volatile fraction is proportionately large, and more viscous if it is small (Langenheim; 2003, p. 35). The volatile fraction of plant resin, also known as essential oil when extracted and sold commercially, is naturally lost over time. However, the non-volatile fraction is more likely to survive in an archaeological context. Therefore, the analysis of resins for archaeological purposes focuses on the non-volatile fraction, usually composed of large lipid molecules, mainly either higher terpenes or phenols.

All resin-producing conifers and most resin-producing angiosperm trees synthesize terpenoid resin (Langenheim; 2003, p. 101). Therefore, the majority of the resins produced and used are terpenic, although some important resins are primarily phenolic. Monocot plants in subtropical to tropical habitats produce phenolic balsam-type resin, including *Xanthorrhoea* and *Dracaena* (grass tree) or *Daemonorops* (vine) producing resin known as 'dragon's blood' (Langenheim; 2003, p. 101-2). Phenolic resins occur sporadically throughout the resin-producing plant population and in some rare cases, for example 'storax' there are both phenolic and terpenoid components in the resin (Langenheim; 2003, p. 347).

Terpenoids

Terpenoids are secondary metabolites in plants, produced for non-essential functions such as protection from microbial and other external attacks (see Langenheim; 2003). They comprise the largest family of natural products with over 23,000 described (as of 2007, Pollard et al.; 2007, p. 153) and many more to yet be isolated. Terpenoids form the major

component of resins and are the source of the valuable properties that have drawn humans to exploit resin for such a long time and for a number of different purposes (see Pollard et al.; 2007; Langenheim; 1990; Pollard and Heron; 1996, p. 239-70).

Terpenoids are grouped by the number of isoprene units they consist of, and the number of corresponding carbon atoms within them. Monoterpenoids and sesquiterpenoids have two and three isoprene units, with 10 and 15 carbon atoms, respectively. These are fairly volatile compounds that can be lost more easily over time. Di- and triterpenoids have four and six isoprene units, with 20 and 30 carbon atoms, respectively. These larger compounds are non-volatile and have a higher chance of preservation in archaeological contexts. Terpenic or terpenoid resins contain a significant component of either diterpenoids or triterpenoids, which rarely occur together in the same plants (Pollard et al.; 2007, p. 154) forming two distinct categories: diterpenoid and triterpenoid resins (Evershed et al.; 2001, p. 345).

Terpenoids are relatively easy to extract, analyse and identify by characteristic molecular fragmentation, using GC-MS (Pollard et al.; 2007, p. 153; Pollard and Heron; 1996, p. 239-70). The main constituents for several resins have already been identified. The non-volatile fraction of diterpenoid resins is mostly composed of tricyclic diterpenoid acids with either abietane or pimarane type skeletons, at least in the case of resins from the Pinaceae family (Colombini and Modugno; 2009, p. 14). Triterpenoid resins consist of mixtures of mainly pentacyclic and tetracyclic triterpene skeletons (Colombini and Modugno; 2009, p. 14).

Terpenoids have been found to preserve well for organic materials and prove to be excellent biomarkers when their origin is associated with a restricted or unique source (Pollard et al.; 2007, p153). The non-volatile diterpenes and triterpenes are the key to characterising and potentially being able to identify resins to some level, possibly to species, even when aged and degraded. The variation and pattern in type, including positioning of double bonds

(Mills and White; 1994, p. 95), and abundance of terpenes display a 'fingerprint' for each individual resin. Therefore, it is practical to focus on these larger terpenes for molecular analysis of archaeological material. Terpenoids in resin are discussed in more detail by Colombini and Modugno (2009, p. 14-17), Langenheim (2003, p. 37-39) and Mills and White (1994).

Biomarkers

Compounds that are unique to the resin of a specific source can sometimes be identified and used as molecular markers for that specific resin type, that is, the species or genus that the marker compound is unique to (Reber and Evershed; 2004, p. 400). This is known as the biomarker method. Pollard et al. (2007, p. 148) describe the biomarker approach in archaeology as "the matching of a specific organic compound, or preferably a group of compounds, to that of a contemporary plant or animal product". In archaeological samples there can be significant alteration of the material through anthropogenic changes, ageing and degradation, particularly oxidation and polymerisation, and changes due to microbial activity (Pollard and Heron; 1996, p. 247). Importantly, biomarkers are considered as diagnostically stable molecules present in the original material and preserved intact in archaeological environments or formed over the centuries due to ageing (Modugno and Ribechini; 2009, p. 216). Biomarkers can be used to detect materials such as resin in a mixture or in an aged or degraded sample, and sometimes identify it as the resin from a particular family, genus or even species of plant.

GC-MS is a highly accurate chemical analysis technique with separation (GC) prior to the detection (MS) making it particularly appropriate for complex, organic compounds (Pollard et al.; 2007). GC-MS can be used to separate and identify individual components within a sample, such as terpenoids, and therefore can be used to recognise existing and potential

biomarkers for specific resin types, and processes. Theoretically, using familial-, generic- or species-specific biomarkers, the botanical sources of the resins can be identified at the respective taxonomic level, once suitable biomarkers have been established.

Biomarkers can also be used for identifying other materials in a mixture. For example, biomarkers for bitumen are hopanes, stearanes, polycyclic aromatic hydrocarbons (PAH); biomarkers for beeswax include palmitic acid ester, fatty acids; and biomarkers for oils and fats are fatty acids, sterol, tri- and di-acylglycerols (DAG and TAG) (Ménager et al.; 2014).

Ageing, degradation and chemical alteration

Lipids have a much higher preservation potential than other organic material, such as DNA, proteins, and carbohydrates, but are still vulnerable to partial and complete degradation (Pollard et al.; 2007, p. 148). The biomarker concept is based on the idea that when naturally occurring compounds are deposited in a sedimentary environment, they go through changes as a result of diagenesis and maturation, by which they lose functional groups but the basic skeleton remains intact (Modugno and Ribechini; 2009, p. 215). The challange is in recognising the compounds in their final form through deducing the degradation pathways they may have followed.

The natural processes associated with ageing and general degradation need to be acknowledged and understood in order to i) be able to correctly identify aged and degraded resins and ii) be able to deduce which process-induced effects may be anthropogenic. Artificial ageing experiments on resins have been published previously (Dietemann et al.; 2000; 2001; van der Doelen et al.; 1998) resulting in the elucidation of degradation products for some particular resins such as dammar and mastic. However, identification of the resin is even more difficult when the naturally occurring resin has been mixed or thermally altered to form tars, pitches, rosin, paints and varnishes, but with understanding of the alterations it

is still possible to recognise a source (Barker et al.; 2002, p. 136; Modugno and Ribechini; 2009, p. 215).

Identifying structural alteration is another advantage of GC-MS. If alterations can be identified, the original compounds and therefore the source of the product can still be deduced. Structural alterations may also provide biomarkers for certain anthropogenic processes, for example, extensive heating, or burning, which can provide information about the life history of the organic artefact, probable production processes and technological development of the associated period or region (Evershed; 2008, p. 900; Robertson; 2005, p. 66).

1.2.3 Resins from Oceania

The southern hemisphere is home to a much larger range of resin-producing plants than the northern hemisphere, and many of the plants that produce resins have a restricted and distinct natural distribution. Oceania, which is defined here as the region comprising Australia, Papua New Guinea, and the Pacific Islands, has an extremely diverse range of resin-producing plants including many geographically constrained endemic species (Cribb and Cribb; 1981). This unique area of the world has many biomes separated by great distances along with distinct cultures with rich histories of plant exploitation. Many Indigenous communities in the Pacific Islands still use some of the traditional materials and methods for a number of activities (e.g. painting (Hill; 2001)), or at least include members that remember them.

1.2.3.1 Resins of ethnobotanical significance

In this region, plant resin is used for a number of purposes including as hafting cement and general adhesives. There has been much ethnographic interest in this area and thousands

of items have been collected and brought to England since European contact with Oceania, many of which are still kept in museum collections. Botanists were the first to realise that Aboriginal Australians utilised the diverse Australian flora leading to a surge of ethnobotanical studies of the region (Clarke; 2003, p. 2). Clarke (2003, p. 1) provides an excellent overview of Australian ethnobotany, with the definition of ethnobotany as "the study of the cultural use and perception of plants."

Resins have been an important resource for Aboriginal Australians and Torres Strait Islanders, and other First Nations communities in Oceania throughout the past. The main resins that have been documented as used by Indigenous peoples of Oceania are kauri (*Agathis australis*) resin in New Zealand, *Xanthorrhoea* spp., spinifex (*Triodia* spp.) and *Callitris* spp. resins in Australia, and *Canarium* spp. in Papua New Guinea and the Solomon Islands, for uses such as hafting (Clarke; 2012; Blee et al.; 2010). Within Australia, it has been noted that "each plant resin is botanically and geographically specific to the environment in which a particular group of people are living" (Blee et al.; 2010, p. 745), and this likely extends to the whole of Oceania as the flora is so diverse and localised across the region.

Other species of resins, as well as gums and kinos (a type of gum that contains polyphenols (Langenheim; 2003, p. 47)) have been noted as ethnobotanically important in Aboriginal Australia, including *Acacia* spp. (wattles), *Grevillea striata* (beefwood), *Gardenia* spp., *Myoporum platycarpum* (sugarwood), *Artocarpus altilis* (breadfruit), *Erythrophleum chlorostachys* (northern ironwood), and *Eucalyptus* spp. often, but not exclusively, as adhesives for stone tools and weaponry (Clarke; 2007; Blee et al.; 2010). Spinifex and grasstree resins are arguably the two most abundant, iconic, and important plant exudates for use throughout the past in Australia.

1.2.3.2 Sources of Oceanian resins

The resins of the southern hemisphere can be generally divided by source into the two plant groups: non-flowering plants or Gymnosperms; and flowering plants or Angiosperms. Notably, the only non-flowering plants known to produce resin in copious amounts are the conifers.

Gymnosperms

Araucariaceae is a large family of conifers (in the subfamily Coniferae), which are mostly confined to the southern hemisphere, with *Agathis* being the main resin-producing genus, particularly in Australia, New Zealand and the East Indies (Mills and White; 1994, p. 103). Kauri (*Agathis australis*) has been very important to the Maori of New Zealand and is used by them in a variety of ways. Under the name 'copal', *Agathis australis* resin is also commercially very important, and was extremely so in the nineteenth century when the semi-fossilised resin (confusingly often referred to as gum e.g. 'gumdiggers') was collected from the soil of old forests and used in the manufacture of high quality varnishes (Langenheim; 2003, p. 302; Mills and White; 1994, p. 103). Unfortunately, though once abundant in New Zealand, *A. australis* is now reduced to less than 0.5% of its former coverage and confined to small preserves in the north of Auckland due to over-logging in the nineteenth century (Langenheim; 2003, p. 302; Mills and White; 1994, p. 103). Another commercially important resin, Manila copal sourced specifically from *Agathis alba* (synonymous with *A. dammara*), goes under various names reflecting the hardness of the resin: 'melengket'; 'loba'; 'pontianak'; and 'boea', from freshly tapped through to older, harder specimens, respectively (Langenheim; 2003, p. 399; Mills and White; 1994, p. 103).

Another conifer family is the Cupressaceae. The most commercially important of the Cupressaceae resins is sandarac. Sandarac is usually from the North African species *Tetraclinus articula* (formally *Callitris quadrivalvis*), however, the so-called Australian sandarac comes from the Australian cypress pines (various species of *Callitris*) (Mills and White; 1994, 103). *Callitris* is primarily restricted to, but widely distributed within Australia, ranging from the arid tropics to areas of relatively high rainfall, flourishing in areas prone to drought such as savannah woodlands (Langenheim; 2003, p. 384). The main substitutes for African sandarac are resins from the 'black cypress pine' found in southeastern Australia (*Callitris endlicheri*) and the 'Murray River cypress pine' (*C. glauca*). Resins from *C. preissii* and *C. verrucosa* that grow in more arid regions of Australia are also commonly used (Langenheim; 2003, p. 384).

Angiosperms

The resin-producing Angiosperms in Oceania fall into three main groups: Angiosperms that produce triterpenoid resins, which appear throughout Oceania; other eudicot Angiosperms such as desert shrubs that produce a range of terpenoid resins; and the monocot Angiosperms that produce both terpenoid and phenolic resins that are unique to Australia.

Triterpenoid resins are produced by a number of deciduous plant families that are native to Oceania, most notably Burseraceae, which is the same family that the sources of frankincense (*Boswellia* spp.) and myrrh (*Commiphora* spp.) belong to. *Canarium* spp. is the source of elemi resin and is one of the main resin-producing Burseraceae genera in Oceania. Mastic resin is also a triterpenoid resin, and is most commonly sourced from *Pistacia* spp. in Europe. Some resin from the Anacardiaceae, a family native to Oceania, can be categorised as mastic. However the resin from *Pistacia* spp. is more similar to resins from the Burseraceae and Dipterocarpaceae families than many from the Anacardiaceae family

(Langenheim; 2003, p. 357). Dammar resin is a triterpenoid resin usually sourced from the Dipterocarpaceae family that are not native to Oceania, but thrive in neighbouring Southeast Asia.

Numerous desert shrubs also produce resin, probably as protection against desiccation, high-intensity radiation and being eaten by foraging animals (the resin often coats the surface of young leaves and stems) (Langenheim; 2003, p. 473). Of the resin-producing shrubs, the family Myoporaceae is known to be one of the most useful to humans and two of the family's three genera, *Eremophila* and *Myoporum* are prominent in Australia. Resin from some species have been very important to Aboriginal Australians for medicinal and ceremonial purposes, such as *Eremophila alternifolia* and *E. longifolia*, whilst others have been important natural adhesives and sealants, particularly *E. fraseri*, *E. abietina*, *E. ramiflora* and *E. viscida* (Langenheim; 2003, p. 438). *Myoporum platycarpum* is known as sugarwood after its sticky exudate, which is also known to have been used for a range of purposes in Aboriginal Australia (Clarke; 2012).

Monocots are a division of the Angiosperms that have a single leaf and it is the leaf epidermis that exudes resin (Langenheim; 2003). Two monocot genera that are resin-producing are *Triodia* (vernacular name spinifex) and *Xanthorrhoea*, which are both endemic to Australia. The resins from both of these plants have been thoroughly exploited by Aboriginal Australians for thousands of years, particularly for use as a hafting cement fastening together the parts of composite tools and weapons. *Xanthorrhoea* produce phenolic resins, but there is very little information on the chemistry of the resin from *Triodia* but what there is suggests that it may be a diterpenoid resin (Chapter 4).

1.2.3.3 Gums

Gums are polysaccharides and are produced differently from resins although many plants from both the conifers and Angiosperms produce both gums and resins (Langenheim; 2003, p. 46; Mills and White; 1994, p. 76). Similarly to resin tapping, gum production can also be accelerated by deliberate injury to the plant. Some gums, most notably gum arabic or gum acacia (*Acacia senegal*) are also known as wattle gum in Australia and are collected in very large quantities as they have considerable economic importance in several countries (Mills and White; 1994, p. 76). It is reasonably easy to distinguish resins from gums and other plant substances by their different physical properties such as water insolubility, inorganic solvent solubility, thermo-plasticity, and a lack of tendency to shrink on drying (Robertson; 2005, p. 67). Gums are of less use for archaeological investigation due to their water solubility and likelihood of being washed from artefacts by ground water.

1.2.3.4 Chemistry of Oceanian resins

The main resins specifically referred to in ethnographic accounts from Australia and Oceania fall into four groups based on their general chemistry:

1. Diterpenoid resins from large conifers (Gymnosperms). The main sources are *Agathis*, *Araucaria* and *Callitris*. These resins are mainly used in Australia and New Zealand (Clarke; 2012; Akerman et al.; 2002, p. 16).

2. Diterpenoid resins from non-conifers (Angiosperms). Notably produced by the tussock grass *Triodia* (spinifex) (Monocot Angiosperm), which is only found and used in Australia (Akerman et al.; 2002, p. 16).

3. Triterpenoid resins from large deciduous trees (Angiosperm). The main known source in the region is *Canarium*. This resin is mainly used in Papua New Guinea and the Solomon Islands (McClatchey et al.; 2006).

4. Phenolic resins. Notably produced by the grass tree *Xanthorrhoea* (Monocot Angiosperm), which is only found and used in Australia (Maiden; 1889, p. 231).

There is a chapter dedicated to each of these resin categories in this thesis (Chapters 3 to 6). These chapters include the results of this study for the samples most relevant to the chapter category. A more in-depth review of the literature and previous work on each type of resin is included at the beginning, preceding the results of this study, to allow a more informed discussion of the results in each section.

1.3 Context of the project

1.3.1 Previous work by the author

The premise of this project builds on results from the author's MSc project. First and foremost, GC-MS analysis after methylation of solvent extracted resin samples was found to be a successful method for characterising aged resin samples. Whilst acknowledging they are based on very few samples, the results indicated that resins of different plant genera were likely to have been deliberately chosen for their specific uses, such as sealing pottery vessels or as torches (Bradshaw; 2009). Specifically, it was found that the type of resin associated with pottery was consistent between samples, but was very different to that of the dammar torch, and the possible torch by-products. This showed that at least two significantly different resins are likely to have been deliberately selected for their particular intended uses by the occupants at Niah Cave, Sarawak, Southeast Asia. These findings raised the hypothesis that there is a reason behind the choice of resin other than being the most easily attainable, for preferred characteristics of one resin over another, such as fluidity, a high melting point, or ability to burn slowly. This in turn could reflect an understanding of the basic chemistry of resin and a shared knowledge of the surrounding environment by the occupants of the cave.

Possible changes in technological choices regarding resins from pre-Neolithic to the Neolithic were also detected, such as an increased variety of species and mixing of different species of resin. While further elucidation of these temporal and functional trends was not possible owing to the small size of the archaeological assemblage, a major outcome of the study was the recognition of the need for further research to into the material culture of resins, their functional properties and how these are selected and manipulated by past and present populations, and how this informs our understanding of human-environment interactions

and the technological development of the use of plants. These outcomes were the main impetus for this DPhil project, alongside a project proposal by A. M. Pollard and C. Heron to investigate the use of resins on artefacts from Papua New Guinea that are currently housed in the Pitt Rivers Museum. Selected significant results from the pilot study on this collection (see Section 1.4.3.3) have been published (Bradshaw; 2013).

1.3.2 Previous work on the characterisation of Oceanian resins

There has been an academic interest in the chemistry of a handful of Oceanian resins for their medical potential, with publications peaking in the 1980s. Chemical characterisation of resins with ethnobotanical significance in Oceania, however, is rare. Published knowledge of specific resins that have played an important role in the local communities throughout the past, and what these roles are, largely consists of the limited information as gathered and interpreted by the ethnographers of the late 19th/early 20th century. Recent studies on resins and their use have focussed on a few specific areas mainly in Australia (e.g. Carman and Marty; 1970; Powell et al.; 2013) and the Solomon Islands (Smith et al.; 1981). Published chemical analyses of archaeological resinous finds from the region are scarce.

The integration of new scientific data with existing ethnographic accounts offers a way towards a wider understanding of the use of resins in Oceania. The benefit of the approach has been previously demonstrated, for example, by Steigenberger and Herm (2011). The Vigani cabinet is a 300 year old pharmaceutical collection owned by Queen's College, Cambridge, containing several resins labelled with their trade names. Steigenberger and Herm (2011) compared these samples chemically using GC-MS to reference materials of known

botanical sources in order to align the trade names of the samples with modern taxonomy. They found several discrepancies from what would be expected from the descriptions, demonstrating the need for such chemical analyses.

1.4 Research design

1.4.1 Research question

The research design was developed to address the overarching research question:

> How can ethnographic examples of resin on artefacts from Oceania be used to both contribute knowledge about the Indigenous use of plant resin in Oceania, as well as develop a methodological framework for identifying plant resins in materials from an archaeological context?

1.4.2 Aims and objectives

The aim of this project is two-fold. Firstly, to acknowledge the value of resin analysis in archaeological research, which has largely focussed on Europe and Africa, and to explore the potential of the technique for Oceania, where the tropics provide a much wider choice of resinous materials. Secondly, to collect and interrogate data from a selection of artefacts that display a material that appears resinous, from Australia and other parts of Oceania that have previously been collected by ethnographers, and are currently housed in museums, with a focus on the exploitation, technology and function of plant resins in this region.

With these aims, the following research questions will be addressed:

1. Are the main types of plant resin known to have been used in Oceania distinguishable and can they be identified using GC-MS analysis?

2. Can the aged resinous substances associated with artefacts in ethnographic museum collections of c.100 years of age be identified as resin or otherwise, and can the resins be identified to a specific botanical source?

3. Do the resins on ethnographic artefacts in museums reflect what is discussed in the literature on resin use in Oceania?

4. Are there distinct geographical differences in the exploitation of resins associated with ethnographic museum artefacts from Oceania?

5. Are there functional differences in the choice of resins used on different types of artefacts?

6. Are there chemical signals that reflect ethnographic knowledge of resin processing technology?

7. Does the chemical analysis of resins on ethnographic museum artefacts make a valuable contribution to the investigation on the past use of resin in Oceania?

8. Is the chemical analysis of resins on ethnographic museum artefacts useful for future archaeological research?

9. Is chemical analysis by GC-MS a suitable method for routine archaeological resin analysis?

The objectives of the project are:

1. To use a robust and previously successful method of resin analysis, namely gas chromatography-mass spectrometry (GC-MS), for characterising a range of resins from Oceania that have had limited previous investigation, in order to build a reference collection of mass spectral data from ethnobotanically important Oceanian resins that can be used to identify unknown resin samples.

2. To analyse resinous materials from a selection of ethnographic artefacts housed in museums, across a range of artefact types, and a range of geographic origins.

3. To collect ethnographic data related to the selected artefacts and use alongside the new chemical data to address the research questions.

1.4.3 Method development

This project aims to inform the development of a potential method for routine archaeological resin analysis. Therefore simplicity and cost-effectiveness of the methods used are of utmost importance alongside the ability to gain as much information from as small a sample size as possible, with potentially one-shot analysis.

1.4.3.1 Gas chromatography-mass spectrometry (GC-MS)

Gas chromatography-mass spectrometry (GC-MS) is suitable for characterising amorphous organic residues as it is a very powerful technique that can produce a largely comprehensive characterisation of unknowns materials in a single analysis. A number of mass spectral libraries have been developed allowing a large range of organic compounds to be easily identified (for example, NIST, Wiley, MassBank). GC-MS is the most widely adopted analytical approach to study natural resinous materials as this is a high performance separation technique with the ability to quantify separate components within complex mixtures of compounds such as terpenes (Modugno and Ribechini; 2009, p. 215).

The main limitations of using GC-MS are that the samples require pre-treatment before analysis; it is a destructive method; and the method does not have the ability to distinguish between certain isomers. In order to be analysed by GC-MS, the sample needs to be volatile enough to move within the gaseous mobile phase. This is not a problem for volatile substances but many compounds are not suitable as they are too polar or have too high a molecular weight. However, this can be overcome by derivatising the original compounds

into ones that are more volatile, for example TMS ethers and/or esters or methyl esters (Evershed et al.; 1990, p. 1339). This derivitisation pre-treatment, alongside the fact that the sample needs to be introduced to the instrument as a solution, means that an amount of material must be removed from the item being analysed, and the original state of the sample is altered and effectively destroyed. However, because GC-MS is a sensitive technique, the amount of sample used is minimal, usually requiring milligrams at most, and often, in the case of resins, can be non-intrusive (either flakes have already come loose, or the removal of a flake is barely noticeable by eye). Distinguishing between positional isomers is not often necessary for general residue characterisation, however in situations where the positional substitution on aromatic rings needs to be determined, infrared spectroscopy (IR) is a suitable complementary technique for this (Hites; 1997, p. 611).

Alternative techniques

The often considered alternative for the analysis of museum resins is Fourier transform infrared spectroscopy (FTIR) as it is non-destructive in that the sample does not get destroyed in the process, and does not require pre-treatment. However, analysing resins on artefacts *in situ* is problematic for a number of reasons, the main ones being the practicalities of getting the museum items and the FTIR instrument in the same place for the length of time required to do the analysis, and then getting the resinous residue satisfactorily positioned in the infrared beam path. In many cases, it is likely that removing a small sample from the complete artefact may actually be preferable than working with the item itself, particularly if the museum item is delicate, in which case, the benefit over GC-MS is lost. Additionally, FTIR is not suitable for the biomarker method as it detects bond types in compounds within a sample but does not produce a fingerprint for individual compounds.

It is therefore useful for comparing complete samples and using reference materials to identify or confirm the presence of probable components within the samples, but not identifying an individual biomarker, or chemically characterising an unknown material.

Burger et al. (2011) have used a technique borrowed from geochemistry by which each type of compound is separated into fractions and analysed separately. This technique simplifies the chromatograms so they are easier to interpret particularly when tiny amounts of compounds from very small sample sizes are being recorded. This technique is advantageous to the analysis of these "precious archaeological substances, often present in trace amounts in excavation sites" (Burger et al.; 2011, p. 185). There are obvious benefits to this method over a standard single GC-MS analysis, in the simplification of interpreting the results, and an improved resolution for the less significant components within the multi-compound resin, as described by (Burger et al.; 2011, p. 190) "our procedure allowed the separation of complex mixtures and the enrichment of minor family in isolated fractions." However, by requiring four or five analytical runs per original sample, a considerable increase in time, effort and finance must be invested. The question is whether the extra resolution of the lower frequencies of compounds is really necessary and worth the extra cost. Burger et al. (2011) suggest that it is necessary for identifying Dipterocarpaceae resins to species level, "The detection of minor compounds by gas chromatography–mass spectrometry is the mile-stone in this type of archaeological analysis: such molecules may have a key role in the characterization of the sample's origin (taxonomic and/or geographic origin) or degree of alteration", but this has not yet been confirmed necessary for other resins.

FTIR and other observational techniques, such as nuclear magnetic resonance spectroscopy (NMR), are useful complementary techniques to GC-MS for distinguishing isomers and potential co-eluting compounds, as well as for studying the transformation, depletion or formation of specific functional groups in the course of ageing (Modugno and Ribechini;

2009, p. 218). Analytical pyrolysis (Py-GC-MS) has been successfully employed as complementary technique to GC-MS to investigate the insoluble or polymeric fraction of resins (Modugno and Ribechini; 2009, p. 218).

Rationale for using GC-MS

GC-MS instruments are relatively affordable and common, as well as reasonably easily acquired and maintained, whilst providing a large amount of in-depth information in a single analysis. The balance of quality and affordability makes GC-MS a sensible option for a standardised resin analysis method.

With a single analytical run by GC-MS, after derivatisation, a large amount of information is gained, and though the complexity of the chromatograms can be very confusing, if the analyst knows specifically what to look for, this is not a problem, even if the resolution is not ideal. The separation of minor compounds is only a concern if they are the only species-specific biomarkers, for example in the Dipterocarpaceae resins, for which further analysis may be required. However, initial identification of the type of resins if unknown, can be done by GC-MS.

It is argued therefore, that GC-MS analysis after solvent-extraction and methylation of resin samples has been demonstrated as most likely to be the best option for a systematic analysis of resins as a general category. It is also hypothesised to be suitable for distinguishing and identifying the different resins of Oceania, as has previously been demonstrated for those of Europe and South East Asia (Stern, Lampert Moore, Heron and Pollard; 2008; Burger et al.; 2011; Bradshaw et al.; 2016).

1.4.3.2 Derivatisation by methylation

As mentioned earlier, derivatisation is required to make the components within a typical resin sample more volatile and less polar so they can be analysed by GC-MS. Derivatisation is a way to transform non-volatile compounds such as sugars, fatty acids, and carboxylic acids into more volatile derivatives, for example, esters. Most resins consist primarily of terpene hydrocarbons (consisting of just carbon and hydrogen), and terpenoids, which are terpene-like (have an isoprene skeleton) molecules with additional compounds to carbon and hydrogen, as functional groups, for example, the carboxylic acid functional group (COOH) (Fessenden and Fessenden; 1998). The molecules in the terpenic fraction of resinous substances, the diterpenoids and triterpenoids, are more likely to be preserved in aged samples as they are large, aromatic molecules, which are less volatile and more robust (Pollard et al.; 2007). These non-volatile components of resins need to be derivatised for effective analysis by GC-MS.

Derivatives are similar or closely related to the structure of the original chemical compound, but are not the same. Compounds with functional groups with active hydrogens such as -H, -NH and -SH, and -COOH form intermolecular hydrogen bonds more readily. These compounds are known as polar and are more reactive with the column of the GC-MS. Derivatisation increases volatility by eliminating the presence of polar groups. The reduction of polarity by derivatisation minimises detrimental and non-specific column adsorptions leading to better peak shapes and improves analytical potential (Modugno and Ribechini; 2009, p. 216).

Derivatisation of unknown organic materials is often achieved by silylation using BSTFA (*N,O*-bis(trimethylsilyl)triflouroacetamide), which has been successfully applied to archaeological samples (e.g. Evershed et al.; 1997; Regert et al.; 2008). Silylation derivatises

groups with an active/polar proton (OH, NH, SH) into TMS ethers and/or esters (Modugno and Ribechini; 2009, p. 216) and can be conducted reasonably easily. This method is particularly suitable for derivatising a wide range of compounds, including sugars, for example monosaccharides that are found in gums.

Alternatively, the derivatisation of organic acids into methyl esters can be achieved by methylation using diazomethane (Pollard et al.; 2007, p. 142; Stern et al.; 2003; Bradshaw et al.; 2016), which is more suitable for resins as they contain many organic acids. Using diazomethane in ethyl ether is difficult and hazardous, however TMS-diazomethane ((Trimethylsilyl)diazomethane) is a more stable and therefore less explosive alternative to ethereal diazomethane, and can be safely stored rather than having to be made fresh before use every time. However, TMS-diazomethane converts fatty acids and carboxylic acids to methyl esters easily, but not completely, and can create impurities (van 't Erve et al.; 2010). Silylation also derivatises organic acids, but the yield is not always high, and this is only a temporary derivatisation which will revert relatively quickly back to its original form, whereas methylation derivatises the sample into a more stable form, which will not revert back for a much longer period of time (Stern, B.; 2008 pers. comm. during discussions about the author's MSc project). This is particularly useful for a lengthy analysis or if samples need to be re-analysed. TMS-diazomethane is also suitable for derivatising phenols (van 't Erve et al.; 2010), which are a main constituent of some types of resin. TMS-diazomethane has been used successfully for the derivatisation of plant resin by Scalarone and Chiantore (2009, p. 336). For these reasons, TMS-diazomethane has been chosen for the derivatisation of all samples in this project.

1.4.3.3 Pilot study

Fifty-three items from the Pitt Rivers Museum were requested for sampling for a pilot study, chosen based on the description on the museum database where the words "resin," "gum," or "wax" were used to describe the majority or whole of the item. Twenty-nine of these items were approved by the museum conservators for sampling. The aims of this preliminary study were to assess the suitability the proposed instrumental analysis method, of a standard GC-MS analysis after methylation using TMS-diazomethane, with the following aims: to find if the botanical source of the museum resins can be confirmed chemically, and/or identified further, for example to species, and to highlight the most suitable direction for further work.

Pilot study conclusions:

1. Lipids were successfully extracted from aged plant resins from a museum collection, and analysed by GC-MS to produce a molecular 'fingerprint'.

2. The new derivatisation method was successful and suitable for the range of resin types involved. Ethereal diazomethane as often used for methylation (Stern et al.; 2003; Pollard et al.; 2007; Bradshaw; 2009) was deemed too hazardous for routine analysis of a large sample set and the more stable trimethyl(silyl)diazomethane was used instead.

3. The instrument set-up needed to be altered to improve the quality of the data.

4. In most cases the aged museum resins produced a chromatogram similar to what was expected based on the descriptions, and when compared to reference samples, apart from PRM24 which did not produce resin-type components, and PRM27 and PRM28 which appeared to be a *Canarium*-like resin, rather than beeswax as described, therefore some discrepancy between samples and museum records was identified.

5. The chromatograms from different types of resins, namely *Agathis* sp., *Canarium*,

spinifex, and *Xanthorrhoea* were distinguishable, and showed potential, with improved analysis, for the source of the museum resins to be confirmed, and/or identified further, for example to species.

6. The collation of chemical analysis and ethnographic research proved to be valuable for improved knowledge of the museum items as well as ethnobotanical resin studies in Oceania.

Dissemination:

Samples PRM23 to PRM29 were reanalysed and the results were published in *Heritage Science* (Bradshaw; 2013), after presenting the results of the pilot study at the 10th Scientific Methods in Archaeology conference in Denmark (SMIA X). The results of the re-analysis are included in this thesis.

1.4.4 Outcomes

This project is important because of the following outcomes:

1. New chemical characterisations of some ethnobotanically important resins from species native to Oceania.

2. New development of a large dataset of mass spectral information on unknown resin components including terpenoids.

3. New information including possible identifications of resins on ethnographic museum artefacts from Oceania.

4. Improved knowledge of the use of resin in Oceania and the role of resin within Indigenous Oceanian communities.

5. New framework for recognising types of resins likely to be recovered archaeologically in Oceania and potential biomarkers to identify them taxonomically.

This will be the first study to present a full chemical characterisation of resins from a range of different types of artefacts, across different parts of Oceania, using a single analytical method. This thesis will also include the first chemical characterisation of known 'spinifex' specimens, one recorded as a particular species (*Triodia irritans*), and the first chemical characterisation of conifer resins from the genera *Callitris*, *Actinostrobus* and *Prumnopitys*.

The main difference between this project and much of the similar work on archaeology-related resin characterisation previously published is the choice of sample pre-treatment before instrumental analysis by GC-MS, namely simple lipid extraction followed by methylation, which is argued to be more suited towards the analysis of resin specifically (Stern, B.; 2008 pers. comm. during discussions about the author's MSc project). This project will present the largest contribution to a mass spectral reference library for methylated components of plant resins, to date.

1.4.5 Limitations

There are certain limitations to this project that must be acknowledged. The reference collection of ethnobotanical resins (Appendix B) is not exhaustive, and in many cases contains only one example of a particular species. This is an exploratory study to assess the scope of the research question. As such, it was important to get as many positive results as possible and so sampling of ethnographic artefacts was limited to those with materials previously identified as probably resin, gum or wax. The results of this project are therefore not representative of all resin use in Oceania, but rather serve to provide an indication.

Only the solvent-soluble portion of the ethnographic samples is analysed. No characterisation of any polysaccharide gum, kino, polymeric or inorganic components is attempted. Therefore, only conclusions on specifically the solvent-soluble resin components of the analysed samples are within the scope of this study.

The methods and findings of this project are intended to provide a framework for future analysis of archaeological samples of probable resin. However, interpretations of the results in this project are not directly analogous to their archaeological counterparts, but rather act as indications of potential botanical sources and uses.

1.4.6 Contributions to the wider field

This project contributes to the fields of resin analysis and terpenoid science, Oceanian ethnobotanical studies, archaeological resin analysis, hafting and stone tool residue studies and archaeological materiality studies. The results provide additional information to museums on specific ethnographic artefacts and to the First Nations communities of Australia, Torres Strait Islands, and other parts of Oceania on past traditional resin use.

The identification of resin from particular species used for specific purposes can offer insight into past use of natural materials. This is important for research into the early adaptation of humans to various environments, their plant exploitation practices and selection of resin-based materials, early knowledge of chemical properties of resins and development of technologies. It will also be useful for recognising cultural uses of resins related to gender, age, tribe customs and also spiritual beliefs.

1.5 Chapter structure

The main literature review is divided and presented in the relevant individual chapters for the four main resin types based on chemical composition preceding the new data for each type of resin (Chapters 3-6). Discussions of the results in the context of the ethnographic artefacts and overall conclusions are in the subsequent chapters. The proceeding chapters are as follows:

Chapter 2: Methodology

Introduction to the samples of the ethnobotanical resin reference collection and the ethnographic museum samples from Oceania included in this project, along with a description of the sampling strategy. The method for the sample analysis is described.

Chapter 3: Diterpenoid resins from the conifers (Gymnosperms)

Background to the archaeology, ethnobotany and chemistry of the conifer diterpeniod resins, including the trade resins: kauri; Manila copal; and Australian sandarac.
Results from the GC-MS analysis of both the conifer resins from the reference collection, and the ethnographic samples found to contain conifer-type diterpenoid resins.

Chapter 4: Diterpenoid resins from the Angiosperms

Background to two ethnobotanically important resins of Australia, spinifex (*Triodia* spp.) and northern ironwood (*Erythrophleum chlorostachys*), which contain diterpenoids of a different type to the conifers.
Results of the GC-MS analysis on putative spinifex and ironwood samples, and ethnographic museum samples exhibiting non-conifer type diterpenoid resins.

Chapter 5: Triterpenoid resins from the Angiosperms

Review of the archaeological and ethnobotanical importance of the *Canarium* tree and its

resin in Oceania. Background to ethnobotany and chemistry of triterpenoid resins, followed by previous work on *Canarium* resin.

Results from the GC-MS analysis of reference *Canarium* resins, and additional reference triterpenoid resins. Results from the GC-MS analysis of the ethnographic museum samples exhibiting triterpenoid resins, grouped by structure type.

Chapter 6: Phenolic resins from the Angiosperms

Background to *Xanthorrhoea* resin, its archaeological and ethnobotanical importance in Australia, and previous work.

Results from GC-MS analysis of *Xanthorrhoea* species in the ethnobotanical resin reference collection. Results from GC-MS analysis of phenolic resins on ethnographic museum artefacts.

Chapter 7: Discussion of the resin analysis results in context of the ethnographic museum artefacts

Discussion of the use of different resins in different regions, discussed by artefact type.

Chapter 8: Resin use in Oceania: discussion of patterns of use and the implications for future archaeological research.

Discussion of resins used for hafting versus non-hafting purposes, geographical differences in resin use, and a framework for analysing archaeological resins.

Chapter 9: Conclusions and further work.

Chapter 2

Methodology

2.1 Sample collection

2.1.1 The reference collection

A list of resin-producing plant species with ethnobotanical importance in Oceania was developed though a review of the literature. Authenticated specimens of each species were sought for sampling in order to create a reference collection. The majority of these were located and sampled with permission, from the Royal Botanic Garden Sydney, The Australian Botanic Garden Mount Annan, and Blue Mountains Botanic Garden Mount Tomah, the Australian Museum ethnobotanical collection at Mount Annan, and the Economic Botany Collection (EBC) at the Royal Botanic Gardens, Kew. Samples from the Sarawak Forestry department, Southeast Asia, collected for a previous project (Bradshaw; 2009), and a sample of *Agathis macrophylla* from the Plant Sciences department, University of Oxford, were also included in the reference collection.

A total of 146 specimens from 81 different known species, as well as 14 unknown species but known genera of resin-producing plants native to Australia and other parts of Oceania were sampled. These reference samples were given unique sample numbers, which are presented in Appendix A with the corresponding institution and accession/reference numbers, and taxonomic identification. Where a resin specimen has been originally labelled with a synonym species identifier, the current accepted name has been used in this project, according to the International Plant Names Index (IPNI; 2018), where applicable.

2.1.2 The ethnographic samples

Prior to the requests for sampling resinous materials on artefacts in the museums, the online catalogues were searched for suitable artefacts from Australia or Oceania, with "resin", "gum" or "wax" listed as a material. The most relevant items were included in a request to sample on each occasion, firstly to the Pitt Rivers Museum, Oxford, then the Australian Museum, Sydney, Australia, and lastly the Peabody Museum of Ethnology and Anthropology at Harvard University, Massachusetts, USA. The items included in this study were approved for sampling by the relevant museums and Australian Aboriginal representatives, where applicable.

In total, 173 resinous residues were sampled from 147 different museum items, including the samples from the pilot study. Most of the items are ethnographic artefacts, ranging from weapons to ornaments, which include an amorphous material that appears resinous. Some of the items consist entirely of a material previously identified as resin, thought to have been used in a particular ethnographic context. For each item, only the amorphous materials were sampled, where 0.1g, or less was removed from each sample site. A full list of the samples, the items they were sampled from and the main corresponding accession information can be found in Appendix B.

The amorphous resinous material on museum artefacts sampled for this project are from a range of items and represent a variety of different functions, predominantly hafting cement, but also other adhesives, waterproofing agent and torches, amongst others. The types of artefacts with associated resinous materials, selected for this project include:

- Weapons and tools: spears, spearthrowers, adzes, axes, knifes, shark hooks, clubs, bow, arrows, throwing sticks.
- Everyday use items: firesticks, firefans, water-carriers, vessels, medicinal items, ornaments and accessories.
- Ceremonial items: emu feathers, totemic pipes, pointing sticks, mourning nose stick.
- Raw material for use as: adhesive including hafting, torch-making, fuel, fire-starter, incense, narcotics, tattooing pigment.

The geographic regions the artefacts were collected from include New Zealand, Australia, Torres Strait Islands, New Guinea, Solomon Islands, Vanuatu, Micronesia, Polynesia, Fiji (Melanesia), Borneo, Philippines, unknown locations in Oceania.

2.1.3 Sampling strategy

The sampling strategy for this project involved searching museum databases for items with the terms “resin”, “gum’, or “wax” in the description, and applying for permission to sample them for destructive analysis. Artefacts with preserved resinous materials on are of limited availability for study, therefore the sampling strategy employed here is non-probability sampling, where the sample is not intended to be representative of the whole population. The purpose for sampling is to collect preliminary data to provide as much

information as is possible within the limits of the project, with a view to informing the best approach for futher investigation into resin use in Oceania.

The population of this study is effectively all human-made items for which plant resin is included as a material, in all of Oceania, throughout the entire past. The variables are the type of item, the type of resin (plant exploitation), how the resin was used (technology), what purpose the resin was used for (function), where in Oceania, when in the past.

Weaknesses of the sampling strategy are mainly reliability and bias. Reliability is dependent on the existing categorisation of samples into "resin", "wax" or "gum" by whomever accessioned the items into the museum databases, and whomever originally described and categorised the materials of the items.

Bias is inevitable and unavoidable, where sampling of museum artefacts relies on the artefacts being present in the museum. The bias of the collectors selecting which items to collect, the events throughout the lifetime of the artefact causing it to end up in a particular museum, those items being categorised in a particular way, and whether there is enough material present to be sampled, all affects the sample selection. There is then sampling bias on top, as Orton (2000, p. 2) explains, "the subjective choice of sampling units, whether at a regional scale or in a museum store, can easily lead to bias and an inability to quote margins of error for one's results." Therefore, the members of the population, in other words, all of the items ever used by past peoples of Oceania with resin on, did not have an equal chance of being selected and therefore those that were selected are not a representative sample of the entire population, which severely limits any generalisations that can be made about the results of the study.

There is further unreliability and bias in the way the samples are taken (arbitrarily based on least disruption to the appearance and structure of the artefact), and the analysis of the

samples: "The use of instrumentation, even expensive instrumentation, does not remove the possibility of error, but brings its own problems" (Orton; 2000, p. 9). This is true in part for this study due to development of the method and changes in the instrument set up throughout the study, and the choice not to use internal standards due to unknown elution times and unknown abundances of analysable material in the samples.

2.2 Sample preparation and instrumental analysis

A less than 2mg sub-sample of each sample (between 0.4mg and 1.9mg) was taken and transferred into a glass vial. Each sub-sample was solvent extracted in 2:1 dichloromethane:methanol and derivatised via methylation, using trimethylsilyl(diazomethane), reduced to dryness and re-constituted in dichloromethane. The TMS-diazomethane derivatisation protocol was very kindly provided by Dr Ian Bull at the University of Bristol. The full sample preparation method can be found in Appendix C.

The prepared samples were analysed by gas chromatography–mass spectrometry (GC-MS) using an Agilent 7820A GC system with a HP-5 ms 5% phenyl methyl siloxy capillary column, 30 m $\times$ 250 μm $\times$ 0.25 μm, connected to an Agilent 5975 series MSD. Helium was the carrier gas at a constant flow rate of 1.2 mL/min. 1μL of sample was injected onto the column either splitless or at a 2:1, 10:1 or 20:1 split ratio as deemed appropriate, with the GC inlet maintained at 300°C. The temperature of the oven was programmed at 50°C, held for 2 minutes, then increased to 300°C at 10°C/min, where the temperature remained constant for 10 minutes. The column was directly inserted into the MS ion source, maintained at 230°C, where electron impact (EI) spectra were obtained at 70 eV with full scan from m/z 50 to 800.

This study focusses on the resinous and therefore lipid-based (solvent-soluble) fraction of the sampled materials only, due to archaeological relevance based on the increased chance of preservation of such material as opposed to any water-soluble fraction. All analyses are therefore based on relative intensities of compounds within the analysable portion of the sample and not quantitative as original amounts of analysable material vary and are unknown, and the samples would not be comparable. This is effectively a qualitative analysis, although relative proportions of constituents within each sample are considered.

2.3 Data analysis

2.3.1 Gas chromatography-mass spectrometry (GC-MS) data

It was deemed implausible, unnecessary and overly complicated to attempt a fully quantitative analysis of the resin samples. The decision not to use an internal standard for quantifying the amounts of each compound was made for several reasons. Firstly, the presence of a known amount of an internal standard could be misleading in that it would appear that there were different quantities of particular compounds in different samples when the initial amount of sample could not confidently be kept consistent. Although all samples were weighed in order to avoid overloading the GC-MS instrument, the amount of the sample that was solvent extracted was not closely recorded. In the case of ethnographic and archaeological samples, starting with a set amount of sample every time would be almost impossible, due to the restricted amounts of sample available, and the unknown status of the material in the first instance.

Secondly, as the amount of extracted lipids in each sample was likely to vary, the presence of an internal standard could be restrictive in the visual comparison of the chromatographs

as they would be standardised to the largest peak, likely to be internal standard in cases where extractable lipids were minimal.

Thirdly, the unknown contents of the samples would also make choosing an appropriate internal standard very difficult, in that it would have to be suitable for the whole range of resins, without the danger of masking any important components, which would be difficult when these components were unknown.

It was therefore decided to keep the analyses of the resins pure, at least at this stage of investigation. With the aim of finding a way to process and interpret GC-MS data from the analysis of unknown resin samples of unknown quantities in an affordable, reproducible, and time-efficient way, qualitative analysis with an indication of the relative proportions of the compounds in the samples was concluded to be appropriate for this project.

2.3.1.1 Data clean-up

A number of analytical runs were undertaken for many of the reference collection during method development and optimisation. The best chromatogram for each sample was chosen based on the analysts opinion of what showed the most and/or clearest amount of information, and the rest were discarded. Contaminants, where identified, were ignored. The most common identifiable contamination is from plasticisers (phthalates), for example, di(2-ethylhexyl)phthalate, which is recognised by the ions at m/z 149, 167, 279, and is particularly abundant in polyvinylchloride-based products (PVC) (Hites; 1997, p. 618). Phthalates are often transferred to samples from plastic sample bags.

A large hydrocarbon contamination occurred through part of the analysis and was unable to be removed for several samples. This, however, was not problematic as the contamination

peaks were easily identified and disregarded, and did not appear to interfere with the main peaks of interest within the samples affected.

2.3.1.2 Mass spectral interpretation

When a sample is analysed by GC-MS, each of the molecules that is separated out by the gas chromatography is then broken into fragmented ions, detected and recorded by the mass spectrometer. The ionisation process, usually, and in this case, electron ionisation (EI), causes the molecules to fragment in characteristic ways, which when recorded, produces a molecular 'fingerprint'. The 'fingerprint' is represented graphically as a mass spectrum, showing the relative abundances of mass to charge ratio (m/z) measurements, which can be communicated non-graphically by an m/z number sequence, sometimes with relative abundances in brackets.

Many compounds can be identified by comparing their unique mass spectrum to a library of known compounds. Commercial libraries are available for the identification of common compounds, such as from the National Institute of Standards and Technology (NIST). However, many of the compounds in resins have not yet been well documented and are not included in commercial mass spectral libraries. In most cases, the identification of the molecular components of resins relies on mass spectral analysis and interpretation, owing to the complexity of chromatographic profiles, and limited commercial availability of natural terpene standards (Modugno and Ribechini; 2009, p. 216). The fragments of underivatised molecules may not have much diagnostic value but derivative compounds often form diagnostic fragmentations (Modugno and Ribechini; 2009, p. 216). For example, as Azevedo et al. (1994) note: m/z 74 is a key ion for linear carboxylic acid methyl esters; m/z 88 and m/z 101 are key ions for isoprenoid carboxylic acid methyl esters; m/z 191 is a key ion for tricyclic terpenoid carboxylic acid methyl esters. Additionally, a sequence of

ions can be diagnostic of a more specific material, for example, m/z 145, 203, 217, 231, 245, 273, 287, 329, 343 plus 357 are the characteristic ions for the aromatic tricyclic carboxylic acid methyl esters of Tasmanian tasmanite bitumen (Azevedo et al.; 1994). Diagnostic m/z sequences found in previous published works such as this is helpful in interpreting the mass spectral data for unknown compounds.

Theoretically, and with the correct expertise, interpretation of the mass spectra can lead to the identification of the compounds from the fragmentation 'fingerprint'. However, even without identification of the molecule itself, the mass spectra can be used to identify the presence of the same compounds in different samples, and key compounds can be recognised as important taxonomic markers.

Individual compounds in both the reference samples and ethnographic resin samples in this project were identified where possible, by comparison with the NIST11 mass spectral library. With a view to comparing the mass spectra of unknown compounds across different samples, in order to match the samples for a potential identification of unknown resins, and for identifying potential taxonomic markers, the mass spectral data was noted for each compound and compared manually.

2.3.1.3 Interpretation of data

GC-MS data is interpreted by the visual profile of the chromatogram, in conjunction with the mass spectral fingerprint for each compound represented as a peak on the chromatogram. The data from unknown samples is directly compared to the data from known reference samples. Mass spectral data is compared with a library of data provided by NIST.

2.3.1.4 Development of a mass spectral library using ChemStation

After many attempts to record and compare individual unidentified peaks from different samples, the necessity for a quicker and more accurate, reliable, and repeatable way to compare peaks became apparent. The data analysis software, ChemStation, used for identifying known peaks, also has the ability to compare selected unknown peaks by creating a new library and inputting the peaks of interest from existing chromatograms. Significant un-recognised peaks from the samples being analysed were added to the new library, which was updated throughout the data analysis process. This worked well for quicker recognition of similar peaks across different samples. However, it will require more work on deconvoluting, clarifying, and potentially identifying or at least naming individual compounds before the new library is a suitable tool for use as a publicly available mass spectral library.

2.3.2 Historical ethnography

Documented ethnographic accounts of Indigenous communities in Australia and other parts of Oceania were sought and collated, focussing on descriptions of the use of resin. This includes some from primary ethnographic accounts from the late 19th and early 20th centuries, but also the collected works of researchers such as Philip A. Clarke. Connections to the museum catalogue descriptions of the items that were sampled in this project were of particular interest, as were connections to the collectors of the items, the type of artefacts, and the area from which the artefacts were collected.

Chapter 3

Diterpenoid resins from the conifers (Gymnosperms)

3.1 Introduction

This chapter will provide a brief background to, and discussion of the diterpenoid resins from conifer species of ethnobotanical importance in Oceania. Previous findings of conifer resins in the archaeological record are outlined, followed by a discussion on the ethnographic record of conifer resin use in Oceania. Some individual species are mentioned in the ethnographic literature.

Previous work on the identification of conifer resins and the difficulty in distinguishing resins at species level is summarised. This is followed by the results from this project, using GC-MS data firstly to compare the chemical fingerprint of different conifer resins, and secondly for the exploration of the range of conifer-type resins in the ethnographic artefact collection.

3.2 Background to conifer-type diterpenoid resins

3.2.1 The conifer families

The conifer families are the only gymnosperms (non-flowering plants) that produce resin (as per the definition in Chapter 1) (Langenheim; 2003, p. 52). Five of the seven extant conifer families produce resin, but only Pinaceae in the northern hemisphere, and Araucariaceae in the southern hemisphere, produce it in copious amounts (Langenheim; 2003, p. 52, 99). Resins from these two families are known to have been used by humans throughout the past, as well as resin from a few species from the other three families. The other resin-producing families in the southern hemisphere are Cupressaceae and Podocarpaceae (Langenheim; 2003, p. 52). The most well-known conifer resins from Oceania are often referred to by the trade names "kauri" and "Manila copal" from the Araucariaceae, and "Australian sandarac" from the Cupressaceae family.

The Araucariaceae family has a fossil record stretching back to the Triassic period (251.902 to 199.6 million years ago), and it may have been established in New Zealand much earlier than that[1], making it one of the oldest extant families of the Coniferae (Ecroyd; 1982, p. 32). Members of this family are found today in warm temperate regions on all the major landmasses of the southern hemisphere apart from South Africa (Brophy et al.; 2000, p. 564-5). Species of the Araucariaceae are mainly found in the lowland rainforests of Malesia and New Caledonia with some species in Fiji, New Zealand, Australia and South America (Brophy et al.; 2000, p. 564-5). The Araucariaceae family comprises three genera, *Agathis*, *Araucaria*, and the recently discovered *Wollemia* that resembles fossil specimens

[1] From New Zealand amber, we know there have been resin-producing trees, and probably members of the Araucariaceae family since the Triassic (251.902 to 199.6 million years ago), when modern gymnosperms, including the conifers, first appeared in their current recognisable forms (Polly et al.; 1993).

of ancient Araucariaceae trees, and has become known as the living fossil. Plant fossils suggest that *Agathis* have also held a long presence in Oceania[2].

Agathis species are today mostly confined to the tropics, with *A. robusta* and *A. australis* being the only species that extend to the sub-tropics of southern Queensland and northern New Zealand respectively (Langenheim; 2003, p. 59,60). Within this mostly tropical habitat, *Agathis* occurs at a wide range of lowland soil types, length of dry season, and elevations up to 2000-2500 m (Langenheim; 2003, p. 59,60).

The Cupressaceae family extends across both the northern and southern hemispheres, and is the largest and most widespread conifer family (Langenheim; 2003, p. 64). *Callitris* is a southern hemisphere genus in the Cupressaceae family, known as cypress pine, which is a major feature of the Australian landscape from rainforest to desert, but particularly in the arid zones. The genus comprises several species, including two that occur naturally in New Caledonia (Langenheim; 2003, p. 64). The resin from *Callitris* spp. is known commercially as Australian sandarac. Another southern hemisphere genus that produces copious quantities of resin is *Actinostrobus*, which is native and restricted to Western Australia.

The Podocarpaceae is essentially a southern hemisphere family, although there are some occurrences in the northern hemisphere, with a fossil record showing a similar distribution

[2]There is certainly a long history of the *Agathis* genus in New Zealand with fossils from the mid Cretaceous, prior to its separation from Gondowana, and even earlier in Australia, with probable *Agathis* fossils from the Lower Cretaceous (145.5 to 99.6 mya) of south-eastern Australia (Lee et al.; 2007, p. 574). *Agathis* becomes evident as a distinct genus in the upper Cretaceous (99.6 to 65.5 million years ago), alongside fossils of the first flowering plants or angiosperms, at the same time as the pollen record shows that a substantial number of genera of the modern flora appeared (Ecroyd; 1982, p. 32).

Agathis leaf fossils have been confirmed from late-Oligocene/early Miocene (Oligocene = 33.9 to 23.03 mya, Miocene = 23.02 to 5.332 mya), of which it has been suggested that "the *Agathis* leaf fossils have some affinities with extant *Agathis australis*" (Lee et al.; 2007, p. 565). *Agathis* fossils appear from the early Tertiary (former term for 65 to 2.58 mya, now split into the Paleogene and Neogene (comprising the Eocene, Oligocece, Miocene and Pliocene)), with some later ones thought to be specifically *Agathis australis*. Other araucarian species are thought to be present at the same time but there is a difficulty distinguishing between species, though agathic acid (characteristic of *A. australis* and "1 or 2 other *Agathis* species") isolated from the resin still carried by the stems was used to confirm the identity of the fossils (Ecroyd; 1982, p. 32). If acceptable to use the agathis-acid-bearing resins as a proxy for *Agathis* in New Zealand then it can be said that "the genus is most likely to have been present in the region continuously from the Cretaceous to the present day" (Lee et al.; 2007, p. 574).

(Langenheim; 2003, p. 63). Several Podocarpaceae genera produce terpenoid resin in a moderate amount, including *Prumnopitys*, which occurs in parts of South America, New Zealand and New Caledonia (Langenheim; 2003, p. 478).

3.2.2 Identifying conifer resins

The resin produced by the conifers is a diterpenic resin, meaning it is rich in diterpenes (terpene molecules with 20 carbons, see Chapter 1). Diterpenes have many active properties, including deterring microbial and fungal growth, and have been found specifically to inhibit the feeding of insects (Atta-ur-Rahman; 2001, p. 242). These anti-pesticide, -microbial, and -fungal properties alongside other useful qualities such as water-insolubility, adhesiveness, and sweet aroma, have made the conifer resins invaluable to the peoples of Oceania throughout the past. The diterpenic component of these resins is the most recognisable and most likely to be preserved over time, making it a suitable focus for chemical analysis. Some diterpenoids have a tendency to combine to form larger polymers, known as polymerisation, making the resin more robust and likely to preserve longer, but also making that portion of the resin more difficult to analyse chemically. The GC-MS method in this project is used to analyse the free diterpenic acids, along with any other significant terpenoids and phenols, but not the polymeric fraction of the resin. In chromatography, mono- and sesquiterpenoids elute early, diterpenic acids elute towards the end of the the analysis, with the diterpenic fragments eluting just before (Scalarone and Chiantore; 2009, p. 334).

The resins from conifers are significant historically, particularly in terms of trade and commerce, and also archaeologically, including local use and trade, pre-European contact. These resins include the hardened (polymerised, and sometimes semi-fossilised) resins traded as copals, and fossilised resins known as amber. Particularly important as exported

trade commodities are Manila copal, specifically from the Philippines, and later the Dutch Indies, kauri, specifically from New Zealand, and Australian sandarac from the genus *Callitris*. The former two trade resins are predominantly sourced from species from *Agathis* of the Aracuariaceae family, however a number of different species produce similar resins that are traded under the same name and the botanical source is not always clear. Resin from a number of these other species are also known to have been used by local communities throughout the past, and a range of different conifer resins may be found on ethnographic and archaeological items. All of these resins are potentially visible on such artefacts as a colourless, or white through to a yellow transparent resin, or even a milky resin. The use of resin from other specific species is less well documented.

It is important to be able to identify the specific botanical source of conifer resins for a number of reasons, many of which have been highlighted by Burkill et al. (1935, p. 63), such as: to track the commercial use and trade of resin and the trees it comes from; for botanical interest and conservation studies; in the reconstruction of past environments; and for contributing towards the study of ambers. It is also important for investigating the local ethnographic and archaeological significance of both the resins and the trees they come from. The significance of identifying the botanical source lies in acsertaining information about local species distribution, local trade systems, and the effort of exploitation and technology invested in order to make use of the resin. For example, in southeast Asia, *Agathis alba* is not found wild below 330m and so is relatively inaccessible and not easy for villagers to exploit it, therefore only a small amount of resin would be collected and likely to be used locally or sold as dammar amongst the more lucrative Dipterocarp resins (Burkill et al.; 1935, p. 63).

The distribution of conifers is quite widespread in Oceania, but there are several species endemic to specific areas and the identification of resin source to species could be invaluable

for many of these reasons. The need to identify resins to species for archaeological research has been prevalent for long time, but is only just starting to become a possibility, certainly for any systematic study, with recent technological advances in analytical chemistry.

3.2.3 Conifer resins in the archaeological record

There are so far no published finds of resin in the archaeological record of Oceania that have been identified as having come from a coniferous source, to the authors knowledge. However, we know that conifer resins have been used by Indigenous communities in more recent times from ethnographic documentation, as discussed in the next section. We also know that conifer resins can be visible in residues when recovered archaeologically from extensive research on the identification of Pinaceae resin and pine pitches from several archaeological finds in the northern hemisphere. These finds show that conifer resins were a useful resource for a number of purposes.

Coniferous resins are known to have been used by the Egyptians and have been identified as the base of the embalming fluid sampled from wrappings on an Egyptian mummy from the Roman period (100-350 AD) (Proefke and Rinehart; 1992). Pinaceae resin has also been identified in a Roman mortuary context in Britain (Brettell et al.; 2015), and found to be used to line transport vessels in the Roman period (Pollard and Heron; 1996, p. 247). Evidence of Pinaceae resin, both un-heated and heated extensively to form pine pitch, was detected in paint samples from the waterproofing and caulking materials on the hulls of ships from an Etruscan and Roman (2nd century BC - 5th century AD) archaeological wreck site in a harbour in Pisa (Colombini et al.; 2003). Pine pitch has also previously been identified on and associated with other shipwrecks (Beck et al.; 1989; Pollard and Heron; 1996, p. 248). Additionally, a Roman pitch production site in the Pyrenees has been reported and discussed elsewhere (Orengo et al.; 2013).

In North America, Reber and Hart (2008) found evidence of extensive resin-sealing over a long period of time in prehistoric central New York State (from 1256–998 cal BC to 1417-626 cal AD), from resin residues in pottery sherds including some identified as pine (*Pinus*) resin. Eerkens (2002) also found evidence of resin in pottery in prehistoric western Great Basin, but identified it as piñon (pinyon) resin (from *Pinus monophylla* or *Pinus edulis*), which is different to most *Pinus* resin in that it is dominated by delta-8(9)-isopimaric acid and pimarane acids, rather than abietane acids (see 3.4.2 Chemistry section below). Eerkens (2002, p. 103) also found indicators of heating and concluded the pot was used for boiling the resin to make pitch. Piñon resin has previously been identified on archaeological and ethnographic materials from the southwestern Great Basin in North America (Fox et al.; 1995).

Another type of pine has been identified in an archaeological context elsewhere in North America. All the hafting residue from projectile points recovered from a site from melting ice patches in northwestern Canada, was found to be spruce resin, and was dated to up to around eight thousand years ago (Helwig et al.; 2014, p. 663-4). The hafting residues were from both parts of the composite throwing darts, the chipped stone points and dart shaft, as well as an antler slotted point that would hold chipped stone micro-blades, and some arrows (Helwig et al.; 2014).

As demonstrated by these examples, different types of pine resin have been successfully identified in archaeological contexts, in different parts of the world. As pine is a type of conifer, it is not unreasonable to expect that other conifer resins also have the potential to survive in archaeological contexts, in a state that they too can be identified.

3.2.4 Ethnographic accounts of conifer resin use in Oceania

Although archaeological evidence for conifer resin use in Oceania is yet to be found, there is plenty of ethnographic information on the use of such resins by Indigenous communities in Oceania, at least in the last 200 years or so.

According to Clarke (2012, p. 143), North Queensland kauri pine (*Agathis atropurpurea*) and black kauri pine (*Agathis microstachya*) were used in Cairns-Yarrabah area of northern Queensland for hafting spears and illumination, "A form of slow-burning torch was made by coating a branch in these resins and setting them alight." Cribb and Cribb (1981, p. 81), also note the use of three species of what they refer to as Queensland kauri, *Agathis atropurpurea* and *A. microstachya* both used in northern Queensland only, and *A. robusta* also used in the Wide Bay district of Queensland.

Lampert (2003) provides an excellent report on the use of resin to glaze pottery in different regions over the world from the ethnographic literature, with particular mention of *Agathis* being preferred in Fiji and Tiwi, and in the Philippines alongside *Pinus* resin. *Agathis philippinensis* was noted as being used on Kalinga pottery, and in Luzon in the Philippines (Longacre; 1981). Fiji kauri (*Agathis vitiensis*, now considered a synonym for *A. macrophylla*) was used as a glaze for pottery and may be lit as a torch, according to Wilkinson and Elevitch (2000, p. 15).

Kauri resin is also known as "Cowdee gum" in New Zealand, according to Prideaux (1838), who provides an extensive early description of the resin and its chemical behaviour, with a declaration for its suitability as a varnish. The employment of the gum-diggers by European settlers and major commercial export of Kauri gum from New Zealand follows the European discovery of the oleo-resin of *Agathis australis* resin in New Zealand, "This industry began in the 1850s and 6000-7000 gum diggers were employed recovering fossil gum from the

gumfields of northern New Zealand by 1893" and production reached its peak in 1905 (Ecroyd; 1982, p. 33).

In pre-European times, however, the Maori used the *A. australis* resin for torches, as a firelighter and for burning in certain religious rites, as well as for chewing, and burning to obtain lampblack used as a tattooing pigment (Burkill et al.; 1935, p. 62; Langenheim; 2003, p. 404; Ecroyd; 1982, p. 33).

In addition to resins from members of the *Agathis* genus, it is apparent that those from species of the genus *Araucaria* were also used. According to Roth (1904), in the region of Brisbane River, southeast Queensland, sources of hafting adhesive included hoop pine (*Araucauria cunninghamii*) resin. Hoop pine is distributed throughout Queensland and New South Wales and the resin can be warmed up and worked by fingers to be made pliable (Cribb and Cribb; 1981, p. 82). Bunya pine (*Araucaria bidwillii*) resin is also noted in the ethnographic literature (Robertson; 2005, p. 378).

The use of *Araucaria* by the Dugum Dani of West Papua for hafting fishing spears and adzes is reported by (Heider; 1970, p. 276-7) "The stone is set with the pitch of the *Araucaria* tree." *Araucaria* pitch was also used to treat rodent-bite wounds on pigs, by plastering it over the open wound and covering with ashes (Heider; 1970, p. 50), and the *Araucaria* tree was considered sacred so the burning of *Araucaria* wood was not allowed (Heider; 1970, p. 217).

Apart from the Araucariaceae resins (from *Agathis* and *Araucaria*), the only other type of conifers with ethnographic reference to the use of the resin is the cypress pine (*Callitris* spp.). Cypress pine resin was used extensively across temperate Australia as an adhesive cement in tool-making, specifically for hafting stone hatchet heads and knife blades to their wooden handles, and heads on spears, and *Callitris preissii* (common cypress pine)

resin is known to have been widely used as an adhesive for these purposes (Clarke; 2012, p. 142). Clarke (2012, p. 142) summarises ethnographic references to the use of resin from some other species, namley: *C. verrucosa* (scrub cypress pine) that was used in Victoria in hafting spears and stone hatchets, and in South Australia in the Ooldea area on the western coast for hafting stone blades to spearthrowers, and as adhesive for other artefacts; *C. columellaris* (western cypress pine) that was used in the arid western zone of Australia as a wax or cement, after adding ash as a temper; and *C. glaucophylla* (northern cypress pine) that was used in the tropics as an adhesive for cementing pegs onto spearthrowers and heads onto spears. Clarke (2012, p. 142) also mentions a negative side to the use of *Callitris* resin, in that it has some unpleasant characteristics, and was thought to be harmful to smell and caused the stomach to swell up if ingested, and so children were not allowed to use it. However, *C. columellaris* resin mixed with animal fat is noted as being used by the Alyawara of Central Australia, as a medicinal salve by Connell et al. (1983, p. 102).

Conifer resins have evidently been used in a number of situations in Oceania, and are likely to be present on ethnographic museum artefacts. Chemical analysis of these resins, alongside the information from the ethnographic literature offers to enhance our understanding of the use of conifer resins in the context of particular items, in particular areas, and contribute to a wider understanding of the past exploitation and technologies of conifer resins in Oceania.

The reference collection in this project has been formed by resin samples from known species of ethnobotanically significant conifers as informed by the ethnographic literature.

3.2.5 Previous work

The relationship between the trade names of resins and taxonomy of the botanical sources of those resins can be complex. The conifer resins discussed in this chapter, and the possible botanical sources of such resins are outlined below. This is followed by previous work on the chemistry of particular conifer resins from the three southern hemisphere families, and a discussion on the ageing and degradation processes of these types of resins, as reported in the literature.

3.2.5.1 Taxonomy

Kauri

Kauri resin (also known as kauri gum or kauri copal) is strictly speaking the resin from only one species, the kauri pine of New Zealand (*Agathis australis* (D.Don) Lindl.) (Mantell; 1950, p. 234). However other similar resins produced by conifers across Oceania, though usually also from the genus *Agathis*, have been referred to as kauri, mainly by the non-native explorers and ethnographers as a way to relate the similar resins from different regions to something familiar: the commercially available kauri resin (*Agathis australis*).

Manila copal

Another commercially available resin is Manila copal. There has been much debate over the main source of Manila copal, mainly as either *A. alba* or *A. dammara*, and also if *A. borneensis* is included as a main source (Langenheim; 2003, p. 401). It is particularly confusing with taxonomies changing as *A. alba* has been used previously as a synonym of *A. dammara*. Additionally, the polymerising resin of the conifers are not strictly speaking copals. Copals are technically semi-fossilised resins, and many authors consider only those

issued from Leguminosae plants growing in Africa, in the inter-tropical zone, as genuine copals (Regert et al.; 2008, p. 670).

The confusion of taxonomy over the history of chemical investigation of the resins has not helped, for example, as stated in Langenheim (2003, p. 401):

> Other *Agathis* species (to kauri) have several different diterpene acid compositional patterns, which influence their usability. For example, *A. dammara* (syn. *A. alba*) has communic acid and sandaracopimaric acid but large proportions of agathic acid and the acetate of agatholic acid in one compositional type but large amounts of torulosic acid characterizing another compositional type.

This apparent intra-species compositional variation may in fact represent the differences between the now accepted *A. alba* and *A. dammara*. Alternatively, the variation may be true for *A. dammara* as it is then noted that "This kind of diterpene compositional variation is similar to that seen in mono- and sesquiterpenes of other conifers" (Langenheim; 2003, p. 401) and is discussed in more detail elsewhere in the publication. However, diterpenes are significantly more robust than the more volatile mono- and sesquiterpenes. Either way, further research is required to clarify the nature of compositional variation of resins from within and between different species of conifer.

Australian sandarac

The resin from *Callitris* spp., (Cypress pine), is referred to commercially as Australian sandarac (usually but not exclusively from *Callitris verrucosa*) due to its similarities with the commercially more common sandarac resin from *Tertraclinis articulata* (Vahl) Mast., also from the Cupressaceae family but native to parts of Africa and the Mediterranean.

3.2.5.2 Botanical resin sources

***Agathis*, *Araucaria* and *Wollemia* (Araucariaceae)**

Agathis are large, evergreen, emergent trees up to 50m tall, occurring in a variety of rainforest habitats at a range of elevations (Thomas; 2017). *Agathis* contains by far the most important resin-producing species of Araucariaceae, and is mostly confined to the tropics, with only *A. robusta* in southern Queensland, Australia, and *A. australis* in northern New Zealand extending into the subtropics (Langenheim; 2003, p. 59-60).

Araucaria are also large, emergent, evergreens and can be even taller than *Agathis*, some reaching 60m, and are usually found in sub-tropical rainforests (Thomas; 2017).

Wollemia, commonly known as Wollemi, occur in two undisclosed small groves in a remote part of Wollemi National Park, within 200km north-west of Sydney, in the Central Tablelands of New South Wales. There is only one known species of *Wollemia*, *W. nobilis* W.G.Jones, K.D.Hill and J.M.Allen. *Wollemia* is a sister group to *Agathis* shown through DNA sequences (Brophy et al.; 2000, p. 564).

***Callitris* (Cupressaceae)**

Callitris are medium sized, evergreen shrub trees up to 25m tall, occurring on poor quality soils, often sandy or stony. They grow in range of habitats, both coastal and inland, at sea level and in mountainous areas of altitudes up to 1300m asl (Thomas; 2017). There are eighteen species of *Callitris* spread across Australia, and the remaining two species of the genus are endemic to New Caledonia (Brophy et al.; 2007, p. 58).

***Actinostrobus* (Cupressaceae)**

Actinostrobus are small, erect, evergreen shrub trees up to 8m tall, confined to Western

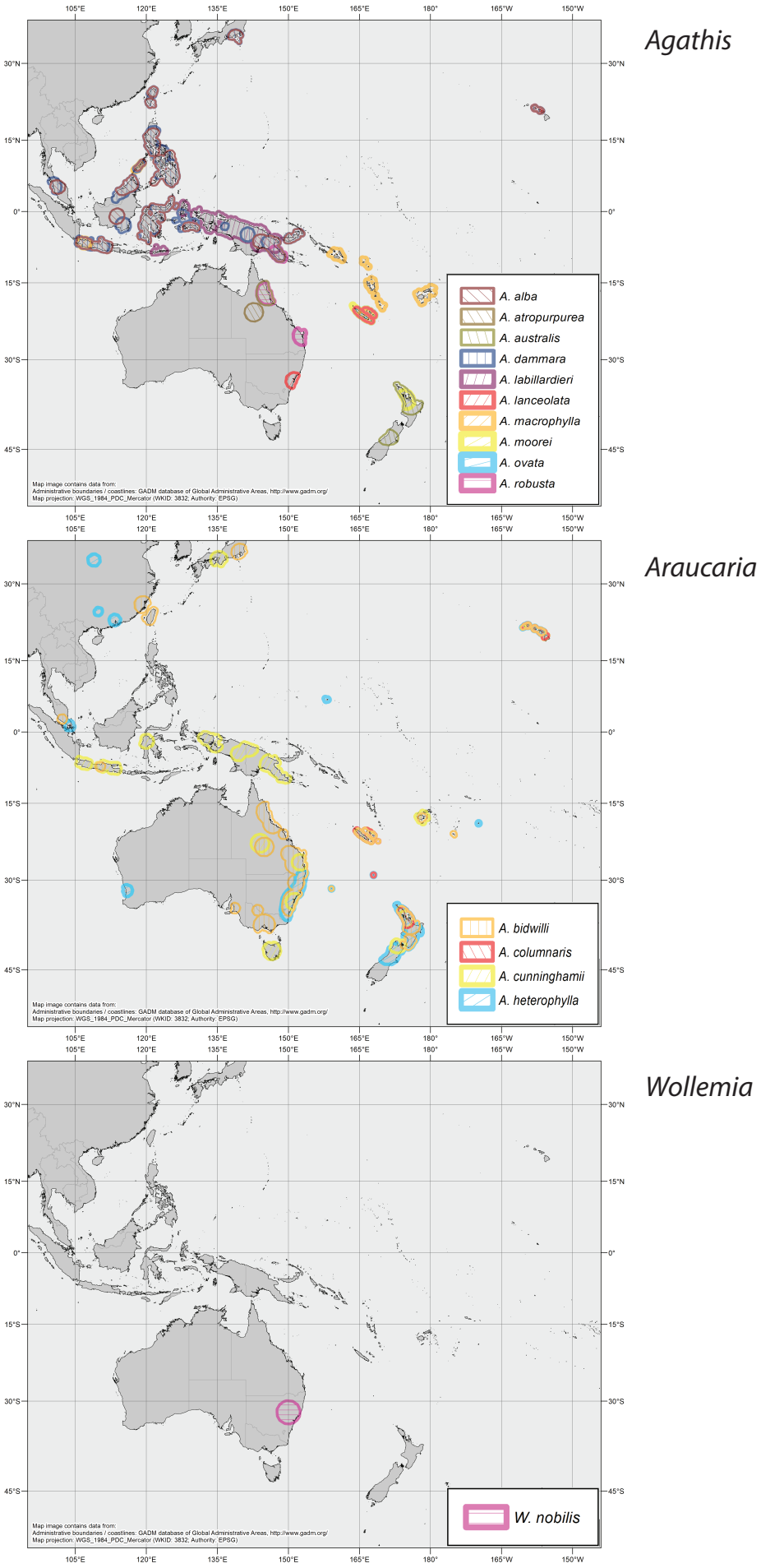


FIGURE 3.1: Maps of distributions of Araucariaceae species included in the reference collection

Distribution data from ALA (2018); GBIF (2018)

Australia (Saxton; 1913; Brophy et al.; 2004). From pollen records, they are known to grow in open canopy, evergreen, xerophytic, low-medium woodland to tall scrublands (<2m), and thus in very different habitats to the Araucariaceae (Pickett et al.; 2004).

The genus *Actinostrobus* is very closely related to *Callitris* (Banks and Pulsford; 2001, p. 31; Brophy et al.; 2007, p. 58), so closely related that Piggin and Bruhl (2010) have proposed that *Actinostrobus* be included in the *Callitris* genus. However, Heady and Evans (2005, p. 89) found that the common occurrence of frost rings in *Actinostrobus* could provide a means of separating *Actinostrobus* from *Callitris*, but further work into frost rings in *Callitris* is required. They do however conclude that the differences in the wood anatomy support the separation of *Actinostrobus* from *Callitris* (Heady and Evans; 2005, p. 89).

There are three known species in the *Actinostrobus* genus: *A. acuminatus* Parl.; *A. arenarius* C.A.Gardner; and *A. pyramidalis* Miq. Resin samples from the latter two are included in this project.

***Prumnopitys* (Podocarpaceae)**

The genus *Prumnopitys* Phil. is native to New Caledonia and Australasia, as well as Southern America. *Dacrydium*, *Podocarpus* and *Prumnopitys* (all in the Podocarpaceae family) also have occurred in New Zealand (Ogden et al.; 2003, p. 759). *Prumnopitys ladei* (F.M.Bailey) de Laub. (brown pine; Mount Spurgeon black pine) is a large podocarp tree up to 30m high, and the only species occurring in Australia and is endemic (Brophy et al.; 2006, p. 212).

3.2.5.3 Chemistry of conifer resin

Distinguishing between the resins from different species is particularly difficult for the numerous conifers of the southern hemisphere. These difficulties within the Araucariaceae family are reflected by the difficulties in distinguishing the species apart based on the wood anatomy (Heady et al.; 2002, p. 356), and other botanical features like the resin canal patterns which are also complicated across the family (Suzuki; 1979).

Resins from the non-Araucariaceae conifers share similar chemical components to those within the Araucariaceae, also polymerising and changing with age and degradation. Many of the same issues in distinguishing species are assumed to also apply to these other conifer resins, though not as much research has been conducted to date.

Previous work on the chemistry of the Araucariaceae and non-Araucariaceae resins is summarised here.

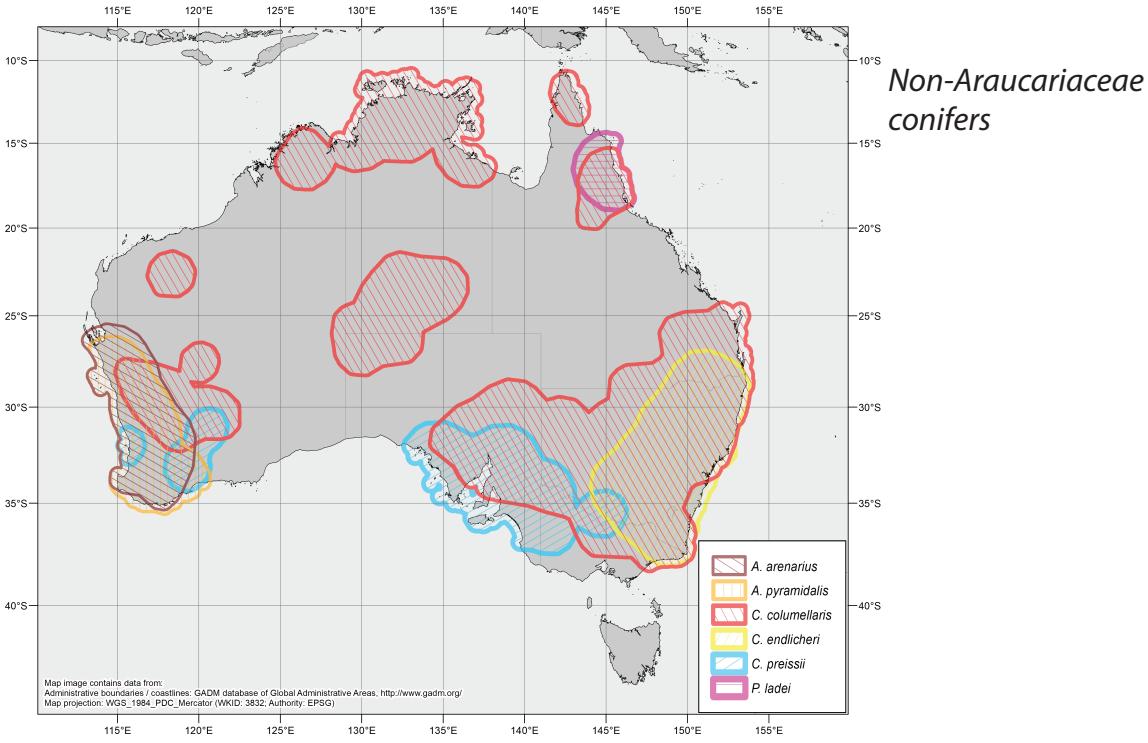


FIGURE 3.2: Map of distributions of non-Araucariaceae conifer species included in the reference collection
Distribution data from ALA (2018); GBIF (2018)

Araucariaceae resin

There is a complex taxonomical relationship in terms of resin chemistry within the Araucariaceae family, as the resins are all very similar with only minor differences between resins of different species across the genera. Identifying and distinguishing between the resins from different species becomes more difficult as the resins can change chemically as they mature.

Different analytical methods are able to focus on different aspects of the resin. The study of diterpenoids from conifers, often from the essential oils (including from the leaf), has been touched upon in the literature but is fairly sporadic in terms of the species studied and the methods used. Previous studies that have been published on diterpenoids from the Araucariaceae[3] are shown in Table 3.1.

Cox et al. (2007, p. 347), report that Araucariaceae resin consists of labdane-type compounds including the readily polymerisable communic acids, pimarane-type and abietane type-compounds, but with no evidence of for the presence of phenolic diterpenes from their analysis by GC-MS.

Previous chemical analysis of the resin from different species of *Agathis* shows that it is possible to distinguish chemically between three kauris in northern Queensland, black, bull and north Queensland kauri (*A. atropurpurea*, *A. microstachya*, and *A. robusta*) (Carman and Marty; 1970). Smith et al. (1981) identify the diterpene acids in two further pacific kauris, *A. lanceolata*, and*A. macrophylla* (also *A. vitiensis* but this is now classed as a synonym of *A, macrophylla*). Matheson and McCollum (2014) analysed a number of resins by FTIR and GC-MS, including *A. bidwillii*, *A. cunninghamii* and *A. heterophylla*, though none were found on any of the museum artefacts in the study, and the details were not published.

[3]Correct at time of writing, up to 2014. Edit: Seyfullah et al. (2015) published their FTIR analyses of several of the Araucariaceae resins, including *Wollemia nobilis* in their paper on New Zealand amber.

TABLE 3.1: Previous studies on diterpenoids from Araucariaceae

		Species included in this study																								
		Unknown Agathis sp.	Agathis alba (Lam.)Foxw.	Agathis atropurpurea B.Hyland	Agathis australis (D.Don) Lindl.	Agathis dammara (Lamb.)Rich.&Rich.	Agathis labillardieri Warb.	Agathis lanceolata Warb.	Agathis macrophylla (Lindl.)Mast.	Agathis microstachya J.FBailey&C..T.White	Agathis moorei (Lindl.)Mast.	Agathis ovata (C.Moore ex Vieill.)Warb.	Argathis robusta (C.Moore ex F.Muell.)F.M.Bailey	Araucaria bidwillii Hook.	Araucaria columnaris (G.Forst.)Hook.	Araucaria cunninghamii Mudie	Araucaria heterophylla (Salisb.)Franco	Wollemia nobilis W.G.Jones, K.D.Hill&J.M.Allen	Actinostrobus arenarius C.A.Gardner	Actinostrobus pyramidalis Miq.	Callitris columellaris F.Muell.	Callitris endlicheri (Parl.)F.M.Bailey	Callitris pressii Miq.	Prumnopitys ladei (F.M.Bailey)de Laub.
NMR	Smith et al. 1981							X	X																	
	Anderson et al. 1992																									
	Thomas 1966				X																					
	Brophy et al. 2000			X	X				X	X	X	X	X	X	X	X	X	X								
	Lambert et al. 2005			X	X			X	X		X				X	X		X								
	Lambert et al. 2007			X	X						X		X		X	X	X	X				X		X		
	Lambert et al. 2008																									
	Lyons et al. 2009				X																					
	Lambert et al. 2011																									
FTIR	Poinar Jr & Havercamp 1985																									
	Lambert et al. 2008																									
	Lyons et al. 2009				X																					
	Matheson & McCollum 2014													X		X	X	X				X	X			
GC	Thomas 1966				X																					
	Carman & Marty 1970			(X)						X			X													
	Smith et al. 1981							X	X																	
	Lebouvier et al. 2013										X	X			X											
MS	Regert et al. 2008		X		X																					
GC-MS	Brophy et al. 2000			X	X				X	X	X	X	X	X	X	X	X	X								
	Brophy et al. 2004																			X	X					
	Brophy et al. 2007																					X	X	X		
	Cox et al. 2007				X								X	X	X	X						X		X		
	Lambert et al. 2008																									
	Regert et al. 2008		X		X																					
	Lebouvier et al. 2013										X	X			X											
	Matheson & McCollum 2014													X		X	X	X				X	X			
	Romero-Noguera et al. 2014					X																				
Py-MS	Poinar Jr & Havercamp 1985																									
Py-GC-MS	Anderson et al. 1992																									
	Scalarone et al. 2003	X																								
	Regert et al. 2008		X		X																					
	Romero-Noguera et al. 2014					X																				

		Species not included in this study																								
		Araucaria angustifolia	Araucaria araucana	Araucaria humboldtensis	Araucaria hunsteinii	Araucaria laubenfelsii	Araucaria luxurians	Araucaria montana	Araucaria muelleri	Araucaria scopulorum	Callitris baileyi	Callitris canescens	Callitris drummondii	Callitris glaucophylla	Callitris gracilis	Callitris intratropica	Callitris macleayana	Callitris monticola	Callitris muelleri	Callitris oblonga	Callitris sulcata	Callitris pancheri	Callitris rhomboidea	Callitris roei	Callitris tuberculata	Callitris verrucosa	Actinostrobus acuminatus	Prumnopitys andinus
NMR	Smith et al. 1981																											
	Anderson et al. 1992																											
	Thomas 1966																											
	Brophy et al. 2000	X			X		X	X	X	X																		
	Lambert et al. 2005		X			X																						
	Lambert et al. 2007	X	X	X		X																						X
	Lambert et al. 2008																											
	Lyons et al. 2009																											
	Lambert et al. 2011																											
FTIR	Poinar Jr & Havercamp 1985																											
	Lambert et al. 2008																											
	Lyons et al. 2009																											
	Matheson & McCollum 2014															X												
GC	Thomas 1966																											
	Carman & Marty 1970																											
	Smith et al. 1981																											
	Lebouvier et al. 2013																											
MS	Regert et al. 2008																											
GC-MS	Brophy et al. 2000	X			X		X	X	X	X																		
	Brophy et al. 2004																										X	
	Brophy et al. 2007												X	X	X	X	X	X	X	X			X	X	X	X		
	Cox et al. 2007							X																				
	Lambert et al. 2008																											
	Regert et al. 2008																											
	Lebouvier et al. 2013															X												
	Matheson & McCollum 2014																											
	Romero-Noguera et al. 2014																											
Py-MS	Poinar Jr & Havercamp 1985																											
Py-GC-MS	Anderson et al. 1992																											
	Scalarone et al. 2003																											
	Regert et al. 2008																											
	Romero-Noguera et al. 2014																											

Several of the *Araucaria* species are gum-resins, meaning they contain a polysaccharide portion. The gum fraction has been analysed and reported elsewhere (Anderson and Munro; 1969; Aspinall and Mckenna; 1968), and is not of significance to this project due to its water-solubility and thus low chance of archaeological preservation. As concluded by Langenheim (2003, p. 59) previous analyses shows that "There is relatively little variability in the gum fraction of resin from different species of *Araucaria*, the terpenoid fraction, however, has received little study." Mills and White (1977, p. 18) summarise that the *Araucaria* resins are rather varied with labdane compounds predominating.

There are considerable gaps in the published research. According to Coulerie and Poullain (2015, p. 896) of the 44 endemic conifers to New Caledonia, only a few have been subjected to extended study of their chemistry. Twenty of these species still remain with no data in the literature at all, and only 18 publications are specifically on the chemical constituents, mostly from the leaves and wood, of the endemic New Caledonian conifers. The only resin analyses reported were those of *Agathis lanceolata*, noting that diterpenes and agathic acids are the main sonstituents, and *Araucaria columnaris* noting the large range of sesquiterpenes in the resin essential oils Coulerie and Poullain (2015, p. 853). Research on these conifer species is important to gain insight to encourage cultivation and enlarge their population as all of the New Caledonian species are currently classed as endangered (Coulerie and Poullain; 2015, p. 896).

Previous work on *Wollemia nobilis* suggests that the species is both similar to and distinct from the *Agathis* and *Araucaria* species (Brophy et al.; 2000; Heady et al.; 2002; Seyfullah et al.; 2015).

Cupressaceae resin

Previous chemical analysis of both types of sandarac resin (*Tertraclinis articulata* (Vahl)

Mast. from North Africa and *Callitris verrucosa* R.Br. from NSW and QLD) found them to contain 70% polymerised polycommunic acid. Remaining diterpenoids included sandaracopimaric acid (major component) together with its 12-acetoxy derivative, as well as some phenols including totarol, and some minor labdanoid compounds (Regert et al.; 2008, p. 673).

Early chemical study of the resin from *Callitris columellaris* F.Muller found it to contain "inter alia cis- and trans-communic acids and a related acid with the conjugated diene side-chain" (Mills and White; 1977). Proton magnetic resonance analysis of *Callitris columellaria* (assumed to be *C. columellaris*) and *C. preissii* resins, by Lambert et al. (2007, p. 1286-7) demonstrated "important differences from those of the Araucariaceae" and found the chemistry of *Callitris* resin to be more similar to that of the *Pinaceae* family.

Cox et al. (2007) found that ferruginol derivatives dominated the phenolic compounds in Cupressaceae. Similarly, Steigenberger and Herm (2011, p. 1772) conclude that "Phenols, such as totarol and ferruginol are highly characteristic for sandarac, but they are difficult to detect when a methylation agent is used for the GC-MS analysis" and that "Sandarac contains various characteristic compounds but it is also known to change very much through ageing" (Steigenberger and Herm; 2011, p. 1773).

Cox et al. (2007) also found that callitrisic acid is only found in *Callitris* sp. Callitrisic acid is therefore a significant taxonomic marker for the genus. Callitrisic acid (+-4-Epidehydroabietic acid) is described in the literature (Gough; 1968; Mori and Matsui; 1968). Importantly, the methylated derivative, callitrisic acid, methyl ester, is very similar in its mass spectrum to dehydroabietic acid, methyl ester (Gough; 1968, p. 295).

No literature on the resins of *Actinostrobus* has been found to date. The woods of all three species (*A. acuminatus*, *A. arenarius*, and *A. pyramidalis*) have been found to be

anatomically similar with no qualitative differences to distinguish each species from another, although there were quantitative differences between the analytical results for each species (Heady and Evans; 2005, p. 89).

Brophy et al. (2007, p. 69) highlighted that diterpene hydrocarbons were either not detected, or were present at very low levels, in the leaf oils of several species in the Cupressaceae family, including *Actinostrobus* spp. They described the composition of the leaf oils of *Actinostrobus* as mirroring that of the majority of species within the *Callitris* in its large amounts of monoterpene hydrocarbons, particularly [alpha]-pinene and limonene (Brophy et al.; 2007, p. 69).

Podocarpaceae resin

Some chemistry has been reported on *Prumnopitys* spp., particularly on *P. ladei* (Brophy et al.; 2006; Smith et al.; 2008), but none on the resin. Analysis of the leaf oils of *P. ladei* by Brophy et al. (2006, p. 213) found it to contain approximately equal amounts of mon-, sesqui- and diterpenes, the major diterpenes being: rimuene, kaurene, beyerene, 13-isopimaradiene (in order of abundance). All the diterpenes identified in *P. ladei* were also found in *P. ferruginea* and *P. taxifolia* but there was some variation in the sesquiterpenes (Brophy et al.; 2006, p. 213). The foliage of *P. ferruginea*, the New Zealand species, has been found by Clarke et al. (1994) to contain similar diterpenes.

Podocarpus is another genus in the Podocarpaceae family. Cox et al. (2007) found that *Podocarpus* samples were dominated by totarol derivatives and structures related to ferruginol, while other members of Podocarpaceae were dominated by quite different compound types, though this did not include *Prumnopitys*. Further literature on Podocarpaceae chemistry describes the presence of totarol derivatives, podocarpic acid, and sitosterol (Coulerie

and Poullain; 2015, p. 848) but there is not much specific to *Prumnopitys*. The New Caledonian species *P. ferruginoide*, along with many of the other New Caledonian Podocarpaceae species still remains unexplored (Coulerie and Poullain; 2015, 851).

The chemistry of the resin from any Podocarpaceae species is yet to be published.

3.2.5.4 Chemical alterations in conifer resin

In order to understand the chemistry of the resin from the conifers, to be able to distinguish between different genera or species, and to identify these types of resins in aged, including archaeological, samples, the changes that occur over time need to be considered. Ageing and degradation occurs in all resins, like any other organic material, but the changes that occur in the conifer-type diterpenic resins are particularly prominent. To be able to recognise an aged and degraded version of conifer resin, the natural degradation pathways need to be understood.

Exposure to light and air

The diterpenoid resins of the conifers, containing communic or ozic acids, start to polymerise on exposure to light and air as soon as they exude from the tree, and can become hardened very quickly (Langenheim; 2003; Regert et al.; 2008, p. 670). Fossil resins are known to be resistant to further maturation changes, once they have reached this stage (Thomas; 1969). Semi-fossilised resins, such as the kauri that was harvested from the ground by the gum-diggers, are hundreds to thousands of years old, but have not yet reached complete fossilisation. Previous work on the maturation and organic geochemistry of New Zealand and Australian fossil resins has been published by Thomas (1969) and Lyons et al. (2009). There is also plenty of general literature on fossilised resins or amber,

and resinites (Anderson et al.; 1992; Lambert et al.; 2008, 2011; Poinar Jr. and Haverkamp; 1985; Langenheim and Beck; 1965; Langenheim; 1969; Larsson; 1978).

Many of the free diterpenoids (not polymerised) identified by GC-MS that have been detected in fresh samples of conifer resin totally disappear in aged samples, including sandaracompimaric acid, agathic acid and its monomethyl ester (methylated to dimethyl agathate), agathalic acid, acetoxy agatholic acid, cis- and trans-communic acid (Scalarone et al.; 2003a, p. 120). However, Scalarone et al. (2003a, p. 131) found that other free diterpenoids that were absent in the un-aged resins were identified in the aged resins. These compounds, thought to be degradation products derived from original components of the resins, are: 19-norlabda-8(20),13-dien-15-oic acid, which might derive from agathalic and agathic acids by loss of aldehyde and carboxylic groups in C4; 19-norlabda-4,8(20), 13-trien-15-oic acid, a dehydrogenation product of methyl 19-norlabda-8(20), 13-dien-15-oate and its isomer; and agatholic acid, which is reasonably the hydrolysis product of acetoxy agatholic acid (Scalarone et al.; 2003a, p. 131).

Ageing and heating

The only previous work specifically on the effects of ageing and heating degradation on the chemistry of conifer resins has been the study of the biodeterioration in varnish from works of art, focussing on colophony from the pine resins, mainly from the genus *Pinus* (Pinaceae), which is composed of abietane and pimarane acids, as summarised by Scalarone and Chiantore (2009, p. 333). The characteristic marker compounds for *Pinus*, especially in the aged resins and seen in archaeological resins, are the oxidation products of abietic acid, such as dehydroabietic acid (DHA), 7-oxo-DHA, 7-hydroxy-DHA, 15-hydroxy-DHA and 15-hydroxy-7-oxo-DHA (Scalarone and Chiantore; 2009, p. 333; Pollard and Heron; 1996, p. 247; Mills and White; 1994; Modugno and Ribechini; 2009, p. 221; Echard et al.;

2007, p. 175). Pimarane acids are generally more stable than abietic acid (Fox et al.; 1995, p. 369) As Auraucariaceae resin also consists of abietane and pimarane acids, the same oxidation products are likely to occur, but it also contains labdane-type compounds.

Occurrence of methylated diterpenoid acids can indicate a pyrolytic treatment of, for example, resinous pine wood to form pine pitch "The methanol released in the hard heating of wood reacts easily with the diterpenic acids to produce, above all, methyl dehydroabietate (the methyl ester of dehydroabietic acid (DHA)), which is absent in pitch produced by heating resin alone" (Modugno and Ribechini; 2009, p. 221). A down side of using methylation to derivatise the resin acids means that the presence of methyl esters in the original material can be masked, however, unlike in the Mediterranean, the process of making pitch from the Araucariaceae wood is not commonly documented in Oceania.

Retene (7-isopropyl-1-methylphenanthrene) can also be an indicator of thermal treatments of abietane acids, as it is a dialkyl-substituted polyaromatic hydrocarbon (PAH) derived thermally and microbially from dehydroabietic acid (Modugno and Ribechini; 2009, p. 221; Leppänen and Oikari; 1999) and is a stable defunctionalised end-product (Pollard and Heron; 1996, p. 248). Pine tar boiled for pitch often produces retene and other aromatic compounds such as norabietatrienes and 1,2,3,4-tetrahydroretene (Reber and Hart; 2008). 7-oxo-dehydrodehydroabietic acid has also been identified as an atypical oxidation product that also indicates excessive heating of resin with abietane-type compounds (Baumer et al.; 2009, p. 137).

The main component (over 70%) of both sandarac (Tetraclinis articulata - similar to the Australian sandarac of *Callitris* spp.) and Manila copal (*Agathis dammara*) is communic acid, which is a bicyclical diterpenoid of labdanic structure which polymerises spontaneously to polycommunic acid (Romero-Noguera et al.; 2014, p. 99). The main degradation

processes involved in the ageing of sandarac and Manila copal, are a "combination of cross-linking and cleavage reactions, mostly affecting the polymeric component, and isomerisation and defunctionalisation of the low-molecular weight components" (Scalarone et al.; 2003a, p. 131). Romero-Noguera et al. (2014, p. 99) concludes that "Polycommunic acid is responsible for the polar character and the low solubility exhibited by these resins after ageing, and makes them clearly different from other natural diterpenic resins such as colophony" from *Pinus*.

An awareness of these changes that are likely to occur in the samples will help to recognise signs of the presence of conifer resins in the aged ethnographic museum samples.

3.3 Results from GC-MS analysis of the conifer resin reference collection

3.3.1 Araucariaceae resin samples

There are three genera in the Araucariaceae family and they all produce very similar resins.

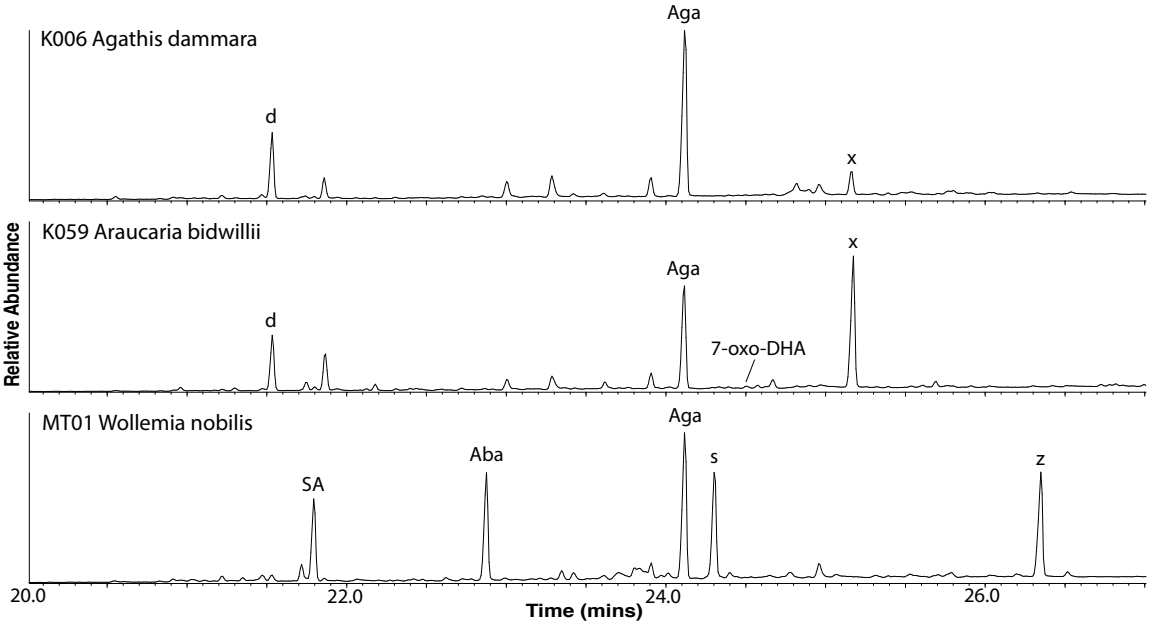


FIGURE 3.3: Partial chromatograms of resin samples K006 *Agathis dammara*, K059 *Araucaria bidwillii* and MT01 *Wollemia nobilis*

The similarities of these resins is demonstrated in Figure 3.3 showing the partial chromatograms of the diterpenic region (elution period of 20-27 minutes) of a resin sample from each of the three Araucariaceae genera. The chromatograms for all of the Araucariaceae resin samples can be found in Appendix H.

The differences in composition between the different Araucariaceae samples can be seen in Table 3.2 and the mass spectral data can be found in Appendix D.

TABLE 3.2: Presence of the main compounds in the resin of different species of the Araucariaceae family

Relative peak size L = large M = medium S = small T=Trace Peak	*A. alba*	*A. atropurpurea*	*A. australis*	*A. dammara*	*A. labillardierei*	*A. lanceolata*	*A. macrophylla*	*A. microstachya*	*A. moorei*	*A. ovata*	*A. robusta*	*A. sp.*	*A. sp.*	*Ar. bidwillii*	*Ar. columnaris*	*Ar. cunninghamii*	*Ar. heterophylla*	*W. nobilis*
b	M																	
tCA		M			M	M	L	M		M	L	M			M	M		
d				M	M	M								M		S		
SA	M		L			M	M	L		M	L	L	L				M	L
e	L		M					M			M				M		L	
Di-DHA			M								M							
Aba		L				S	M	L		M	M	M	M					L
p		M	M			S			M	M								
Aga	L	L	L	L	L	L	L	M		L		L	L	L	L	M	M	L
s	S																M	L
7-oxo-DHA		M	L			S	S	M		M	M	M		T	M			
x	S			S						M				L		M		
15H7-oxo-DHA		M	M			T	S	M			S	M	M					

Agathis resin

Agathic acid, detected as its methyl ester, was found in most of the *Agathis* resin samples as expected. The samples from *A. moorei* and *A. robusta* did not contain any agathic acid.

Based on the premise that the presence of agathic acid separates the *Agathis* spp. into at least two distinguishable groups, it can be taken that the two refence *Agathis* samples of unknown species: K058, and SWF06, are unlikely to be *A. moorei* or *A. robusta*.

Araucaria resin

The *Araucaria* samples also contain a large proportion of agathic acid, and are very similar in composition to the majority of the *Agathis* samples.

***Wollemia* resin**

Wollemia nobilis (the living fossil) is also very similar in chemical composition to the other Araucariaceae species, which is in line with the morphological similarities described in the literature. Similarly to the *Agathis* and *Araucaria* samples, *W. nobilis* contains a large amount of agathic acid, but also displays another peak just after agathic acid (peak s), that appears to be related to sandaracopimaric acid, which is not in most of the *Agathis* and *Araucaria* samples. Similarly to many of the other conifer resins it contains sandaracopimaric acid, and similarly to several *Agathis* species, but unlike *Araucaria*, in proportionally large quantities.

3.3.2 Non-Araucariaceae conifer resin samples

The non-Araucariaceae conifer species included in this study are from the genera *Callitris, Actinostrobus* and *Prumnopitys*. This study includes the first characterisation of resin from several species from these genera, as far as the author is aware.

***Callitris* resin**

The *Callitris* resin samples appear to be characterised by the presence of trans-communic acid, and sandaracopimaric acid, as well as callitrisic acid in varying proportions. Callitrisic acid has previously been noted as a taxonomic marker for *Callitris* resins (Cox et al.; 2007), which is supported by the results of this study. Although when methylated the mass spectrum for callitrisic acid is very similar to that of dehydroabietic acid (Gough; 1968), the retention times are different, with callitrisic acid, methyl ester eluting significantly earlier than dehydroabietic acid, methyl ester.

The three species analysed here, *C. endlicheri, C. preissii* and *C. columellaris*, appear to have peaks that distinguish each species from the others, as shown in Figure 3.4, and

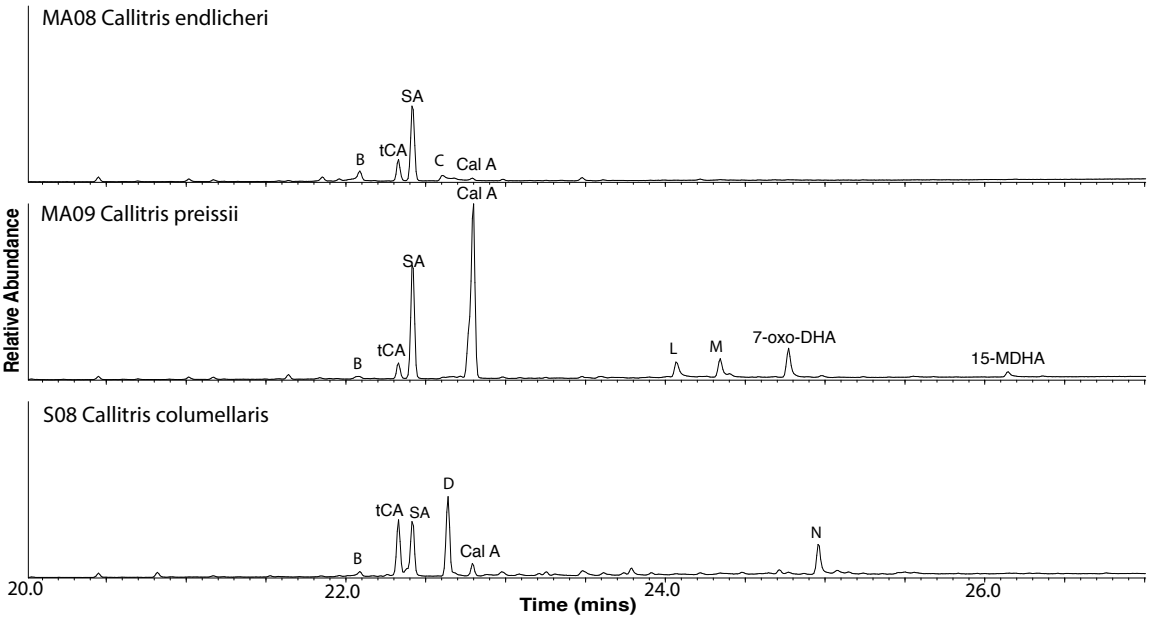


FIGURE 3.4: Partial chromatograms of *Callitris* resin samples from three different species, MA08 *C. endlicheri*, MA09 *C. preissii* and S08 *C. columellaris*

are consistent across multiple samples of the same species. Based on the chromatographic differences between the species, it is suggested that some of the samples from the Kew EBC be reassigned. Samples K041 labelled as *Callitris columellaris*, and K042 labelled as *C. endlicheri* are believed to have been wrongly identified as the chemical profiles of the resin are inconsistent with the other samples of those species, but are consistent with other samples of *C. preissii*. Therefore, samples K041 and K042 are both concluded to be from *C. preissii*.

Additionally, sample K063 was labelled as a fossil specimen of *Callitris* sp., however, the absence of callitrisic acid and the presence of agathic acid (detected as methyl esters), suggest it is more likely to be from a species in the Araucariaceae family. Analysis of the polymerised fraction via pyrolisis-GC-MS may be necessary to identify this sample to botanical origin.

Actinostrobus resin

The *Actinostrobus* samples all show peaks for the methyl esters of both sandaracopimaric acid (SA) and isopimaric acid (IPA), as well as ferruginol (F).

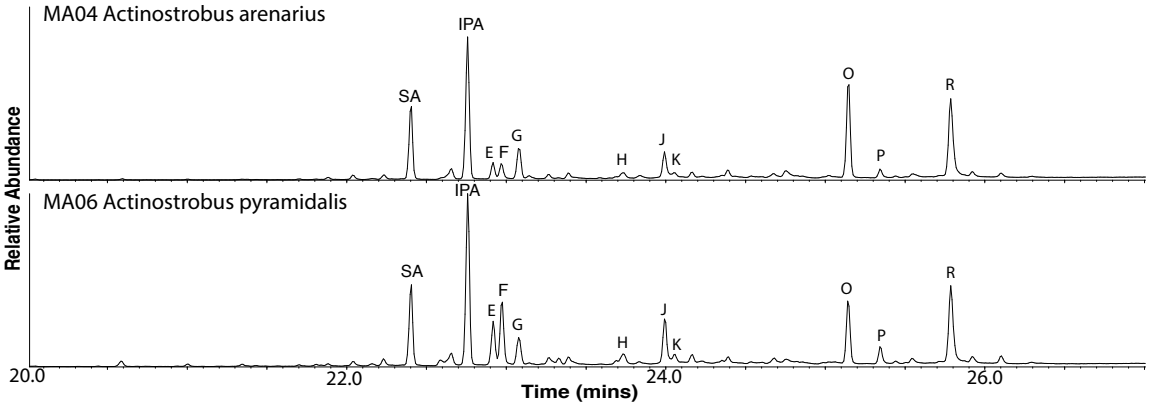


FIGURE 3.5: Partial chromatograms of *Actinostrobus* resin samples from two different species, MA04 *A. arenarius* and MA06 *A. pyramidalis*

There are several other unknown compounds that are consistent across all three *Actinostrobus* samples, as shown in Figure 3.5. The only noticable difference between the two species is the proportion of ferriginol compared to the unknown compound (peak E) that elutes just before it.

Prumnopitys resin

One resin sample from this genus was analysed and is presented here for the first time.

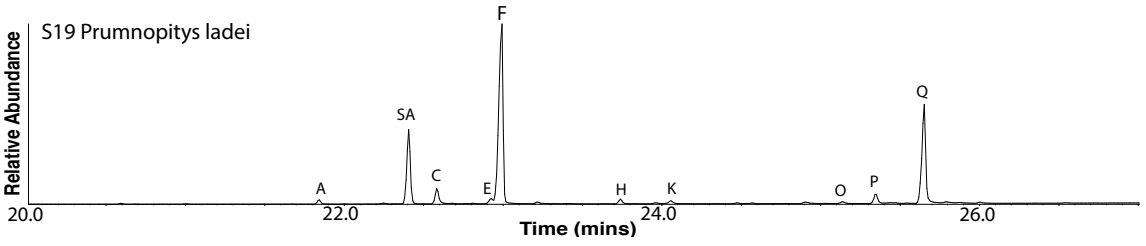


FIGURE 3.6: Partial chromatogram of *Prumnopitys ladei* resin, sample S19

The one *Prumnopitys ladei* resin sample suggests that resins from this species, or potentially the genus, may be characterised by a large amount of ferruginol compared to sandaracopimaric acid, as well as an abundance of an unknown compound depicted by peak Q (Figure

3.6). However, more samples of *Prumnopitys* resin would need to be analysed to reinforce this characterisation and strengthen such a hypothesis.

3.4 Results from GC-MS analysis of ethnographic museum artefacts with conifer-type diterpenoid resins

3.4.1 Araucariaceae resins

Several of the ethnographic resin samples, analysed by GC-MS after methylation, produced chromatograms that resembled those of the known conifer resins. A few of these were identifiable to species level. Pictures of all the ethnographic artefacts included in this thesis, and the chromatograms for each of the samples analysed, are presented in the adjoining catalogue. The significant mass spectral data for the ethnographic samples containing conifer resins are presented in Appendix D. The results of the findings are summarised here.

3.4.1.1 Species-level identification

***Agathis australis* resin**

All 22 samples from the same or similar source in New Zealand (PRM01-22) produced similar chromatograms to each other, and resembled those of the reference samples of the *Agathis* resins (Figure 3.7).

The samples are chromatographically all very similar but there are some notable variations, of which the most prominent ones can be seen in Figure 3.7. There are some minor variations between most of the samples and on closer comparison, no two are exactly the same. If these variations were indicative of different source species, the identity of resins other than *Agathis australis* resin for use as tattooing pigment would be significant for the study of resin use in New Zealand. However, the overall consistency between the samples, and the close match with the reference *Agathis australis* resin sample is high. The variations in the chemical

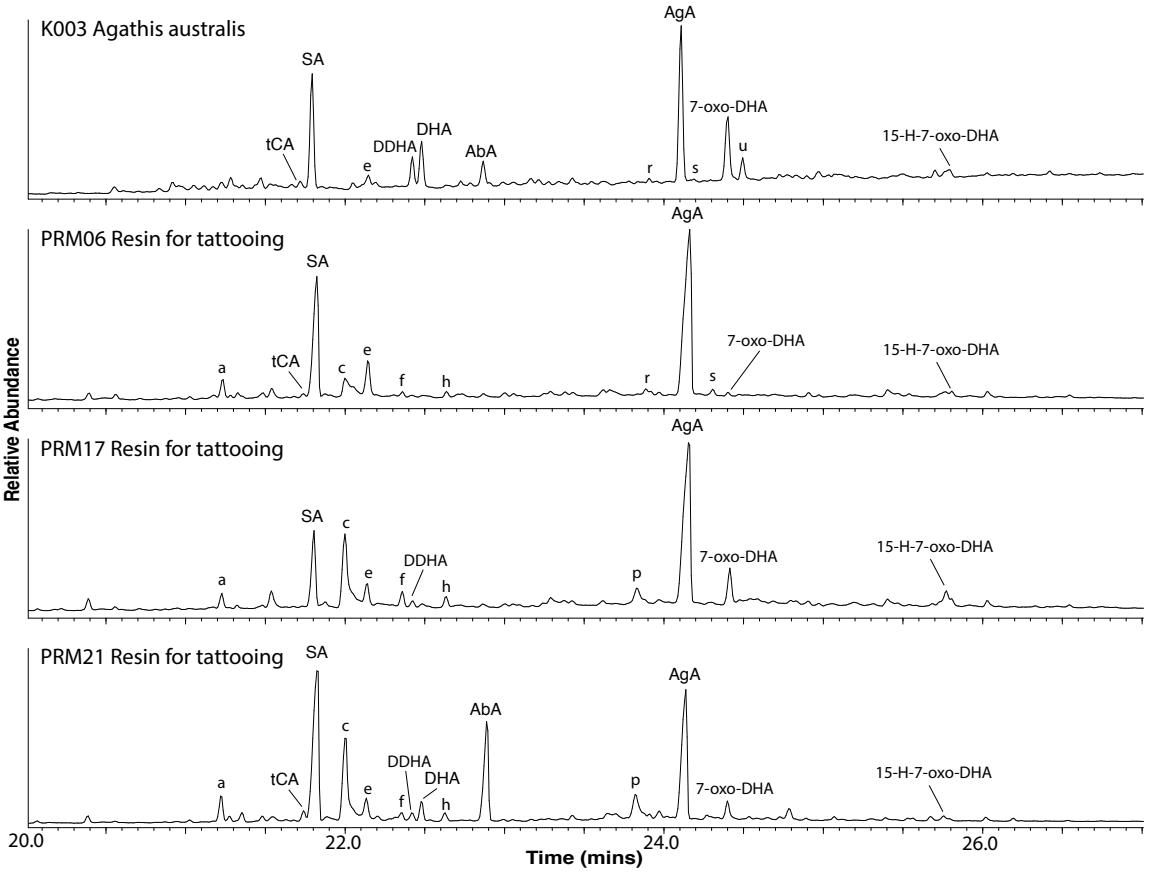


FIGURE 3.7: Partial chromatograms of K003 *Agathis australis* resin and three examples of the PRM1-22 museum resin samples

composition of these samples are more likely to be due to differing levels of degradation, and/or may be indicative of natural intra-species variation, which is interesting in itself and requires further investigation. This chemical variation demonstrates the potential difficulties in identifying *Agathis* resin to species level using this GC-MS method alone.

Samples PRM01-22 are therefore all identified as resin from *Agathis australis*, which is the true 'kauri' tree native to New Zealand. This was the expected outcome and is consistent with the current botanical and ethnobotanical knowledge of New Zealand resin.

***Agathis labillardierei* resin**

The chromatogram produced by AM19 looks very similar to that of PBH024. The chromatograms of both of these samples are consistent with the diterpenic fingerprint of the reference sample from *Agathis labillardierei*, and are therefore identified as such (Figure 3.8).

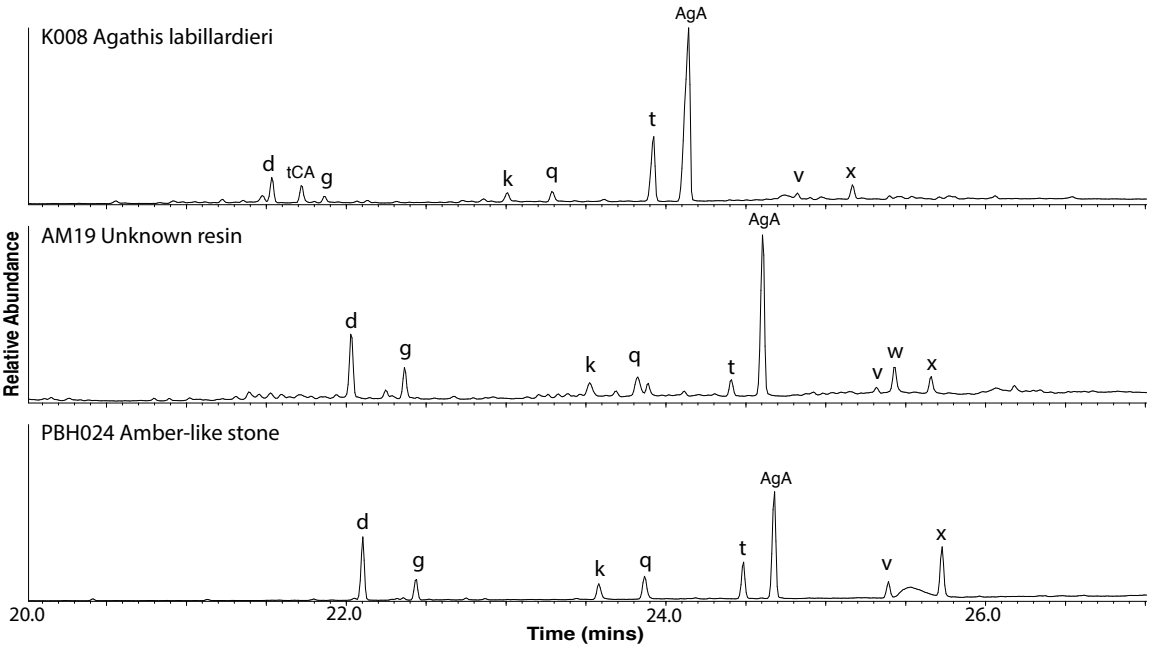


FIGURE 3.8: Partial chromatograms of K008 *Agathis labillardierei* resin with samples AM19 and PBH024
NB Retention time shift due to change in column length in the GC

The minor variations between these samples including the presence of a small amount of trans-communic acid (tCA) only in the herbarium sample and peak w only in sample AM19 can likely be attributed to degradation losses and products, although further investigation would be required to confirm this.

***Agathis macrophylla* resin**

Both samples AM16 and AM17 produced chromatograms that are consistent with that of *Agathis macrophylla* (syn. *Agathis vitiensis*), and have been identified as such (Figure 3.9).

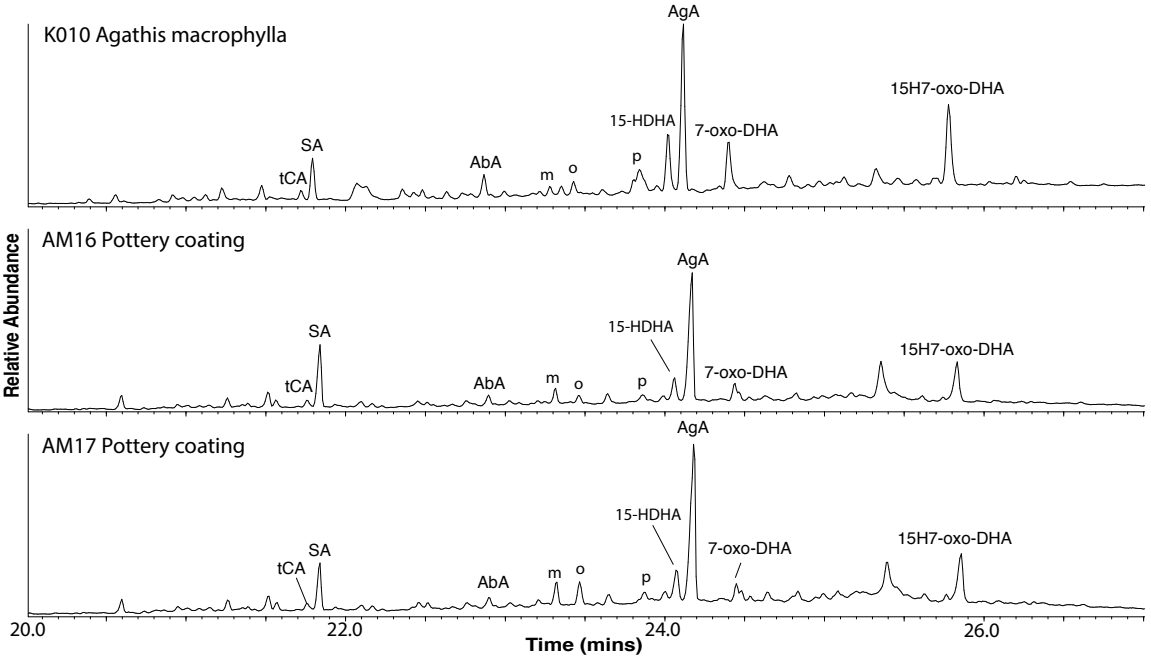


FIGURE 3.9: Partial chromatograms of K010 *Agathis macrophylla* resin with samples AM16 and AM17

Agathis alba resin

The chromatogram produced by PBH051 is similar to those of the *Agathis* reference samples, but apart from a large agathic acid methyl ester peak, there is not much else detected. However, the trace peaks match those of *Agathis alba*, though in far less abundance relative to the methyl ester of agathic acid. PBH051 is cautiously identified as *A. alba* (Figure 3.10).

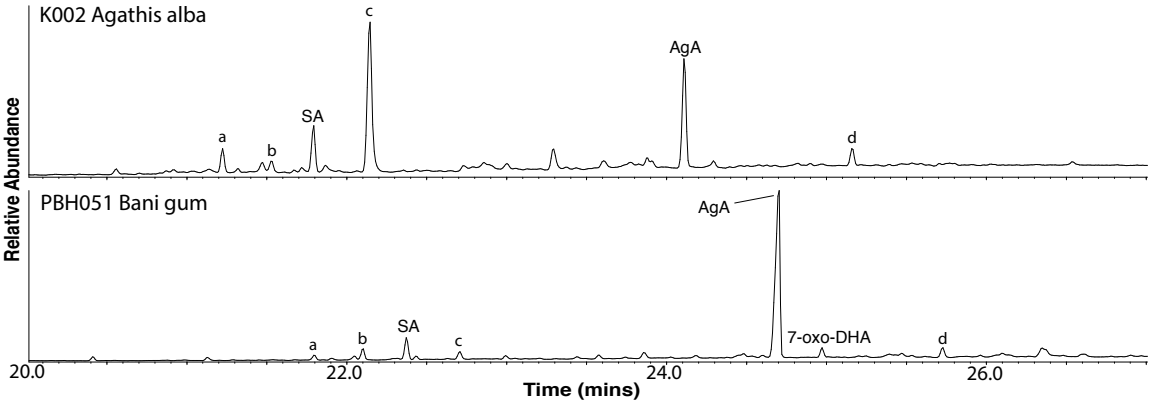


FIGURE 3.10: Partial chromatograms of K002 *Agathis alba* resin and sample PBH051 NB Retention time shift due to change in column length in the GC

3.4.1.2 Other Araucariaceae resins

Samples PBH107, PBH112 , PBH113 have very similar chromatographic profiles showing DHA, 7-oxo-DHA and 15-hydroxy-7-oxo-DHA, detected as methyl esters, as the main components (Figure 3.11).

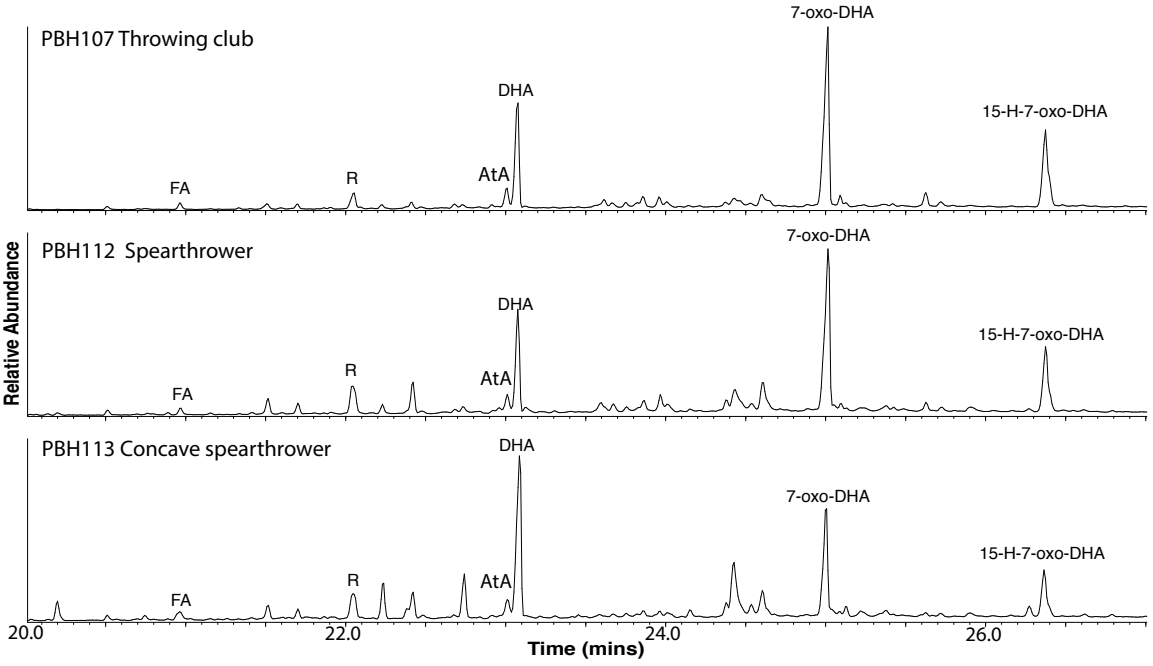


FIGURE 3.11: Partial chromatograms of samples PBH107, PBH112 and PBH113

These are oxidation markers for conifer resins. All three samples show additional smaller peaks including retene (peak R), a marker for thermal degradation of abietane-type compounds. The presence of retene, alongside an increased abundance of 7-oxo-DHA, most likely indicates a heating process in the application of the resin during the manufacture of the items. These compounds have been detected previously in samples interpreted as pine pitch. The only records for the use of pitch in Oceania note only resin from species of *Araucaria* being used, but there is no previous research on the chemical effects of heating on these resins. These compounds are different to the degradation products reported from sandarac and Manila copal by Scalarone et al. (2003b) (see section 3.2.5.4). These samples

may represent the production and use of a pitch-like material using local conifer resin, otherwise it may represent an importation of pine pitch from the northern hemisphere.

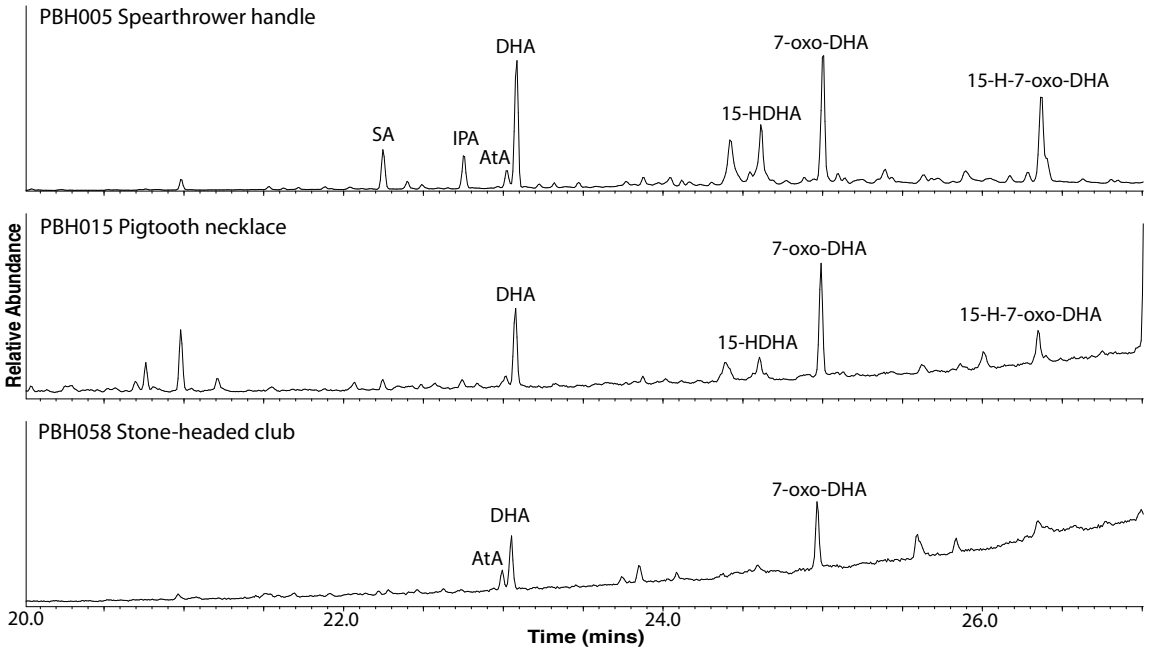


FIGURE 3.12: Partial chromatograms of samples PBH058, PBH005 and PBH015

Samples PBH005, PBH015 and PBH058 also all show the oxidation markers for abietane type compounds, DHA and 7-oxo-DHA, and some additional compounds indicative of conifer resin. These compounds occur in small and trace amounts in PBH015 and PBH058, which may be due to the diterpenic resin being highly polymerised (Figure 3.12). Analysis using a pyrolysis technique would be required to characterise the polymeric fraction of these resins.

3.4.2 Cupressaceae resins

Callitrisic acid, methyl ester (CalA) along with trace amounts of sandaracopimaric acid, methyl ester (SA) and the oxidation product 7-oxo-dehydroabietic acid, methyl ester (7-oxo-DHA) were detected in three of the ethnographic samples, AM07, PBH124, and PBH055. The presence of the compounds represented by these peaks indicates *Callitris* resin (Figure 3.13).

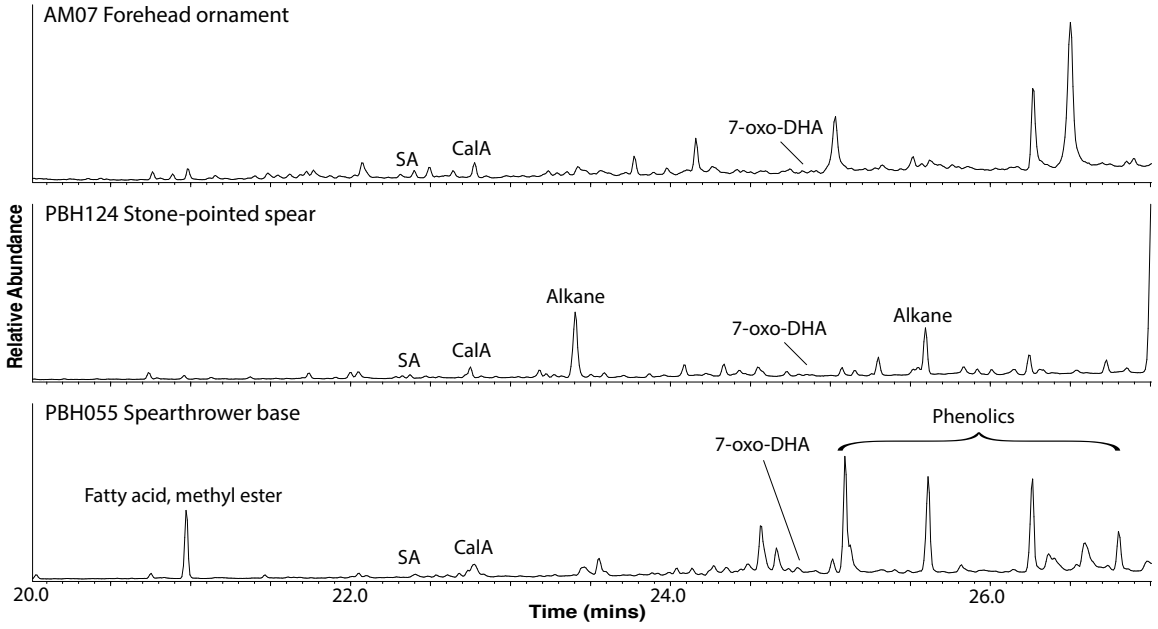


FIGURE 3.13: Partial chromatograms of samples AM07,PBH124 and PBH055

These compounds are at low levels in both samples and identification to species is not possible. The *Callitris* resin appears to be in a mixture with other materials due to the presence of other compounds often in larger relative abundances than the diterpenoid resin acids. A group of unknown compounds in AM07, as well as unknown compounds alongside alkanes in PBH124, suggest the presence of unknown materials. Sample PBH055 appears to be a mixture of the diterpenoid resin with a phenolic resin, possibly *Xanthorrhoea* (see Chapter 6).

3.4.3 Miscellaneous conifer resins

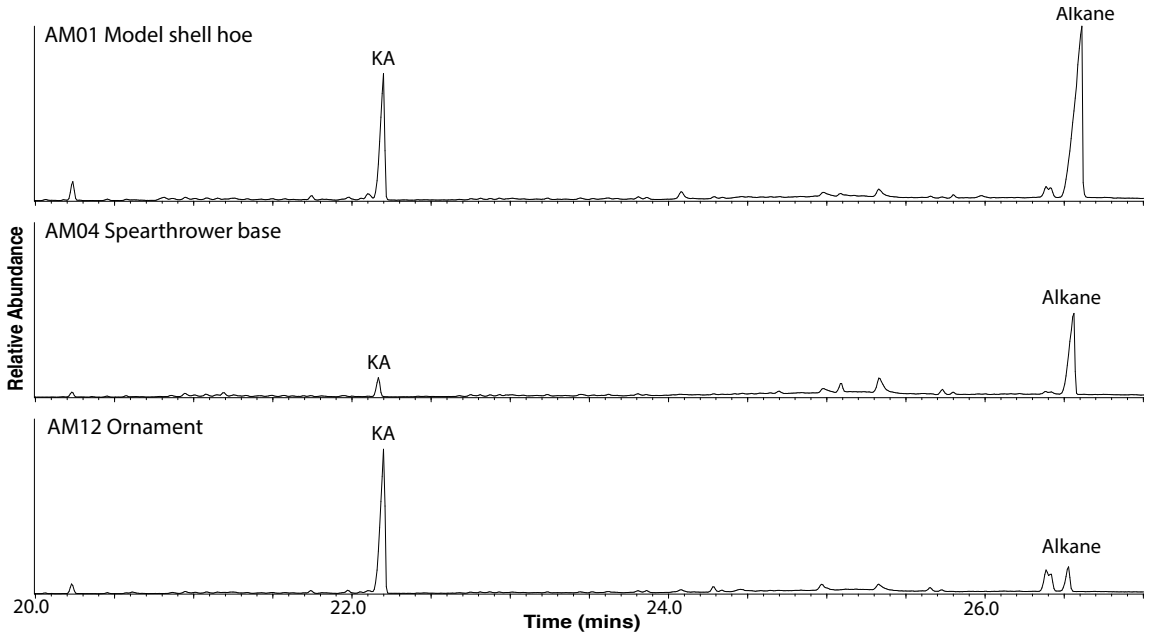


FIGURE 3.14: Partial chromatograms of samples AM01, AM04 and AM12

Samples AM01, AM04, and AM12 contain kaur-16-en-18-oic acid (a kaurane diterpenoid), detected as a methyl ester, and show very little else in the diterpenoid range of the chromatogram (Figure 3.14).

The compound 13-hydroxykaur-16-en-18-oic acid, methyl ester (also known as steviol, methyl ester or methyl steviol) (peak KA-13-H) has been detected in samples PBH098, PBH105, PBH106 and PBH125 (Figure 3.15). This compound occurs via hydroxylation of kaurenoic acid, which is indicative of oxidative degradation in air. It is possible that kaurenoic acid was the original compound in the sample and the oxidation process was catalysed by another compound in the mixture.

A similar compound, kaur-16-en-19 oic acid, methyl ester has been detected in a sample of Balsam Capivi from a collection of historic pharmaceutical samples (Steigenberger and Herm; 2011, p. 1774). Kaurenoic acid is known to be a dominant constituent of *Copaiba* oil and *Copaifera* oleo-resins native to Africa and Southern America, and modern samples of

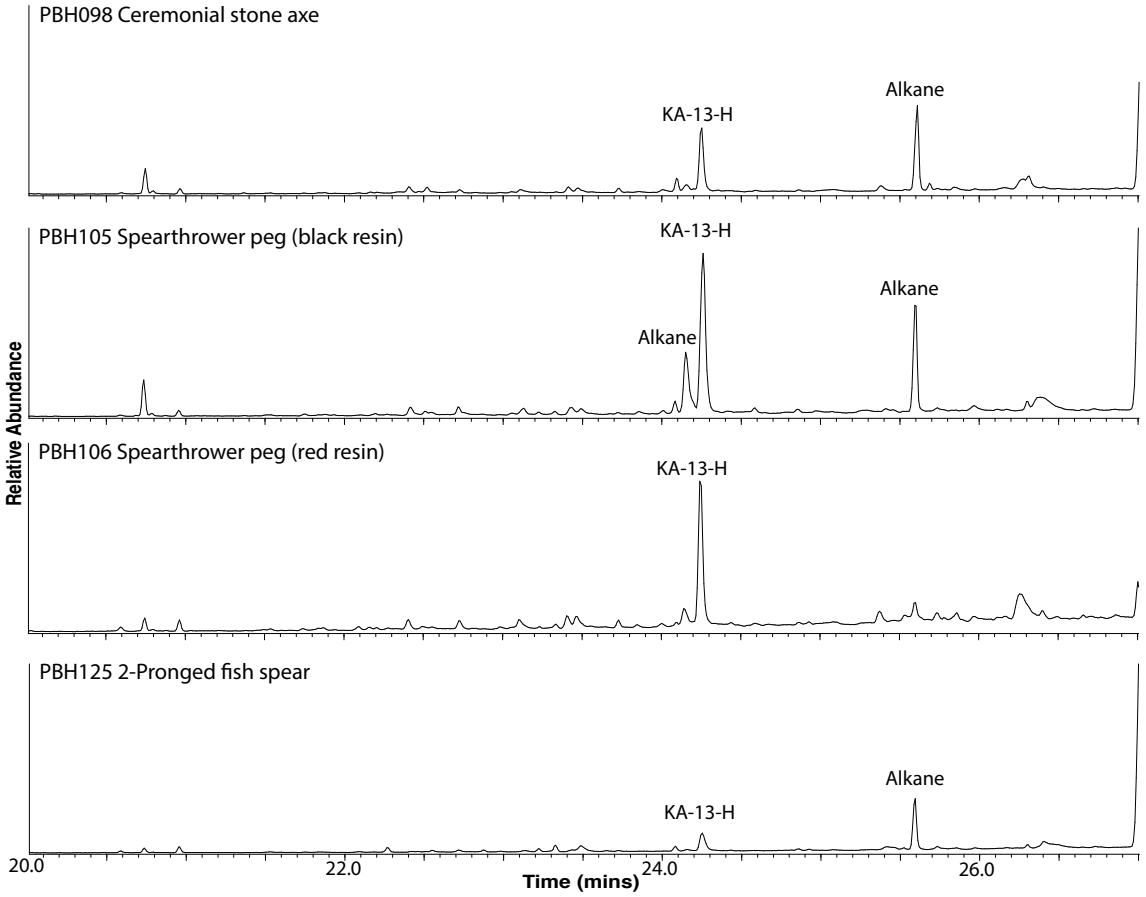


FIGURE 3.15: Partial chromatograms of samples PBH098, PBH105, PBH106 andPBH125

Copaiba balsam are often found to be adulterated with pine resin (Steigenberger and Herm; 2011, p. 1772), suggesting a strong similarity between the resin from these two different sources.

It is hypothesised that these samples represent an unknown pine-like diterpenoid resin. However, no other diterpenoids were detected in the sample, but some triterpenoids were detected in PBH098 and PBH105 (see Chapter 5), and alkanes were present in PBH098, PBH105 and PBH125.

Sample PBH025 is dominated by labdane-related compounds similar to those seen in *Copaifera* sp. resin but no kaurenoic acid was detected. The labdane acids are also dominant in *Araucaria* resin but no abietane or pimarane acids were present in sample PBH025.

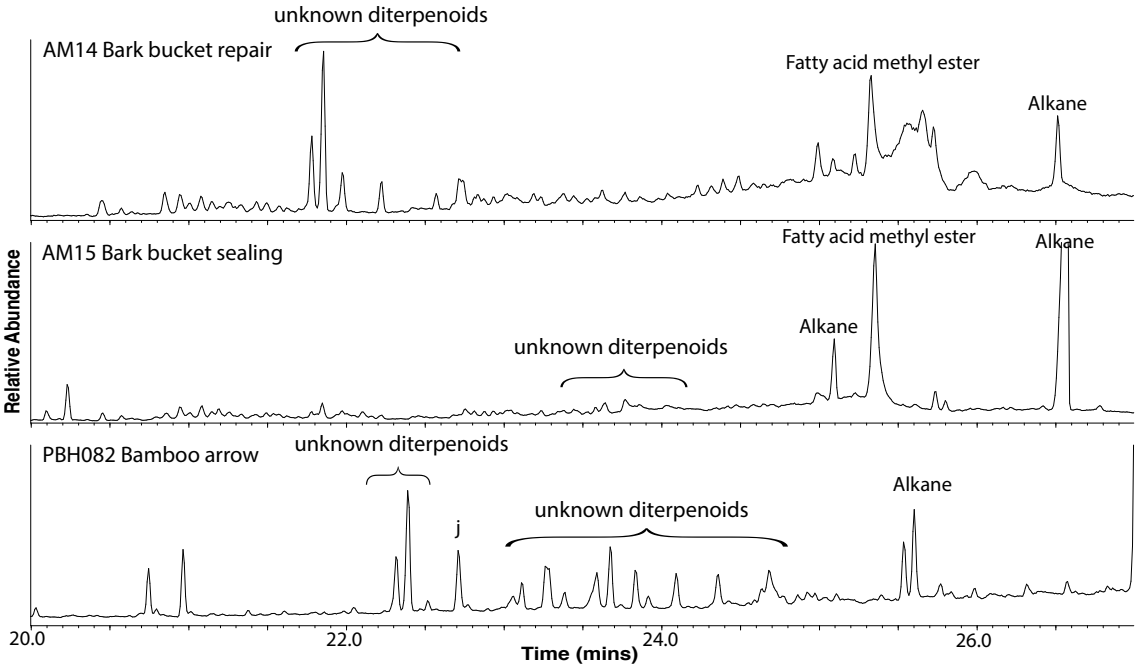


FIGURE 3.16: Partial chromatograms of samples AM14, AM15 and PBH082 j=unknown diterpenoid

Samples AM14, AM15 and PBH082 have trace peaks of unknown compounds in the diterpenoid region of the chromatogram (Figure 3.16). Sample PBH082 also displays alkanes, fatty acids and trace triterpenoids (see Chapter 5).

3.5 Conclusions

The results of the analysis of the museum resins suggests conifer resins play a significant role in Indigenous Oceania. Thirty-five of the total 173 unknown ethnographic museum samples in this project are concluded to contain diterpenic resins of the conifer type. Possible conifer-related diterpenoids have been detected in a further ten samples.

The analysis of the reference conifer samples from previously identified sources in botanic gardens, has contributed to the characterisation of a range of conifer resins from Oceania. Certain *Agathis* resins have been found to be identifiable to species, as the molecular variability between these species is distinct. However, the variation between species is very complex, as is the variation within a species as thought to be demonstrated by the kauri tattooing materials identified as *Agathis australis*. More research on the inter- versus intra-species variability is required. The identification of *Callitris* resins by the presence of callitrisic acid, as suggested in previous literature, is supported, though the data is very limited.

The ethnographic evidence from Oceania shows that particular conifer resins have useful purposes and have definitely been used in Oceania in at least the recent past. Archaeological evidence from other parts of the world, such as the Mediterranean and the Americas, shows that conifer type resins can be identified in an archaeological context, and that different types of conifer resins can potentially be distinguished. There is therefore reasonable potential for finding and being able to identify conifer resins in future Oceanian archaeology. Continued research on the chemistry of these types of resins is invaluable for this prospect, and the analysis of ethnographic museum resins is crucial in understanding the role of conifer resins in past societies in Oceania, which has so far been under-reported.

This study contributes the analysis of a large number of different known species of conifer resins, including the characterisation of resins from *Actinostrobus* and *Prumnopitys* species not previously published to the author's knowledge. There is a need for more chemical research, particularly to resolve taxonomic confusion, as the resin analysis presented in the literature is sporadic and a more consistent analysis is required. Research on endangered species is particularly important for conservation by raising their profile and encouraging local cultivation.

The detection of a series of products from the oxidation of abietane-type compounds in resins from Oceania is of particular interest as they have previously been used as markers for the presence of *Pinus* resin from the Pineaceae family of conifers. This either implies that pine resin, possibly obtained from European commercial sources, was used in the manufacture of the museum items, or that a local source of resin has a similar chemistry to *Pinus*, which potentially has implications for the use of the oxidation compounds as taxonomic markers beyond the Coniferae (or Pinophyta) division of Gymnosperms.

The detection of several markers for high-temperature heating of conifer resins is significant, suggesting that the resin on these items had been processed by heating, possibly during pitch-like production. This technological practice has not been well documented in the ethnographic literature from Oceania, with only two references to the author's knowledge (Heider; 1970; Crosby; 1973). Further research into pitch-making and the effects of heating Oceanian conifer resins would be of significant interest.

Chapter 4

Diterpenoid resins from the Angiosperms

4.1 Introduction

A category of resins that appear chemically similar to the conifer resins but have a completely distinct set of components are hypothesised to also be diterpenoid based. The chemical fingerprint for this type of resin sits within the diterpenoid retention zone on a chromatogram (GC-MS), and although the majority of the compounds are currently unidentified, previous work along with the results of this project, as discussed in this chapter, suggest the presence of diterpenoids. This resin type has therefore been categorised by the author as non-conifer diterpenoid resin. Two well-known sources of resin putatively fall into this category: spinifex resin, produced by various species of the genus *Triodia*; and northern ironwood resin, produced by the single species *Erythrophleum chlorostachys*. Both of these resinous plants produce flowers and therefore belong to the Angiosperms. Use of these resins is well documented and often discussed when referring to hafting in Australia.

This chapter will provide a background to what is known about these two sources of resin, as well as examples of these types of resins in the archaeological and ethnographic record, and how they are identified. Samples from artefacts in this study that fit into this group, diterpenoid-based but dissimilar to the conifer resins, are presented with the results of the chemical analysis and a discussion towards categorising and identifying the potential sources of the resins.

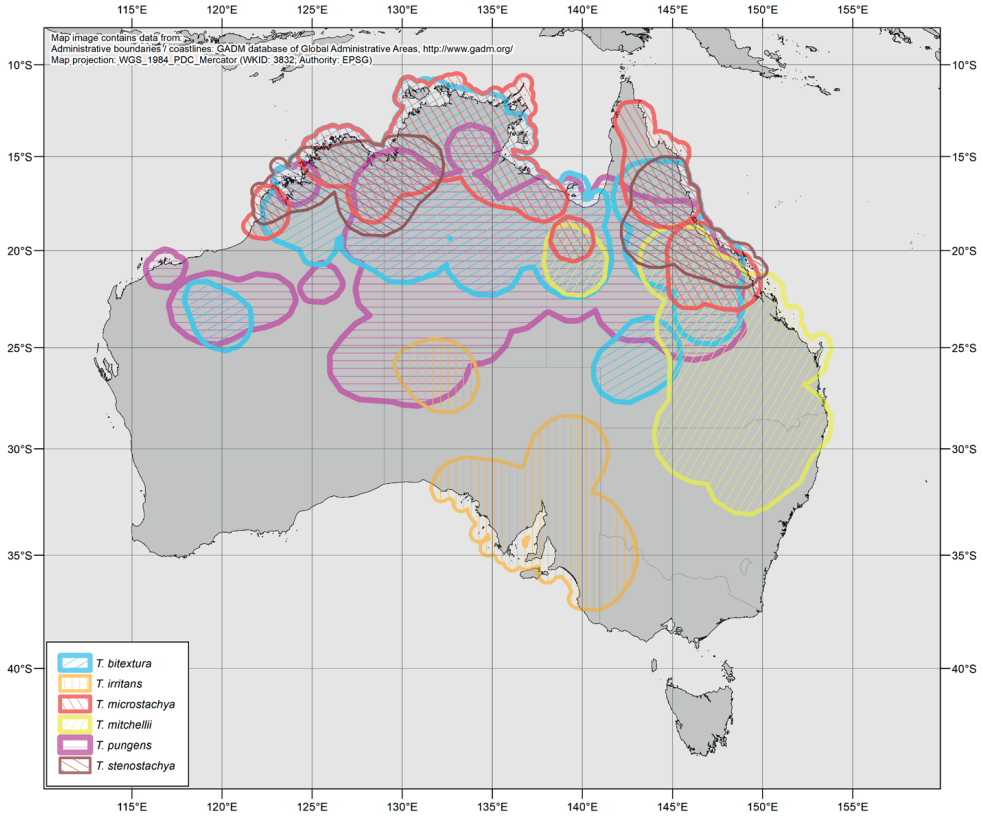
4.2 Background to *Triodia* (spinifex) and *Erythrophleum chlorostachys* (northern ironwood)

4.2.1 *Triodia* (spinifex)

Spinifex, in this context, is the common name for the perennial tussock grass in the genus *Triodia*, in the Poaceae family of the Monocot clade of Angiosperms, not to be confused with the perennial coastal grass genus *Spinifex*, also belonging to the Poaceae family. *Triodia* plants are also often referred to as 'porcupine grass' owing to the long stiff leaves that protrude out from the base in all directions, and have been described as "the scourge of mounted desert explorers", because they irritated the horses' legs (Clarke; 2008, p. 115). In the early 1980s, Cribb and Cribb (1981, p. 87) suggested not using the ambiguous term 'spinifex' for the tussock grass, and using 'porcupine grass' instead, but the use of 'spinifex' is so well engrained in the history of the use of these plants that it cannot be removed from the description of them, or the resin they produce.

The genus *Triodia* is endemic to Australia, and the spinifex plants occur in abundance throughout inland areas, thriving on the arid soils that do not support much plant life, enduring droughts, and surviving bush fires (Gamage et al.; 2012, p. 119). Not all species

More commonly documented resinous *Triodia* species



Less commonly documented resinous *Triodia* species

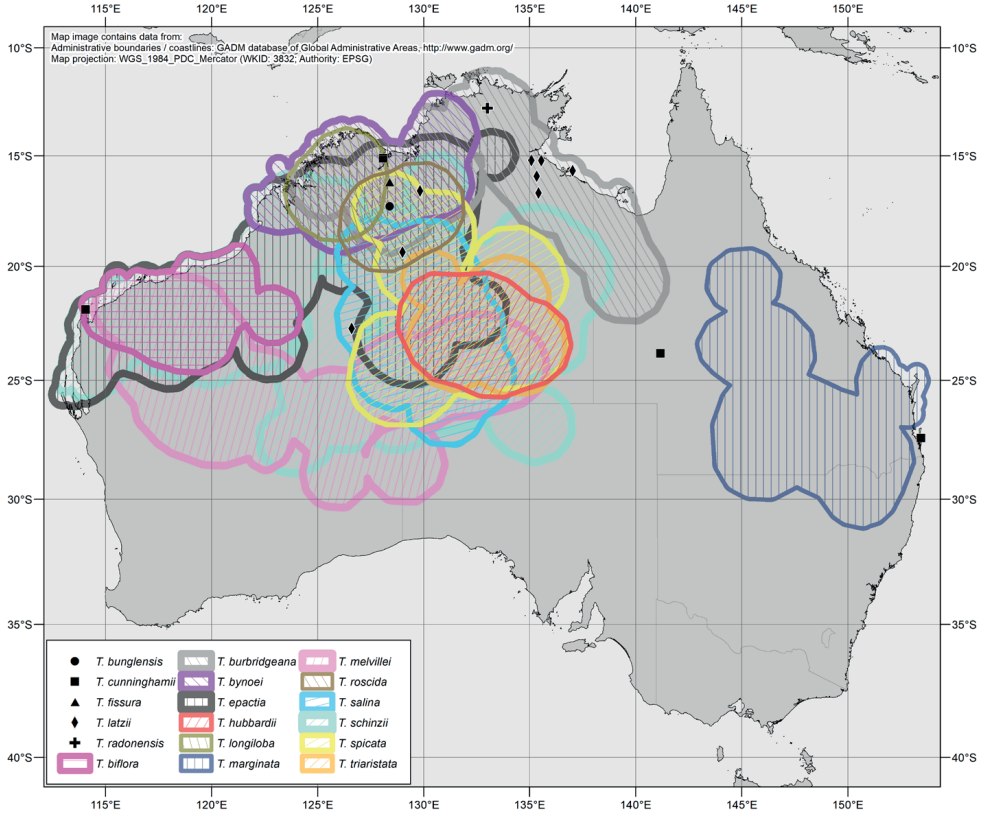


FIGURE 4.1: Maps of the distributions of resinous spinifex species
Distribution data from ALA (2018); GBIF (2018)

of spinifex (*Triodia*) produce resin, which is one of the physiological differences that splits the genus into two groups, the 'hard spinifex', and 'soft spinifex'. Only the 'soft' species are resinous. The soft species are generally more common across northern Australia (Pitman and Wallis; 2012). Figure 4.1 shows the current distribution of the soft spinifex species, based on occurrences collected by Atlas of Living Australia (ALA; 2018) and the Global Biodiversity Information Facility (GBIF; 2018).

Spinifex resin is an extremely useful resource for Aboriginal Australians and there are many ethnographic references to its use throughout the past. The porcupine-like leaves have also been extremely useful to Aboriginal Australians for a number of purposes, as have other parts of the plant. Pitman's thesis (2010) is an excellent overview of the Indigenous use of spinifex in Australia, including but not limited to resin use, with a thorough background to the plant itself and its taxonomy and geography. The wide range of uses for different parts of the *Triodia* plants, and their general economic importance is also discussed by Pitman and Wallis (2012). Spinifex resin, like the rest of the spinifex plant, does not appear to have been used outside of Australia and no reference to its use elsewhere in Oceania has been found to date, by the author.

4.2.2 *Erythrophleum chlorostachys* (northern ironwood)

Ironwood is a term used for many plants. For example, in New Guinea ironwood refers to the species *Casuarina equisetifolia* L, and in Australia, ironwood is sometimes a name for *Acacia estrophiolata*, but this is usually specified as southern ironwood, or ironwood wattle (Clarke; 2012, p. 346). Ironwood, in this thesis, refers to the northern ironwood, or Cooktown ironwood, from the particular species *Erythrophleum chlorostachys* (F.Muell.)Baill., (syn. *Erythrophloeum laboucherii* F.Muell.ex Benth, and *Laboucheria chlorostachya* F.Muell) in the family Fabaceae. This ironwood is native to northern Australia, including parts of Western

Australia, Northern Territory and Queensland. Figure 4.2 shows the current distribution of *Erythrophleum chlorostachys*, highlighting the more densely populated areas, based on occurrences collected by ALA (2018) and GBIF (2018). Other species of the *Erythrophleum* are native to Africa and East Asia, according to The Plant List (TPL; 2013).

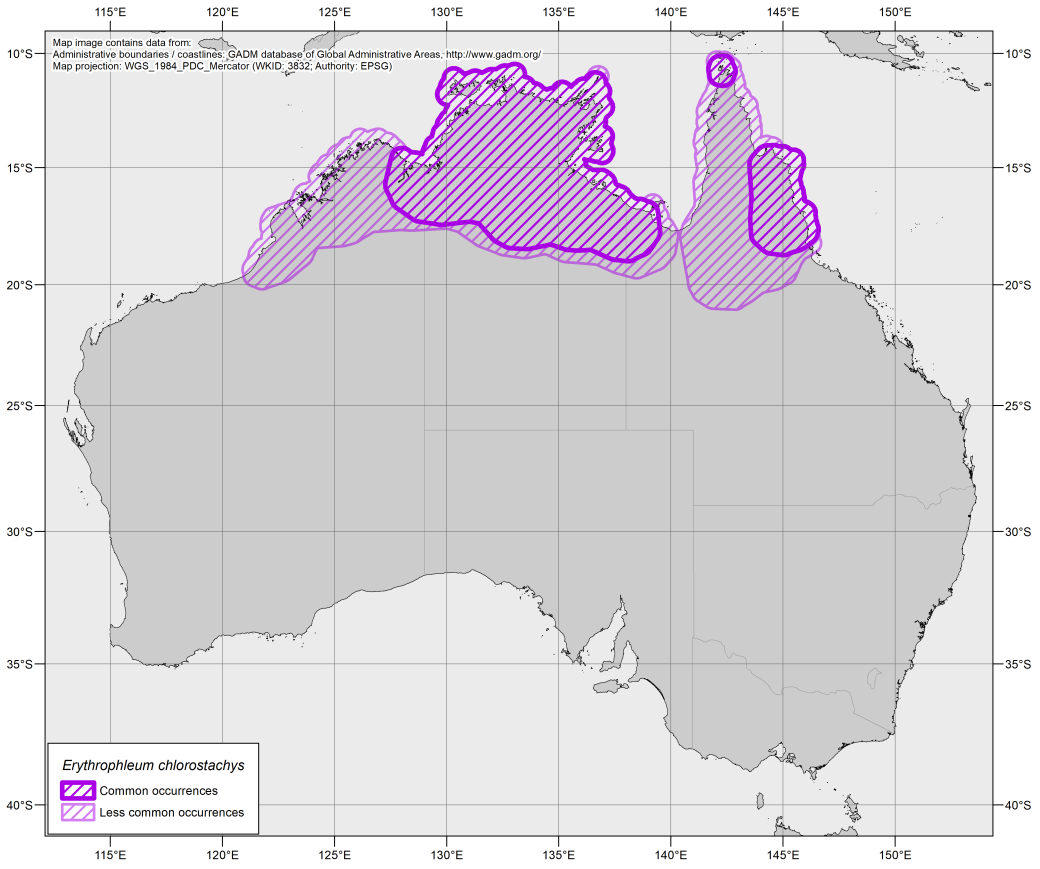


FIGURE 4.2: Map of the distribution of the ironwood species *Erythrophleum chlorostachys* Distribution data from ALA (2018); GBIF (2018)

Erythrophleum chlorostachys (northern ironwood) produces a resin that is known to have been used for hafting in Australia, in a similar way to spinifex resin. The ironwood resin has been referred to as an alternative where spinifex was not available (Parr; 1999, p. 23), yet according to Clarke (2012, p. 141) ironwood resin was the resin of choice across much of the tropics of Australia as it is a particularly strong adhesive cement, but it requires heating to extract the resin from the bark and is toxic in its molten state.

4.2.3 Resin identification

The Aboriginal use of spinifex resin, and to a lesser extent ironwood resin, is well known throughout the field of Australian anthropology and archaeology. However, specimens of resin are rarely identified to species and are often labelled as 'spinifex' without any chemical verification. There has been limited chemical analysis of this type of resin probably because it has gained little interest outside the region due to having never been exported commercially. The spinifex plant as a whole appears to have no specific interest outside Australia, but a long history of the use of spinifex (or similar) resin in Australia is evident from archaeological finds (e.g. Maloney et al.; 2015; Veitch et al.; 2005). Chemical verification of these archaeological finds would be invaluable for understanding this long-standing local importance of these plants.

4.2.4 Spinifex and ironwood resin in the archaeological record

Amorphous material that is putatively spinifex resin is occasionally found in an archaeological context, usually identified by its fairly distinctive appearance: dark, dull, and often with plant inclusions. This type of material is often assumed to be resin from *Triodia pungens*, which is the most widely distributed resin-producing species of *Triodia*. Some such archaeological finds have been summarised below, highlighting the need for continued research into the characterisation of 'spinifex' and *Triodia* resin, as well as the potential for the archaeological interpretation of such finds if the source of the resin is properly identified.

Bindon and Lofgren (1982) describe a spear with hafting residue discovered behind an intact wall section at rock shelters in the semi-arid Pilbara Region of Western Australia. When discovered, the spear was lying on the surface of fallen rocks from the walls, littered with twigs and spinifex (*Triodia* sp.) leaf blades (Bindon and Lofgren; 1982, p. 115),

giving weight to the assumption that the resin used for hafting would have also been from *Triodia* sp. The spear is thought to be of post-contact age, and is registered in the Western Australian Museum collection as A23064 (Bindon and Lofgren; 1982, p. 116). The first ethnographic account of this type of spear was by Clement and Schmelz in 1903, and the unusual hafting of this spear is described in detail by Bindon and Lofgren (1982, p. 119). Chemical identification of the resin used for this haft would shed light on the study of the development of spears and hafting techniques in the Pilbara.

Thorley (1999, p. 45) describes a rare archaeological find; a stone flake with an intact resin haft recovered from the upper levels of the deposit from Amngu Rockshelter at the middle of Palmer River (Alice Springs, NT) during excavations in 1996:

> The stone flake is made on dendritic chert of a non-local source while the haft is probably spinifex resin (sometimes referred to as spinifex 'wax') from *Triodia pungens* which grows on local sand hills. . . The resin haft has survived amazingly well. The colour has faded from black to a mottled light brown and the resin has become cracked and brittle but the shape of the haft remains otherwise intact.

The assignment of this resin to *Triodia* sp. may well be correct, as there are probably very few other resin-producing plants in the arid vicinity of Amngu Rockshelter. Indeed *Triodia pungens* is common in that area, but there are several other resin-producing species of *Triodia* also known to grow locally to Alice Springs: *T. irritans, T. hubbardii, T. salina, T. schinzii, T. spicata* and *T. triaristata*. Analysis of this specimen, with comparison to modern examples of resin collected from *Triodia pungens* and the other local species, could shed much light on the processing of spinifex resin, and its use in this region.

In the Kimberley region of northern Western Australia, there have been a few archaeological finds of the distinctive and toponymously named Kimberley points, recovered with hafting residue thought to be spinifex resin. Smith (2001) discusses archaeological finds at a site where European manufactured material had been adopted for traditional uses. A metal spear point was identified by Richard Fullagar as having traces of spinifex resin from hafting on its surface (Smith; 2001, p. 28). Maloney and O'Connor (2014) explore the direct dating of hafting resin on point technology and provide an overview of the long history of hafted Kimberley points noting their common presence in the archaeological record from around 1000 cal. BP. In 2015, a distal point fragment with a "sizeable portion" of adhering resin was excavaed from a site in the southern Kimberley and directly dated to 3160-2954 cal. BP, providing a rare demonstration of hafting technology in the prehistoric period (Maloney et al.; 2015). Chemical analysis of these finds could provide geographic data in addition to the temporal data, potentially narrowing down where the resin was sourced from, based on natural distributions of different species, and highlighting any trade of the material in and out of the Kimberley.

Archaeological examples of ironwood resin are rare, largely because the resins are either not usually identified but recorded simply as resin, or where identifications are attempted they are often assumed to be 'spinifex', as the general appearance may be similar. One find of interest is a hafted axe made from the wood of ironwood, found at a site in western Arnhem land (Langley et al.; 2016, p. 107). Although the hafting material was not described, it would be interesting to know if the resin used was from the same botanical source as the wood. In the same study, a wooden spear thrower and a digging stick with resinous residues were also described, the latter thought to be beeswax applied by European collectors for preservation of the wood (Langley et al.; 2016, p. 114). Chemical analysis of these residues would be beneficial to confirm the identifications and explore the different uses of such

materials for hafting versus conservation.

With routine chemical screening of archaeological amorphous materials becoming more common, it is likely that many more examples of spinifex resin will be identified in the archaeological record. Chemical analysis of existing archaeological examples of putative spinifex resin would not only provide additional information relevant to the context in which they were excavated, but also assist the analysis of future archaeological resin samples. Additionally, the analysis of ethnographic material can provide a framework for the type of resins likely to have been used in particular areas, indicating how best to analyse archaeological samples, as well as offer insights into the technologies behind the manufacture of such items.

4.2.5 Ethnographic accounts of spinifex and ironwood resin use in Australia

4.2.5.1 Spinifex resin

Similarly to the archaeological finds, most cases of hafting on ethnographic items are described as spinifex, with no further details. However, spinifex appears regularly in the Australian ethnographic literature and occasionally there are references to specific species of *Triodia*. There is some confusion about which species are resinous, and correlating vernacular and taxonomic names can be difficult (see section 4.2.6).

Despite these limitations, ethnographic accounts of the preparation and use of spinifex can be rich in detail, for example, an account by Binford (1984)[1] describes threshing and

[1] From his time with the Alyawara people of Central Australia, Binford (1984, p. 166) describes the heating of the spinifex resin after threshing and winnowing to leave the cleaned resin dust in a bark tray: "The men stirred the resin dust with small sticks; as the heat increased the dust began to be transformed into little lumpy balls. As this happened the men would pick the lumps out, molding them into a growing round ball."

winnowing the spinifex leaves, then heating the cleaned resin dust, whilst stirring until it formed small lumps, which were then moulded together and ironed until the resin was transformed into a "tar-like gum" (also see Powell et al.; 2013; Pitman; 2010 for more on spinifex processing).

Binford (1984, p. 172) also discusses the role of women in the manufacture of knives among the Alyawara people of Central Australia, and what he perceived his hosts's view to be on the importance of resin collection and processing[2]. It is notable that among the Alyawara the gathering and preparing of the spinifex resin was normally done by the women, and likely that boys learned the process of resin collection from their mothers. It was then the men who used the processed resin for manufacturing the knives (Binford; 1984, p. 172).

An ethnographic account by Maiden (1890, p. 639) describes a sample of spinifex resin as probably coming from *Triodia irritans R.Br.* (spinifex, porcupine grass):

He describes further "The fire was fanned with Sandy's hat, so that the three small stones got quite hot. Jacob then took two of the previously prepared sticks and removed one of the flat stones, now hot, from the fire and placed it on top of the resin ball that was sitting on the flat table rock in front of Jacob. Jacob placed his stick across the flat rock and began "ironing" the ball with the hot rock. As the hot rock was moved across the ball, rocking back and forth, the gray resin ball was transformed into a black, tar-like substance that shone and glistened around the edges of the hot rock. Jacob would put the rock back on the fire and then fold the black, glistening gum into the center of the ball, exposing more gray resin on the surface. This ironing, folding, and ironing again continued until the round, gray ball was transformed into a black, tar-like gum tablet, $6\frac{1}{2}$ inches long and 2 inches wide at the widest point, with rounded edges and rather flat top and bottom surfaces" (Binford; 1984, p. 168). See Binford (1984) for some informative photos of this process.

[2] "It will be recalled that after it was decided that we should be exposed to more traditional knowledge regarding the manufacture of men's knives, there was an episode where Jacob was said to have been in the boy's camp and then later commented that "the women had not gathered the material for the mastic." On questioning, Jacob had indicated that gathering the resin was normally a woman's task. Clearly preparing the spinifex gum is basic to the making of men's knives, yet it would appear that they had not intended to demonstrate its manufacture. My first guess was that this was a case of "abbreviation," in that the men, while having agreed to show us "everything" about making men's knives, had judged that we were not really interested in everything. On the other hand, if in the course of things the women or boys normally brought in the resin, then the men were simply behaving normally and modeling the normal adult male way of dealing with the situation. In their eyes this may not have been an abbreviation, since the collection of spinifex resin was normally done by women or boys. Nevertheless, as the events of the day demonstrated, the men were both skilled and knowledgeable about collecting and processing the resin. Several facts obtained later lead me to believe that boys normally learn how to do this not from their male teachers but from their mothers, while they still live in the women's camp, and accompany women on their daily foraging trips. The manufacture of resin is not learned from his male sponsor after a boy leaves the women's camp and moves into the novice camp, where the men take over most of the cultural instruction. I would guess that what we saw in the resin processing demonstration was most likely abnormal from the Aborgines'[*sic*] perspective" (Binford; 1984, p. 172)

> Last year Sir William Macleay was kind enough to give me "a sample of gum used by the blacks for cementing the heads of spears, and prepared from Spinifex roots," which had been collected by Mr. Walter Froggatt in the Napier Range (locally called Barrier Range), 100 miles inland from Derby, North-west Australia. I was dubious as to it being the product of a "Spinifex," never having heard of a grass yielding a resin, but Mr. Froggatt is emphatic that he is not mistaken, nor is so experienced a collector likely to be. The Spinifex is probably *Triodia irritans, R.Br.*, but further information on the subject, giving the mode of preparation of the resin would be very acceptable. Mr. Froggatt states that it is obtained from the roots, and local Europeans and aboriginals all make similar statements as to its origin. It is in a cake about 4 inches in diameter, and 1 1/4 inch in thickness. The smell is something like beeswax, but at the same time it has an exceedingly disagreeable and persistent odour which is not easily described. It reminds one of the smell of the fabric known as corduroy. It is of especial interest because it is of aboriginal preparation. Its colour is that of a dirty dark bronze-green, or almost of a slaty colour with a little green in it. To the naked eye it looks very like finely chopped hay or grass- seed cemented into a compact mass. It is exceedingly tough, a sharp blow with a hammer on a cold chisel being necessary to fracture it.
>
> The heads of spears from Western Australia in my collection are coated with a hard gum, forming a ridge on one side, in which pieces of glass are impacted. Mr. Froggatt informs me that Spinifex resin is put to such a purpose in the locality from which he obtained it.

According to some accounts, spinifex resin from *Triodia* spp. is the strongest and most malleable out of the Australian plant exudates (Parr; 1999, p. 23), appearing to be often

preferred over other exudates for purposes such as hafting. According to Pitman and Wallis (2012, p. 112), other exudates are only used in areas where spinifex resin is not available. Conversely, Clarke (2012, p. 146) records:

> At Groote Eylandt, Levitt described the use of porcupine grass (white tussock grass): When heated in ashes, a sticky gum is exuded that can be used to stick spear heads to the shafts, also the pegs of woomeras [spearthrowers]. It was only used when Ironwood or Cypress Pine gum was not available as it was not as satisfactory.

This account states that ironwood and cypress pine resins are preferable to spinifex resin for hafting purposes. These inconsistencies in the perceived quality of spinifex resin may reflect the differences in the various species of *Triodia*, as the resin from some may well be better suited to hafting than others.

The two species of *Triodia* most commonly documented as being exploited by Aboriginal Australians for the resin are *T. pungens* and *T. irritans* (Cribb and Cribb; 1981; Clarke; 2012), which are also the two most widespread of the resin-producing species. However, Pitman and Wallis (2012, p. 112) highlighted that whilst many early accounts recognised just three resinous species; *T. basedowii; T. irritans* or *T. pungens*, many others are now known to exist (4.2.6).

Powell et al. (2013, p. 211) explore some hypotheses for the restricted nature of the ethnographic accounts of *Triodia* species used for hafting resin, and why only certain species may have been chosen for use. Furthermore, experimental research by Powell et al. (2013) found that not all spinifex resin was suitable for hafting after processing using traditional techniques. Of six resinous species tested (*T. pungens* R.Br., *T. bitextura* Lazarides, *T. stenostachya* Domin, *T. microstachya* R.Br., *T. mitchellii* Benth and *T. marginata* N.T.Burb),

from which they collected resin dust and processed using consistent methods, only *T. pungens* and *T. mitchelli/T. marginata* (too difficult to differentiate) were deemed as 'haftable' based on a congealment criteria[3]. The resin from (*T. bitextura* Lazarides, *T. stenostachya* Domin and *T. microstachya* R.Br) may therefore be unsuitable for functions such as hafting (Powell et al.; 2013).

Pitman (2010, p. 81) notes that the ethnographic accounts are themselves fairly restricted geographically, and hypothesises that the collection and preparation of spinifex resin was actually much more widely distributed than the available records indicate. This hypothesis is based on the fact that resinous *Triodia* species cover the majority of the northern half of Australia, whereas the records associated with spinifex resin manufacture do not. Pitman (2010, p. 81) suggests that geographical biases in the ethnographic literature towards remote desert regions, where people continued to live a semi-traditional lifestyle for longer, may underestimate the widespread importance of *Triodia* resin, and that it was probably used much more widely across northern Australia. If this is the case, archaeological evidence in the areas less favoured by ethnographers, and the ability to identify any surviving resin residues, will be extremely significant.

The regular use of *Triodia* sp. resin is thought to be generally restricted to the arid zones of Australia (see map in Clarke; 2012, p. 9). As Clarke (2012, p. 143) explains, "Apart from its desirable traits, the Aboriginal use of spinifex [in general] was favoured by its extensive distribution and its dominant position in the vegetation of many arid areas, where spinifex tussocks often form dense stands on rocky hillsides." Clarke (2007, p. 121 and see references within) describes *Triodia pungens* (Clarke; 2007, p. 186) as the main source of cementing material used by "desert dwellers" for making and mending artefacts. Binford's

[3]The criteria: requires minimal to some, but not strong, compression to congeal, and surface not easily scratched by fingernail (Powell et al.; 2013, p. 215).

(1984, p. 161) observation of spinifex collecting and processing describes searching for the particular grass they needed, which tended to grow on rocky areas.

It can generally be assumed that spinifex resin would have been used by people who live locally to where it grows. Powell et al. (2013, p. 218) found that in Queensland, spinifex only appears to have been used for hafting north of the Tropic of Capricorn. They concluded that haftable resin may be restricted to plant sources in semi-arid regions of 600mm rainfall per annum or less (Powell et al.; 2013, p. 218). However, across Australia, species of *Triodia* were widely used for artefact making in the subtropics (Clarke; 2012, p. 143), and in reference to *T. irritans*, Clarke (2012, p. 317) notes that *Triodia* resin is used as cement by Aboriginal groups in the Mallee district of temperate Australia (Clarke; 2012, p. 143). It is possible that processed spinifex resin was traded across Australia, beyond the immediate vicity of the plants themselves.

4.2.5.2 Ironwood resin

Ethnographic descriptions of hafting occasionally specifically refer to the use of northern ironwood resin. In northern Australia, including north Queensland, the dark gum obtained from the northern ironwood tree (*Erythrophleum chlorostachys*) was made into an adhesive when attaching spearheads to shafts and pegs to spearthrowers (Clarke; 2007, p. 121; Maloney et al.; 2015, p. 37). According to Roth's research, the local Gunanni people living around the Mitchell and Staaten Rivers called ironwood resin 'aldema', and manufactured it as follows:

> [..]first roots of the ironwood tree were dug out and cut into small pieces. The outer sticky covering on these pieces of root was scraped off with a bark strip. It was then roasted over a fire and hammered between two stones. The roasting

> and hammering continued until the material was quite soft, when it was ready for use. Any leftover resin was left to cool and harden, ready to be used at another time.
>
> Khan; 2004, p. 79

There are several accounts of the wood of the ironwood tree being used in the making of artefacts, for example in the Roth collection (Khan; 2004), but not so many direct references to the resin. A collection of spearthrowers from the Kokomini people of around the Middle Palmer River including an item from the Australian Museum (E.14368), as well as at Maytown, are made from ironwood. The spearthrowers have a hafted Melo shell (from the sea snail species *Melo diadema* now known as *Melo amphora*) at one end, which probably had been bartered from the Musgrave River region. The hafting adhesive is recorded as being resin from either the ironwood (specifically *Erythrophleum* sp.) or roots of the young beefwood tree (*Grevillea striata*), and the peg join would be covered in the resin (Khan; 2004, p. 39). The use of ironwood resin was also recorded by Spencer (1914, p. 358):

> The jiboru was approximately 3m long with a hardwood shaft and butt end of bamboo to take a spearthrower. The head of the jiboru consisted of a sharpened bone barb hafted to the shaft with resin from the root of the ironwood tree.

There is significant evidence of both spinifex and ironwood resin being used by Aboriginal Australians, particularly for hafting purposes. It is therefore likely that both will be present on ethnographic artefacts from Australia, particularly hafted ones. To be able to differentiate between them chemically would have additional archaeological value given they appear very similar to the eye, especially when aged and degraded.

4.2.6 Species of *Triodia* as sources of spinifex resin

4.2.6.1 Resinous species by morphology

There are currently 68 recognised species of *Triodia*, according to The Plant List (TPL; 2013) and these are split botanically into two main groups, referred to as 'hard' and 'soft' spinifex. The soft spinifex produce resin, and the hard spinifex do not. Burbidge (1946, p. 222) noted that *T. pungens* differs to "all the other species", largely in that it has a resin secreting epidermis.[4] Since the discovery of more species over the last few decades, it has become apparent that several more species have this resin secreting epidermis, and are all of the 'soft' spinifex variety.

According to the Kew GrassBase (Clayton et al.; 2006 onwards), the following 24 species of *Triodia* are resinous:

1. *T. biflora* Lazarides - leaf-sheaths and leaf-blades resinous
2. *T. bitextura* Lazarides (curly spinifex (Clarke; 2012, p. 366)) - leaf-sheaths and leaf-blades resinous
3. *T. bunglensis* (S.W.L.Jacobs) Lazarides - leaf-blades resinous
4. *T. burbidgeana* S.W.L.Jacobs - leaf-sheaths and leaf-blades resinous
5. *T. bynoei* (C.E.Hubb) Lazarides (giant oat-eared spinifex (Clarke; 2012, p. 366)) - leaf-sheaths and leaf-blades resinous
6. *T. cunninghamii* Benth. - leaf-sheaths resinous

[4] The resin secreting epidermis: "This special tissue is found along the abaxial epidermis of the flange of the sheath. The best development occurs on exposed portions, ... The resiniferous tissue continues up the margin to the auricular ridge, where it is interrupted by the auricular hairs (also epidermal in origin). It is found again on the petiole, but disappears at the base of the lamina" (Burbidge; 1946, p. 222).

7. *T. epactia* S.W.L.Jacobs (soft spinifex (Clarke; 2012, p. 366)) - leaf-sheaths and leaf-blades resinous

8. *T. fissura* Barrett, Wells and Dixon - leaf-blades resinous

9. *T. hubbardii* N.T.Burb - leaf-sheaths and leaf-blades resinous

10. *T. irritans* R.Br. (porcupine grass (Clarke; 2012, p. 366)) - leaf-blade resinous

11. *T. latzii* Lazarides - leaf-sheaths and leaf-blades resinous

12. *T. longiloba* Lazarides - leaf-sheaths and leaf-blades resinous

13. *T. marginata* N.T.Burb - leaf-sheaths resinous

14. *T. melvillei* (C.E.Hubb) Lazarides (soft spinifex (Clarke; 2012, p. 366)) - leaf-sheaths resinous

15. *T. microstachya* R.Br (hummock grass, type of kerosene grass (Clarke; 2007, p. 186)) - leaf-sheaths and leaf-blades resinous

16. *T. mitchellii* Benth. (buck spinifex (Clarke; 2012, p. 366)) - leaf-sheaths and leaf-blades resinous

17. *T. pungens* R.Br. (soft spinifex (Clarke; 2012, p. 366)) - leaf-sheaths resinous

18. *T. radonensis* S.W.L.Jacobs - leaf-blades resinous

19. *T. roscida* N.T.Burb - leaf-blades resinous

20. *T. salina* Lazarides - leaf-blades resinous

21. *T. schinzii* (Henrard) Lazarides -leaf-sheaths and leaf-blades resinous

22. *T. spicata* N.T.Burb - leaf-blades resinous

23. *T. stenostachya* Domin (porcupine grass (Clarke; 2012, p. 366)) - leaf-sheaths resinous

24. *T. triaristata* Lazarides - leaf-blades resinous

4.2.6.2 Ethnographic references to resin from specific species

Ethnographic accounts of the Indigenous use of spinifex resin occasionally mention specific *Triodia* species, though more commonly the information stops at 'spinifex' (e.g. Spencer and Gillen; 1912, and see Chapter 7). There are, however, sporadic references to the use of several different species in the literature, though there is some confusion as to which species of *Triodia* are indeed resinous, and which of those species were actually likely to have been used for purposes such as hafting. The references to species as sources of spinifex resin can also be contradictory and confused in the correlation between local and scientific names.

Triodia pungens R.Br. (gummy spinifex, soft spinifex) is highlighted in several reviews of ethnographic accounts (Thorley; 1999; Clarke; 2007; 2008; 2012), and is universally accepted as both a resinous species of *Triodia*, and an important source of spinifex resin as used by Aboriginal Australians. The species noted by Pitman and Wallis (2012) as soft spinifex include: *T. bynoei, T. helmsii*, and *T. microstachya*. The soft spinifex noted by Clarke (2012) as economically important for uses such as shelter- and bed-making but not necessarily resin are *T. epactia*, and *T. melvillei*.

According to Clarke (2012, p. 146,318), 'spinifex wax' from *Triodia bitextura* (curly spinifex) and *T. microstachya* were both obtained and used in the Katherine area of the Northern Territory, and resin from *T. stenostachya* (porcupine grass) (Clarke; 2012, p. 318), was used as tool-making cement at Victoria River, closer to the Western Australian border (Clarke;

2012, p. 146)[5]. Akerman and Bindon (1984) note the use of resin from spinifex hummock grass (*Triodia* sp.) in the Kimberley region, called Limirr (Nyikina term). This could refer to *T. microstachya*, which is commonly known as hummock grass (Clarke; 2007, p. 152).

Triodia mitchellii is stated as the cement for covering shaft joints of a heavy three-piece spear (local name percha-marro), made by the Pitta-Pitta speaking people of Central West Queensland, which is in the Roth collection (Nugent; 2015, p. 65). However, Powell et al. (2013, p. 215) suggest that Roth's identification of the spinifex as *Triodia mitchellii* may be incorrect, even though *T. mitchellii* does grow locally to Boulia and the Pitta-Pitta people. Powell et al. (2013, p. 215) note that at Boulia, as well as at nearby Glenormiston, prepared gum was called "kanti" (according to Roth), yet at Camooweal, only a few hundred miles north, spinifex gum was known as "anoggora". It is unclear whether these local terms refer to the same "spinifex" resin, or different specific resins, i.e. different species of *Triodia*. This example demonstrates the difficulty in matching local names with taxonomic species. Chemical resin analysis can certainly help to shed some some light in these situations.

There seems to be a discrepancy between accounts in the literature for *T. basedowii, T. helmsii, T. irritans*, and *T. procera*. Pitman (2010) includes *T. basedowii* as a noted source of resin, however Clarke (2012, p. 366) refers to *T. basedowii* as hard spinifex or porcupine grass, and it is not described as resinous in the Kew GrassBase (Clayton et al.; 2006 onwards). *T. helmsii* is included as a soft spinifex by Pitman and Wallis (2012), yet Kew GrassBase does not specify if it is resinous or not. *T. procera* (white tussock grass) resin is mentioned by Clarke (2012, p. 146) as being used when ironwood or cypress pine were not available, but again, *T. procera* is not described as resin-producing on the Kew GrassBase (Clayton et al.; 2006 onwards).

[5] Species such as bull spinifex (*Triodia longiceps*) reportedly bear no resin at all "(Walpiri Lexicography Group 1986a, 55) (Clarke; 2012, p. 317). *T. wiseana* referred to as hard or limestone spinifex by Clarke (2012, p. 366).

There is also some discrepancy in the descriptions of *T. irritans*, as to whether it is resinous or not. According to Burbidge's (1946) description of the genus, *T. basedowii* and *T. irritans* are described as unlike *T. pungens*. Given that *T. pungens* is resinous, this implies that *T. basedowii* and *T. irritans* are not resinous, although there may be an historical discrepency in the assignment of the name *T. irritans*, according to Pitman and Wallis (2012)[6]. According to Kew GrassBase (Clayton et al.; 2006 onwards), *T. irritans* is a resinous species, and Clarke (2012, p. 143, 317) states that *T. irritans* is reportedly used as a source of artefact cement. Furthermore, Hardman (1901, p. 63) notes that *T. irritans* as the source of "spinifer gum," and Cribb and Cribb (1981, p. 87,88) mention only *T. irritans* and *T. pungens* in their discussion of spinifex or porcupine grass resin used as a cement for hafting[7]. As the plant curently named *Triodia irritans* is resinous, it is fairly conclusive that reference to *T. irritans* in most cases is one and the same, and a key source of spinifex resin.

4.2.6.3 The application of chemical analysis to 'spinifex' resin

It has been noted that it is botanically difficult to differentiate the different species of *Triodia* (Pitman and Wallis; 2012, p. 112). This is especially true for non-botanists, but is even the case for specialists unless they are able to examine the reproductive material. Additionally, there has been much renaming and reassignment of species, with some resin-producing *Triodia* species formerly considered as being members of the *Plectrachne* genus (Clarke; 2012, p. 317), confusing matters of species identification even further. Chemical

[6] It is possible that reference to *T. irritans* in the past, may be referring to a similar species that is now classed as *Triodia scariosa* N.T.Burb., which is a 'hard' non-resinous spinifex, or *Triodia compacta* (N.T.Burb.) S.W.L.Jacobs in South Australia, which was originally classed as a subspecies of *T. irritans*, which is also a non-resin producing 'hard' spinifex.

[7] In their description of Aboriginal use of spinifex, they note that the small globules of resin were highly valued by the Aborigines, collected from the 'roots' of the plants', and collected by women (Cribb and Cribb; 1981, p. 87,88).

characterisation of the resins produced by the different species can help towards differentiating between them, as well as identifying which species were likely to have been used by local communities. Translation of the local names used by different Aboriginal groups for different species of *Triodia* is currently based on notes from ethnographic explorers, but through analysis of the resin specimens collected by those ethnographers, chemical characterisation has the potential to clear up some of the confusion. Analysis of the resins associated with artefacts already present in museums can provide an idea of the regularity and range of uses of *Triodia*, and where in Australia it is more commonly used. Analysis can also show the amount of variation there is in the chemical composition of *Triodia*-based adhesives, with implications for the range of species exploited for the resin, and variations in the preparation methods.

4.2.7 Previous work on *Triodia* (spinifex) resin identification

Published analyses of *Triodia* resin are limited. Although spinifex resin has been an extremely important and highly valued commodity in Australia (Cribb and Cribb; 1981, p. 87), it has not had a significant place in commercial export and global trade, and was not subject to the early chemical studies on resins in the way the more common, commercially available, and commercially important resins were (e.g. Dieterich; 1920). Interest in the chemical composition of spinifex resins is therefore more ethnographic and archaeological. Gamage et al. (2012) and Mondal et al. (2012; 2013), however, have found *Triodia* resin to have commercial interest in its potential as a bio-polymer, though their analyses focused on the thermal qualities and behaviour of the resin, rather than the chemical composition.

It is very difficult to analyse raw spinifex resin, as unlike other plant exudates, such as the conifers, that can exist as a pure resinous substance fresh from the tree, the resin from spinifex resembles more of a dust that needs to be processed to become a resinous

mass. For example, spinifex resin is often formed by threshing the resin dust from the chaff and heating it until it becomes congealed. Occasionally, the resin can be found already formed in small globules after a fire, where it has been altered naturally. In most cases, it means that to analyse spinifex resins, a sample needs to either be from processed examples i.e. ethnobotanical samples, or the resin needs to be collected and processed to replicate traditional methods before analysis.

4.2.7.1 Non-chemical analysis of spinifex resin

The methods required for chemical characterisation of resins and similar adhesive substances are to a certain extent intrusive and/or destructive, which may often not be appropriate for the analysis of museum objects, at least initially. Pitman (2010, p. 21) makes this arguement for the analysis of spinifex resins, adding that the addition of other substances in processed spinifex can also complicate the process of identification. To address this, she has devised a non-chemical method for the visual identitification of spinifex on artefacts, with the aim of distinguishing it from other similar materials.

The strategy is based on a series of questions to determine an outcome of a spinifex confidence rating between 1=definitely spinifex and 5=definitely not spinifex. This confidence rating is acheived by rating the material under observation on each of the questions from 1=definitely to 5=definitely not. The eight questions proposed and used[8] by Pitman (2010, p. 29) are:

[8] "The analysis of adhesive samples assisted in confirming, improving and/or correcting museum records for some samples ... This analysis identified some items as spinifex resin which had not been previously classified as such and also identified some objects which were incorrectly labelled as spinifex resin" (Pitman; 2010, p. 41). "This research has assisted, at the SAM [South Australian Museum] in particular, improving the link between the information recorded on the database, information located with the object, and archival records. For example, a wooden container (A12117) on display in the Australian Aboriginal Cultures Gallery, SAM with a mend labelled as spinifex resin has been re-identified as not being spinifex resin but probably beeswax, and a spearhead (A1898 SAM) identified as being hafted with spinifex resin has been identified as being some other adhesive. Two items on display were also re- identified not as spinifex resin but as a resinous insect nest on a stone slab (SAM A58389), and a nest of a small marsupial or rodent (made of resinous spinifex grass which has been melted in a fire; SAM A1882), respectively" (Pitman; 2010, p. 79).

1. Does the object's label or catalogue information state it as being either "spinifex", "porcupine grass" or "*Triodia*"?
2. Was the sample collected from a geographical area known to have resinous spinifex?
3. Are there inclusions of chaff within the sample?
4. Is the sample very hard?
5. Is the sample colour a dark brown-black (not on the GLEY pages of a Munsell Colour Chart)?
6. Does the sample have little or no odour (does not smell of honey)?
7. Is the sample dull-shiny (not glassy)?
8. Is the sample opaque (no sign of translucence)?

It would be interesting to test how these criteria compare with chemically identified spinifex resin samples on ethnographic museum artefacts. A strong correlation would be expected, unless other non-spinifex samples also have the same physical attributes.

4.2.7.2 Chemistry of *Triodia* (spinifex) resin

There are a handful of reports of *Triodia* resin analysis in the literature, from a basic characterisation by Joseph H. Maiden in the 19th century, to some more recent small scale chemical analysis studies.

Maiden (1890, p. 640) described the basic chemical composition of a *T. irritans* sample as a mixture of fat, resin, extractive and salts (soluble in water), and impurities, as well as dirt and particles of chopped grass. Pitman and Wallis (2012, p. 112) have also commented on the physical characteristics, concluding that "Spinifex resin is thermoplastic, meaning that

below its glass transition temperature (about 25°C) it is hard and brittle, and above that temperature it becomes soft and malleable, making it an ideal adhesive." Another account describes the resin as soft at room temperature and requiring a filler or acid treatment to change the behaviour of the resin and allow it to harden at ambient temperature (Mondal et al.; 2013, p. 326). The general characteristics of spinifex seem agreed upon, however, it is likely that there is some variability in behaviour amongst the resins under this umbrella term. The details of chemical composition are even less clear.

Matheson and McCollum (2014) published their GC-MS analysis of a resin sample from an unspecified species of *Triodia* R.Br (after derivatisation using BSTFA), and identified the presence of aromatic hydrocarbons like anthracene and fatty acids including hexadecanoic acid and octadecanoic acid. Matheson and McCollum (2014) and Blee et al. (2010) have both published their FTIR characterisation of unknown *Triodia* samples. Blee et al. (2010) found that spinifex had potentially diagnostic peaks, in the region 1082-1030cm-1 (attributed to in plane C-H bending), that were not present in the most similar spectrum in the study, that of goanna oil. Matheson and McCollum (2014) found that the *Triodia* sp. resin spectrum had some similarities with terpenoid resins, but was most similar to yet distinguishable from the *Erythrophleum chlorostachys* resin sample.

For research on paint binders, Reeves et al. (2013, p. 200) analysed a sample of spinifex resin by pyrolysis-GC-MS and reported it as a triterpenoid resin based on the detection of β-amyrin, and the chromatographic profile presented is definitely similar to that of their sample of Manila elemi. It is notable that they list the spinifex resin sample as coming from the *Spinifex* genus, and originates from "West of Mt. Liebig, South Australia". As spinifex resin is usually thought to come from the genus *Triodia*, which is not common in South Australia, though there is a Mount Liebig in the Northern Territory where *Triodia* is more common, the origin of the sample is brought into question. It is also listed with

accession number A17752 from the South Australian Museum, which is the same sample that was analysed by Blee et al. (2010), who notes that the source species is not provided.

The most detailed report of resin from a specific species of *Triodia* has been published by De Silva et al. (2009). They analysed the methanol-soluble fraction of resin from *Triodia pungens* by chromatography (GC-MS and LC-MS for the polar and non-polar fractions as appropriate) and found it to contain monoterpene, sesquiterpene and diterpene compounds, including: α-phellandrene; camphene; isoborneol; endo-borneol; bornyl formate; α-muurolene; communol; communic acid; abietic acid; difenchyl succinate; dibornyl succinate components; and many others. FTIR was used to confirm that the *T. pungens* resin contains polymer -OH groups, as well as aromatic compounds, -COOH groups, symmetrical and assymetrical C-H bonds in methylene groups, C=C bonds in olefinic groups, and C=O bonds in ketones (de Silva et al.; 2009).

De Silva et al. (2009) postulate that the succinic acid groups presumably act as cross-linking agents, causing the resin to harden. However, polymerisation would occur on exposure to air, causing the resin to harden over time from its initial exposure, similarly to the conifer resins. There are no ethnographic accounts of this hardening in relation to spinifex resin known to the author, whereas there are accounts of re-softening the resin by heating. It is notable that the resin was extracted directly fom the plant stems and not prepared in the traditional way before analysis, perhaps highlighting the importance of the modification process.

It is clear from the literature that much more research on the chemical composition of *Triodia* resins, as well as spinifex resin examples from ethnographic materials is required. The current knowledge of the chemistry of spinifex resin is too sporadic to be able to ascertain confident taxonomic identifications of ethnographic or archaeological samples.

4.2.7.3 Spinifex resin on artefacts

Studies on the identification of spinifex on artefacts are sparse, and summarised as follows. Blee et al. (2010) used FTIR analysis and chemometrics to identify the binder on knife handles from the collections of the South Australian Museum as a way to provenance three broken stone knives. Residues from the handles were analysed and found to contain beeswax as the fixative on two of them, indicating a probable origin of northern Australia or Arnhem land (Blee et al.; 2010, p. 750). Spinifex resin was found to be the probable binder on the third knife handle, indicating an arid or tropical Australian origin, but with the acknowledgement that more data is required to provenance the artefact (Blee et al.; 2010, p. 750).

Using both GC-MS and FTIR, Matheson and McCollum (2014) were able to directly compare resins labelled as spinifex on museum artefacts with a known *Triodia* sp. reference sample. This approach enabled them to confirm the museum identification of several samples, and assign the 'spinifex' identity to two more previously unknown museum resin samples.

To date, both non-chemical and chemical analyses have been used to identify, confirm or discount the presence of spinifex resin on artefacts, but no identification to source species has been attempted.

4.2.8 Previous work on *Erythrophleum chlorostachys* (ironwood) resin

There is very little in the literature about the chemistry of ironwood resin from the native Australian species *Erythrophleum chlorostachys*. However cassaine-type diterpenoids, including taraxerol, have been identified in the leaves and bark of other species of *Erythrophleum* (Tsao et al.; 2008; Dade et al.; 2015).

Current knowledge of *E. chlorostachys* resin is restricted to ethnobotanical studies, and this knowledge is very limited to date. Analysis of an ironwood sample from the South Australian Museum using pyrolysis-GC-MS by Reeves et al. (2013, p. 198) detected an unknown compound, and a derivative of a common wood plant monosaccharide. Blee et al. (2010, p. 748) found that (the same) ironwood resin sample yielded very similar FTIR spectra to acacia gum, beefwood gum resin, and orchid juice, possibly suggesting a polysaccharide component.

Matheson and McCollum (2014) analysed a specimen of resin from *E. chlorostachys* (F.Muell.) Baill. sourced from a botanical garden in Australia, by FTIR and GC-MS. They report the GC-MS results as showing the majority of peaks to be fatty acids, with sterols and plant waxes and include tetradecanoic acid, hexadecanoic acid, octadecanoic acid, 9,10-epoxy-18-hydoxy-octadecanoic acid, anthracene and oxanilic acid (Matheson and McCollum; 2014). They conclude that the exudate from *E. chlorostachys* is a gum or resin-gum, but not a terpenoid resin as it does not have any of the typical resin acids. Their published chromatogram of *E. chlorostachys* shares some similarities with that of their *Triodia* sp. specimen, as does the FTIR analysis, though the FTIR analysis of *Triodia* appears to have aspects that are unique to it.

In Khan's (2004) study of the Roth collection, a description of the properties of the ironwood (*E. chlorostachys*) resin by the curator of what is now the Powerhouse Museum, Sydney, is quoted, and includes the following extract:

> The principal resin is of a dark-brown colour, and is somewhat brittle, and melts at a low temperature; it ignites readily, and burns with a smoky flame, leaving an excess of carbon. It is readily soluble in alcohol, but less so in ether... It is

> remarkable how closely the resin agrees in every respect with the resin obtained from Spinifex.
>
> Khan; 2004, p. 79

This statement is consistent with the similarities found by Matheson and McCollum (2014) between their *E. chlorostachys* and *Triodia* sp. resin samples.

Similarly to the *Triodia* resins, more research is clearly needed to properly characterise the resin of *Erythrophleum chlorostachys*, as well as to be able to distinguish it from spinifex resin, particularly in an ethnographic or archaeological context.

4.3 Results from GC-MS analysis of putative spinifex and ironwood resins

Four samples from the resin collections included in this project were labelled as either *Triodia*, spinifix or ironwood. These samples were analysed by GC-MS after methylation and used cautiously as reference samples for these types of resins. They were found to all contain a number of unidentified compounds that appear to be diterpenoids, therefore fitting into the category of diterpenoid-based resin, but are significantly different to the conifer resins. As there were no authenticated reference samples to compare to, the exact identity of these resins are still unconfirmed.

4.3.1 Putative spinifex resin samples

One resin sample from the Kew Economic Botany Collection (EBC) was labelled as *Triodia irritans* (K070: EBC no.33340). This specimen was donated to Kew's EBC in 1988, noted as from H. Maiden (transcribed from a handwritten label, probably J. H. Maiden, or perhaps a decendant of Joseph Maiden) and is likely to be the sample of spinifex from *Triodia irritans* described by (Maiden; 1890, p. 639), as discussed earlier (see sections 4.2.5.1 and 4.2.7.2). This may be the first chemical characterisation of *Triodia irritans* resin known to date. However, there is some ambiguity over the species identity based on the location where it was collected, if it is the sample in the description by Maiden (1890) (see 8).

The sample K070 '*Triodia irritans*' resin was found to contain the methyl esters of hydrocinnamic acid, β-phenyllactic acid, piperonylic acid, and compounds similar to cinnamic and coumaric acids as well as 4-methoxycinnamaldehyde (see Figure 4.3 for the chromatogram

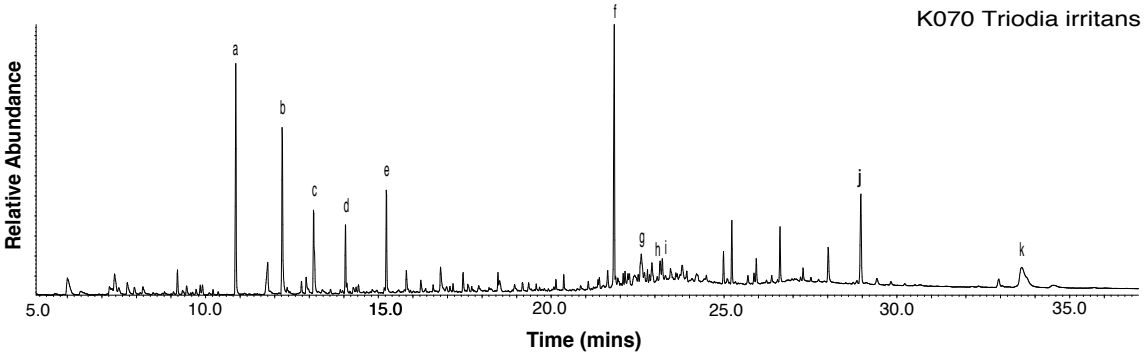


FIGURE 4.3: Chromatogram for K070 *Triodia irritans*

TABLE 4.1: Mass Spectral data for the peaks identified in Figure 4.3 K070 '*Triodia irritans*'

Peak	RT	m/z (base peak in bold)	M+	Compound ID	References
a	10.88	51, 65, 77, 91, **104,** 133, 164	164	Hydrocinnamic acid, methyl ester	NIST11; NIST Chemistry WebBook
b	12.22	51, 65, 77, **91**, 103, 121, 131, 162, 180	180	β-Phenyllactic acid, methyl ester	NIST11; NIST Chemistry WebBook
c	13.12	53, 63, 91, 121, **149**, 180	180	Piperonylic acid, methyl ester	NIST11; NIST Chemistry WebBook
d	14.05	51, 77, 91, 103, 131, **162**	162	Similar to cinnamic acid, methyl ester	NIST11; NIST Chemistry WebBook
e	15.24	53, 63, 91, 119, 147, **178**, 210	178	Similar to coumaric acid, methyl ester	NIST11; NIST Chemistry WebBook
f	21.82	51, 65, 77, 91, 104, 105, 121, 131, **162**	-	Unknown diterpenoid	-
g	22.61	59, 77, **91**, 103, 121, 131, 162, 179, 203, 216, 260	-	Unknown diterpenoid	-
h	23.15	59, 77, 91, 107, 121, 131, 143, **162**, 203, 222, 289	-	Unknown diterpenoid	-
i	23.22	59, 71, 89, **91**, 125, 143, 165, 203, 229, 320	-	Unknown diterpenoid	-
j	28.96	51, 65, 77, 91, 105, 131, 148, **162**	162	Similar to 4-methoxycinnamaldehyde	NIST11
k	33.61	55, 69, 81, 95, 107, 119, 135, 147, 175, **189**, 203, 207, 220, 233, 262, 410, 411, 437, 452, 455, 470	470	Betulinic acid, methyl ester	NIST11; Modugno et al. 2006

and Table 4.1 for the mass spectral data). The presence of this series of compounds loosely resembles the phenolic resins of the *Xanthorrhoea* (see Chapter 6).

There were also several unknown compounds detected within the diterpenoid range of the chromatogram amongst a mass of unresolved compounds, which appears to represent a diterpenoid component. Betulinic acid, methyl ester, which is a triterpenoid, was also detected, as were several methylated long-chain fatty acids. The presence of a triterpenoid is notable in the same sample as diterpenoids and is likely to indicate a mixture of resins, or contamination from a triterpenoid resin. This is a very interesting sample, and unlike anything else in the ethnobotanical reference collection analysed in this project, or elsewhere in the literature to the knowledge of the author.

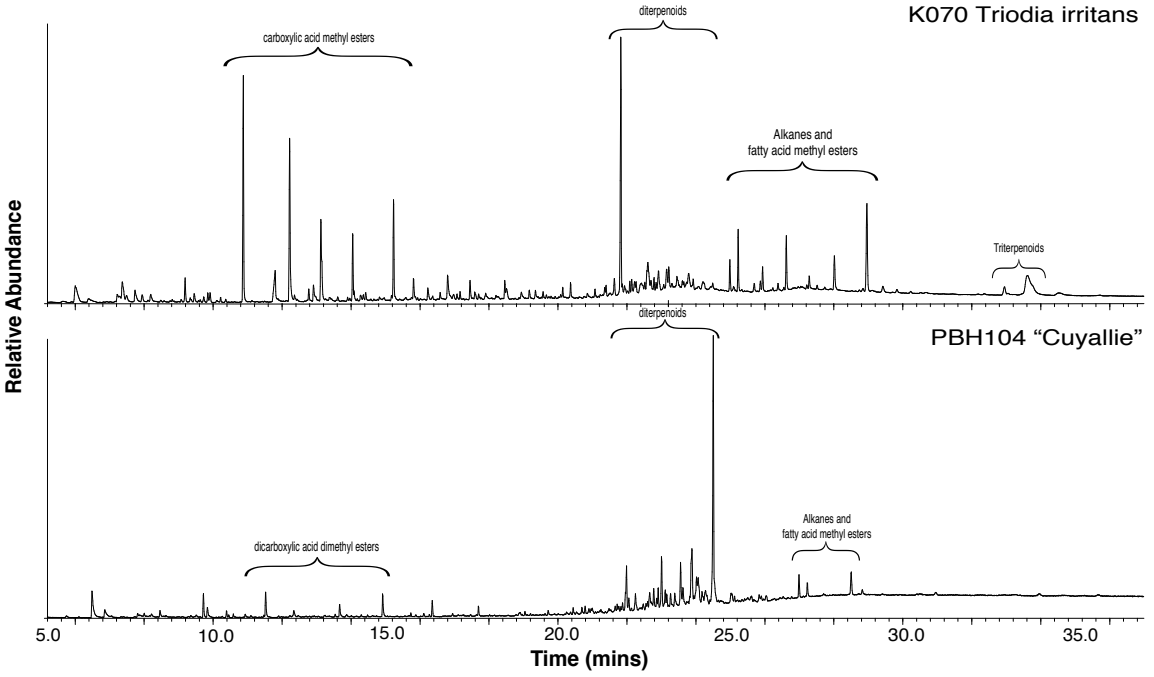


FIGURE 4.4: Partial chromatograms comparing K070 and PBH104

No other reference specimens of *Triodia* resin were successfully sampled for this project, however, some examples of hafting cement clearly labelled as spinifex were in the Peabody Museum at Harvard (PBH) collection. Two items labelled 'spinifex gum', one unrefined with local name 'cuyallie' and the other purified by continued re-melting and squeezing with local name 'burga', were sampled (PBH104; PBH011) and analysed by GC-MS after methylation. The results are consistent with each other, with very little variation between the two samples, suggesting they are likely to be from the same source, and that the processing method of re-melting and squeezing has no effect on the chemistry of the material.

The chromatographic profiles of the two 'spinifex' samples (PBH104 and PBH011) are highly consistent with each other (see section 4.4), but are quite different to that of the putative sample of *Triodia irritans* (K070). The main difference is the presence of the carboxylic acid, methyl esters eluted between 10 and 15 minutes on the chromatogram of K070, which may represent a seperate non-diterpenoid resin. This difference between the samples is continued in the mass spectral data of the diterpenoid fractions. The mass

spectral data for these compounds are listed in Appendix E. The mass spectra for the main diterpenoid peak in each K070 and PBH104 'cuyallie' (the same as in PBH011 'burga') are shown in Figure 4.5.

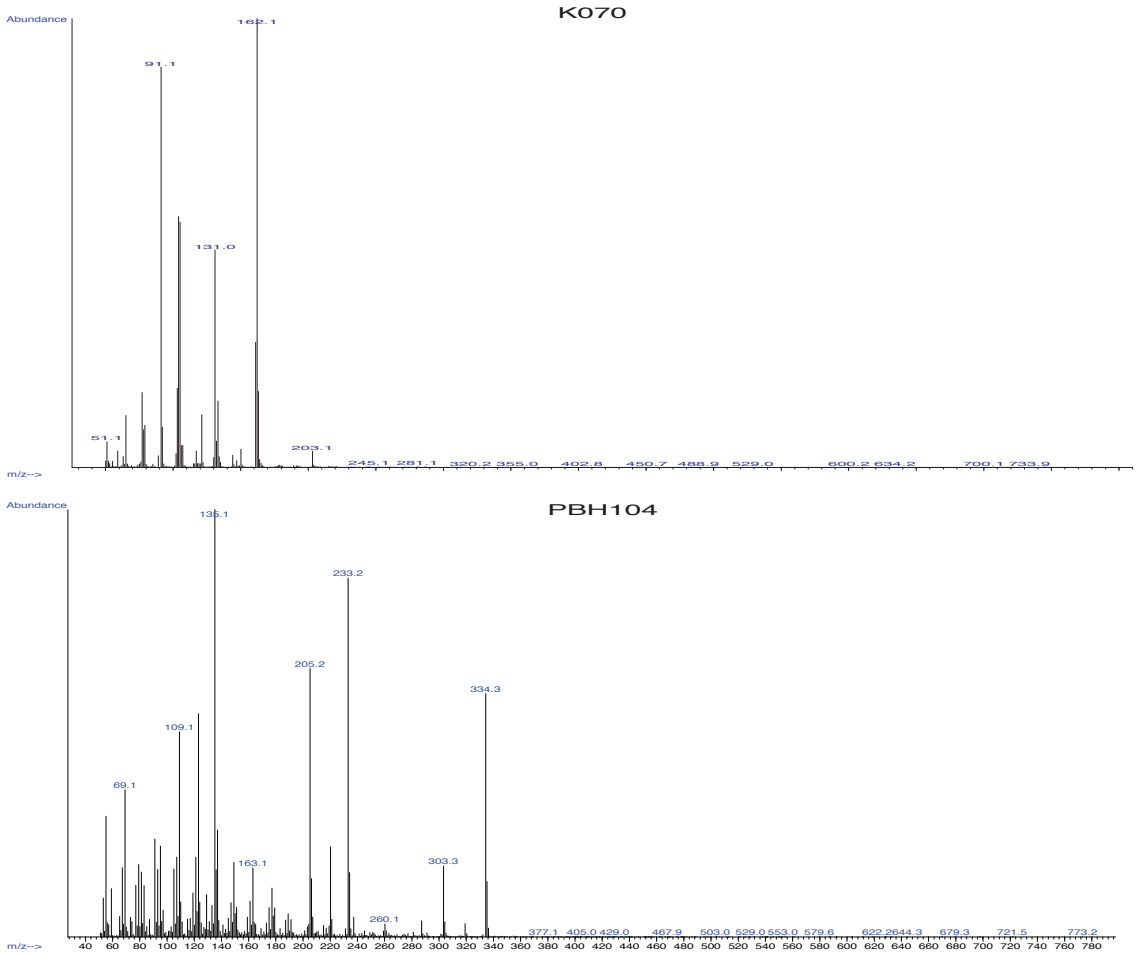


FIGURE 4.5: Mass spectrum for the main diterpenoid peak in K070, at 21.82 minutes (above). Mass spectrum for the main diterpenoid peak in PBH104, at 24.50 minutes (below)

Most of the compounds in these diterpenoid fractions were unable to be identified partly due to poor resolution, but also that the compounds are not commonly recognised and are not in the NIST11 mass spectral database. There may well be several new, unknown compounds, considering such little chemical analysis has been carried out on the spinifex-type resins.

The presence of fatty acids, indicated by the detection of their methyl esters, supports similar finds by Matheson and McCollum (2014). The chromatogram from the resin of *Triodia* sp. published in Matheson and McCollum (2014) loosely resembles what is seen in the *T. irritans* sample, and possibly more closely with that in the ethnographic 'spinifex' samples. However, there are not as many components visible in the Matheson and McCollum (2014) chromatogram, probably due to the derivatisation method (silylation via BSTFA, rather than methylation via TMS-diazomethane). None of the specific compounds identified by de Silva et al. (2009) in *T. pungens* were detected in any of the postulated spinifex/ *Triodia* samples, but the presence of diterpenoids is consistent with their findings.

4.3.2 Putative ironwood resin sample

A further ethnographic sample PBH100 was labelled as being "ironwood rosin [*sic*]", and therefore hypothesised to be *Erythrophleum chlorostachys*, though this needs to be verified by comparison with an authenticated sample, which was not possible within this project. However, the sample was collected from Arnhem Land which is comfortably within the natural distribution of the species (see Figure 4.2).

None of the compounds were identified by comparison with the NIST11 mass spectral database, but all of the main components eluted in the diterpenoid region of the chromatogram, and are shown in Figure 4.6. The m/z values for the unknown peaks are presented in Table 4.2.

The similarities of ironwood resin and spinifex resin described by Matheson and McCollum (2014) are consistent with the findings in this study based on the general chromatographic profie, however with a closer look at the mass spectral data, the individual components are very different with hardly any crossover. Samples similar to this putative *Erythrophleum*

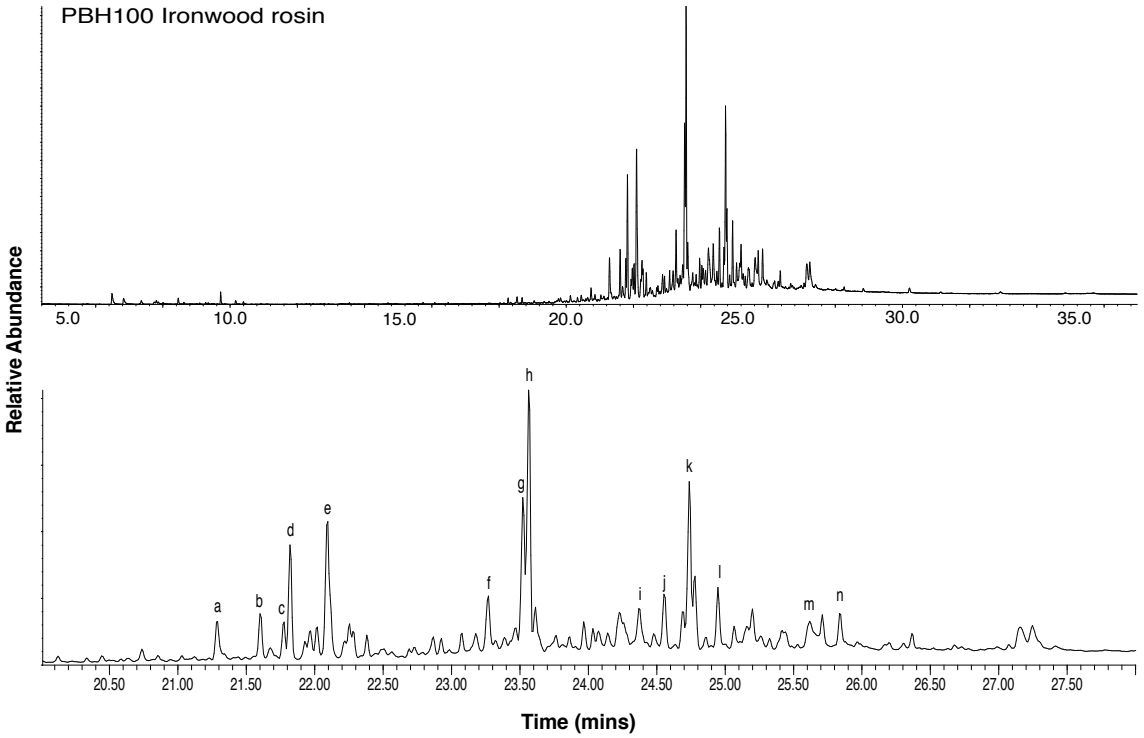


FIGURE 4.6: Full (above) and partial (below) chromatograms for PBH100 Ironwood rosin

TABLE 4.2: Mass spectral data for the peaks identified in Figure 4.6 PBH100 Ironwood rosin

Peak	RT	m/z (base peak in bold)
a	21.28	55, 67, 81, 95, 107, 121, 136, **161**, 179, 203, 221, 235, 253, 264, 296
b	21.61	55, 79, 91, 109, 124, 135, 147, 161, **189**, 205, 231, 278
c	21.78	55, 79, 91, 109, 122, **124**, 135, 147, 161, 189, 205
d	21.83	55, 69, 91, **106**, **110**, 119, 138, 152, 184, 212, 287, 318
e	22.1	55, 69, 81, **95**, 107, 121, 136, 149, 163, 175, **191**, 238, 277, 289, 305, 320
f	23.27	55, 69, 81, 95, **109**, 123, 137, 151, 163, 179, 189, 207, 251, 273, 288, 307
g	23.52	55, 69, 81, 91, 105, 119, 133, 147, 163, 178, 189, 241, **257,** 269, 285, 301, 316
h	23.57	55, 69, 81, 95, **109**, 123, 137, 149, 163, 189, 207, 223, 237, 321
i	24.38	55, 69, 81, 95, 109, 123, 137, 149 , 161, 177, 189, 207, **291**, 352
j	24.57	55, 69, 81, 95, 109, 123, 135, 149, 163, 179, **189**, 207, 251, 275, 289, 307, 339
k	24.74	55, 69, 83, 95, 109, 121, 135, 149, 163, 177, 189, **205**, 287, 303, 319, 334
l	24.96	55, 69, 83, 95, 109, 121, 123, **124**, 135, 149, 163, 177, 205, 250, 303, 316, 334
m	25.6	55, 69, 84, 95, 109, **123**, 137, 149, 163, 189, 207, 225, 300, 322, 354
n	25.85	55, 69, 95, 109, 121, 135, **168**, 189, 207, 217, 251, 281, 319, 346, 382

chlorostachys resin sample are therefore easily distinguishable from the putative spinifex resins by GC-MS, certainly when derivatised by methylation.

4.4 Results of GC-MS analysis of the ethnographic samples with non-conifer type diterpenic resins

4.4.1 Samples with spinifex-type resin

Unknown ethnographic resin samples were compared to the chromatograms of the putative *Triodia irritans*, spinifex and ironwood samples. There are six distinct groups of chromatographically similar looking materials, thought to be spinifex or ironwood resin. The majority of the compounds of note are currently unidentified but the mass spectral data (showing fragments of complex structures) suggests they are likely to be diterpenoids. These samples are therefore categorised as diterpeniod-based resins, but specifically non-conifer diterpenoid resins.

Those samples with similar chromatograms to the ethnographic museum 'spinifex' samples (PBH104 and PBH011) have been characterised as probable *Triodia* sp. based on the consistent connection of the two names in the ethnographic literature. The data show little consistency across all of the samples with visually similar non-conifer diterpenoid type chromatograms, but there is some consistency across several groups of artefacts, which have been arbitrarily labelled A-E. The most notable components of each group, where consistent across two or more samples are labelled in the corresponding chromatograms, and presented in full in Appendix E. The details of the ethnographic samples can be found in Appendices B and H, and are discussed in Chapters 7 and 8.

Group A: PBH104, PBH011, PBH109, PRM24 (see Figure 4.7). The similarities between these samples are more obvious by pulling out the m/z123 ion, as shown in Figure 4.7. Group A comprises samples that are consistent with PBH104, the 'unrefined (cuyallie)' and PBH011, the 'processed (burga)' spinifex samples presumed to be *Triodia* sp. The

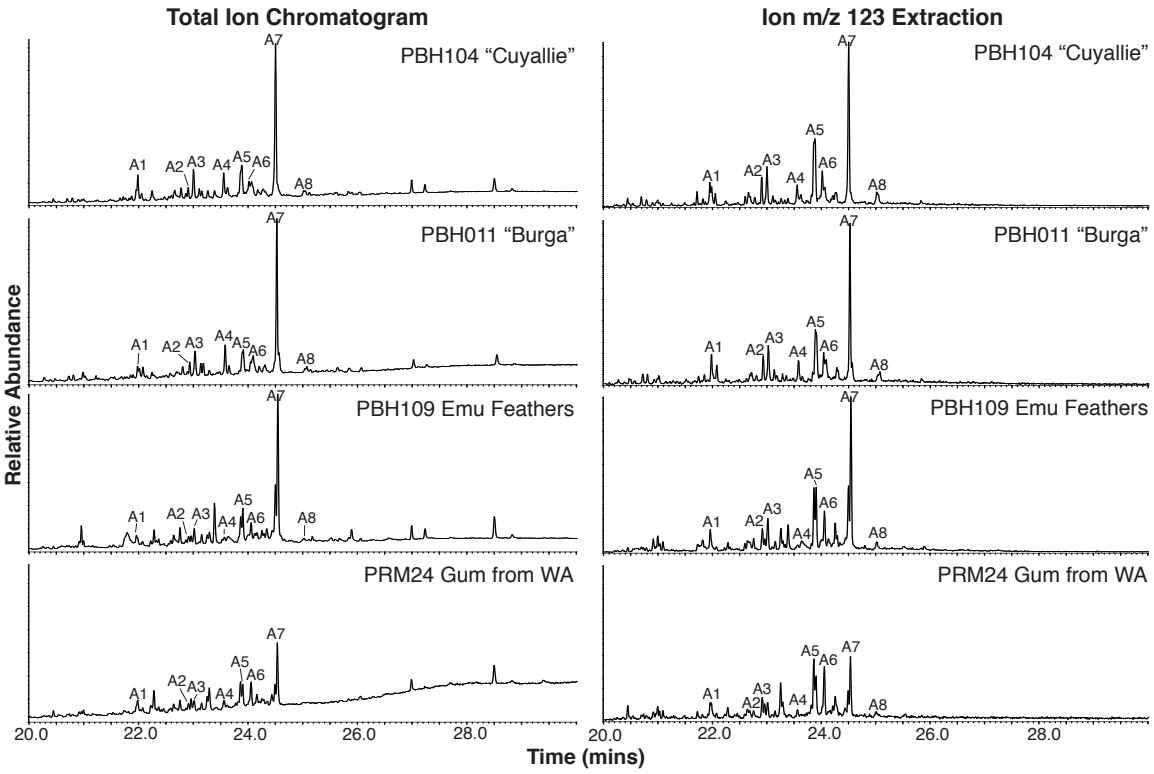


FIGURE 4.7: Spinifex Group A

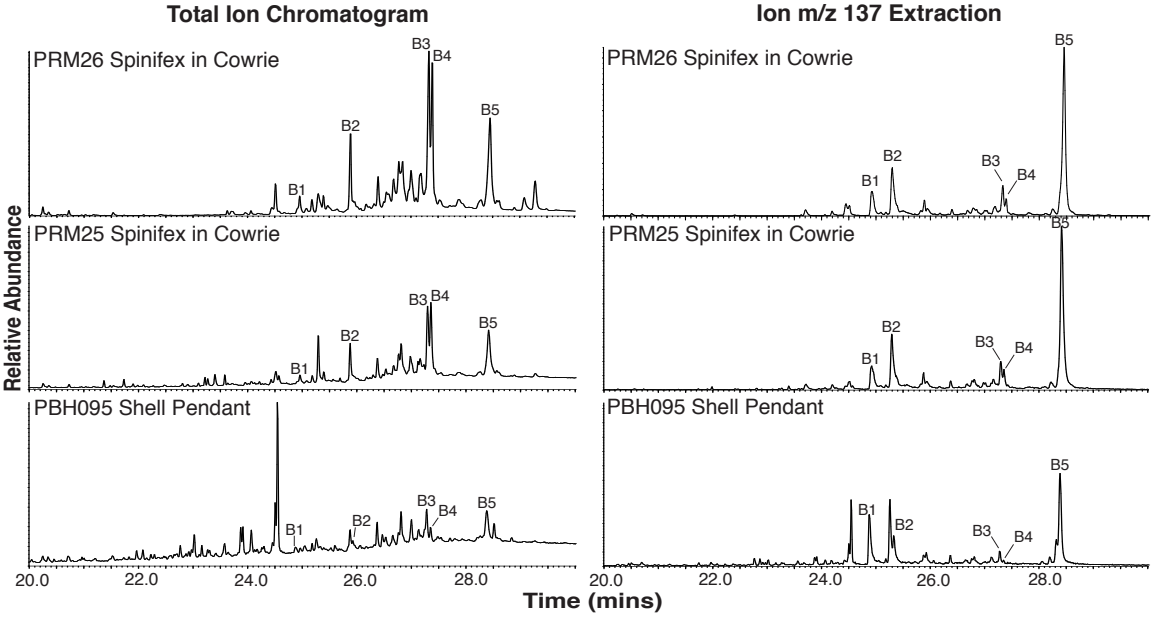


FIGURE 4.8: Spinifex Group B

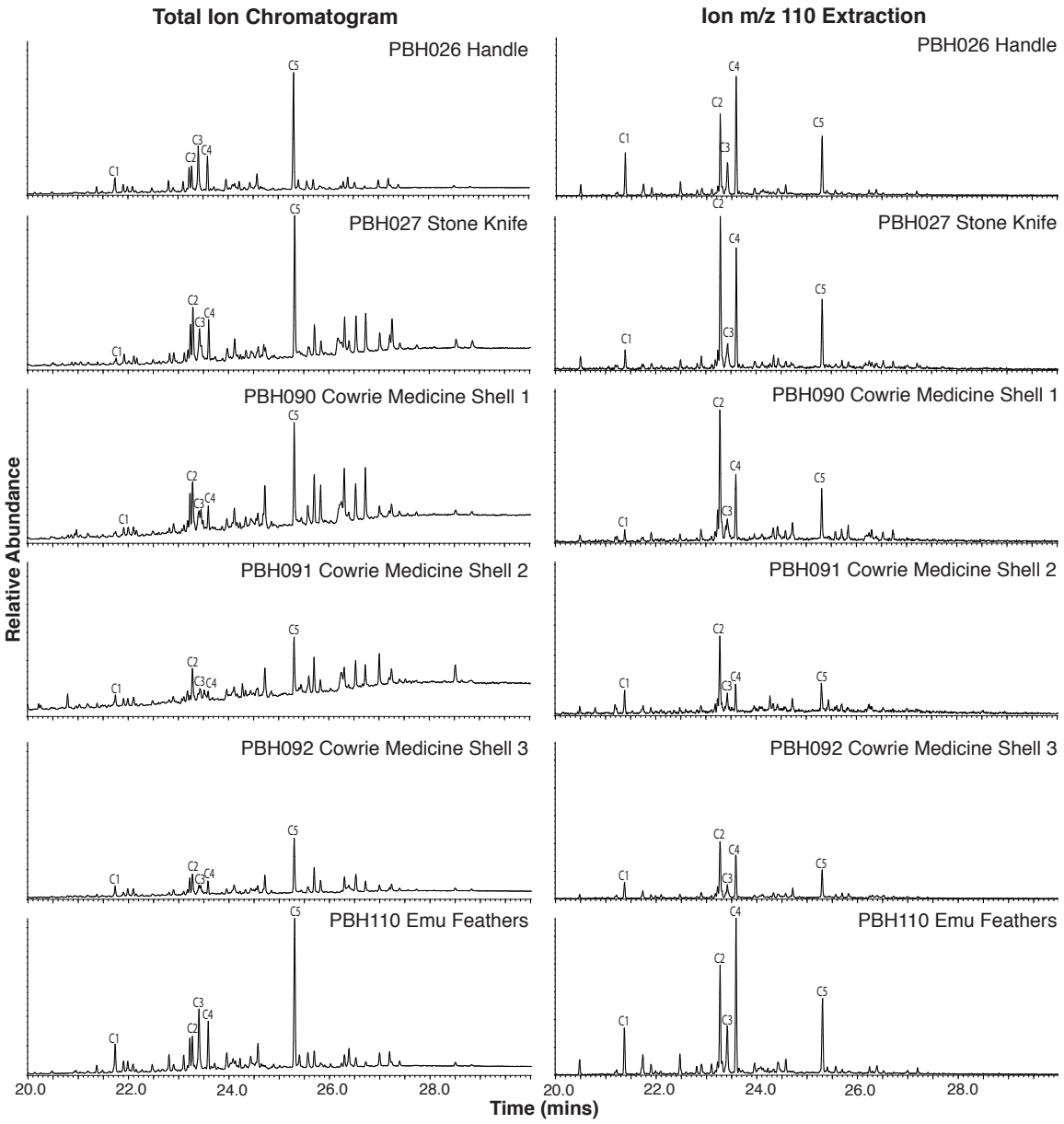


FIGURE 4.9: Spinifex Group C

similarities in the composition of all the samples in spinifex group A indicate that they are likely to be from a similar source.

Group B: PRM26, PRM25, PBH095 (see Figure 4.8). The chromatographic and mass spectral data for these samples are consistent with each other suggesting a similar source, yet different to spinifex group A. The similarities between these samples are more obvious by pulling out the m/z137 ion, as shown in Figure 4.8. Two samples from the Pitt Rivers Museum (PRM25 and PRM26) were labelled as spinifex in the museum records, but no

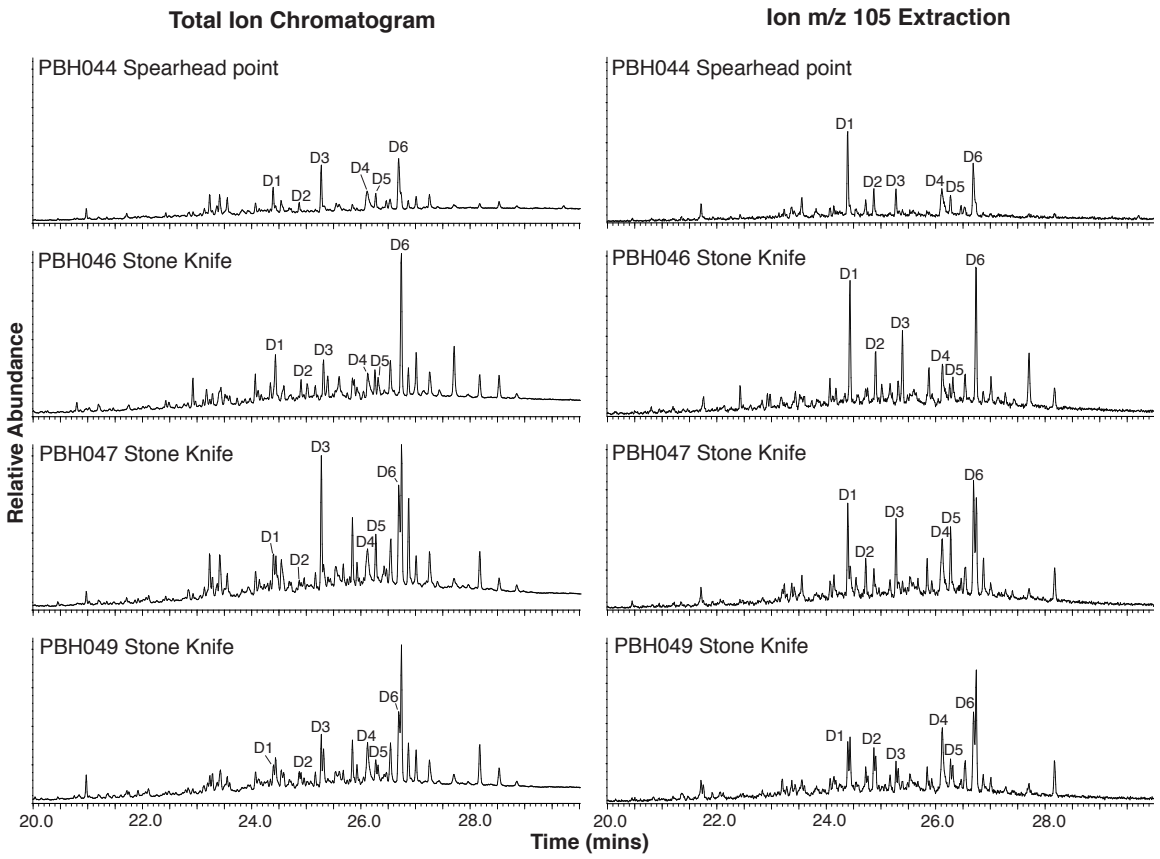


FIGURE 4.10: Spinifex Group D

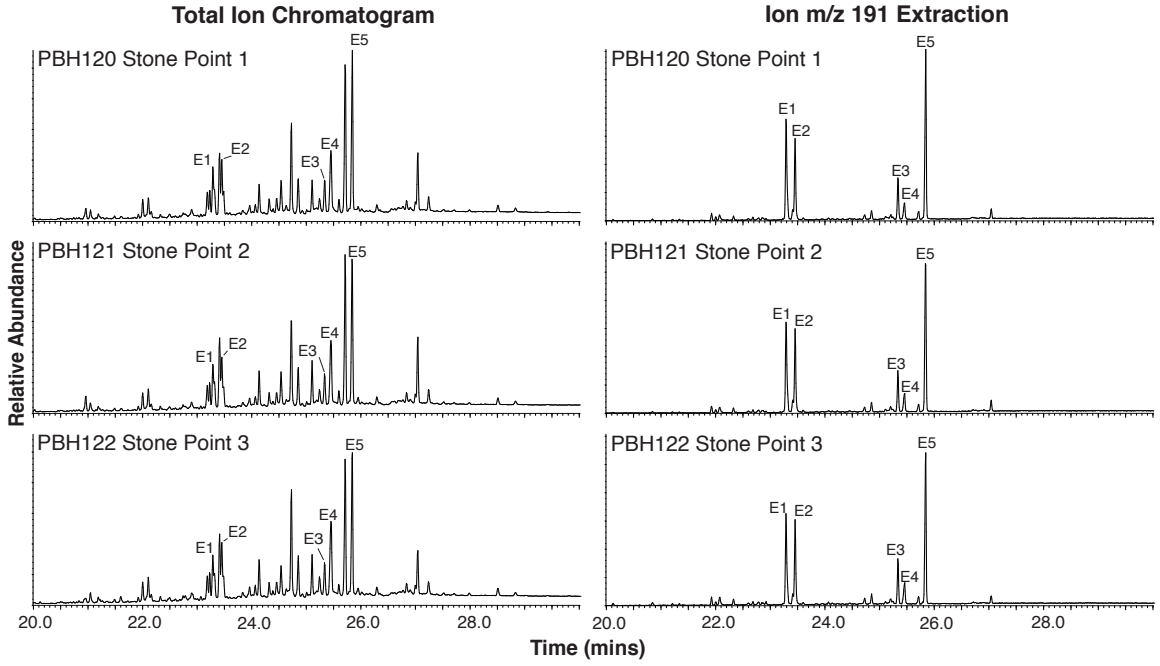


FIGURE 4.11: Spinifex Group E

further ethnographic descriptions of the samples were provided. The practice of using spinifex resin in cowrie shells for medicinal purposes, as is the description for the items these samples were taken from, has been recorded ethnographically and is discussed in Chapter 8. The main peaks present in this type of 'spinifex' resin are still within the diterpenoid range of the chromatogram, but are different in both retention time and fragmentation patterns to those in the group A type of 'spinifex' resin.

Group C: PBH026, PBH027, PBH090, PBH091, PBH092, PBH110 (see Figure 4.9). This is largest group of spinifex type resins of conistent composition, yet different again to both groups A and B. The similarities between these samples are more obvious by pulling out the m/z110 ion, as shown in Figure 4.9.

Group D: PBH044, PBH046, PBH047, PBH049 (see Figure 4.10). Again, different to the other groups, these four samples are consitent with each other. The similarities between these samples are more obvious by pulling out the m/z105 ion, as shown in Figure 4.10.

Group E: PBH120, PBH121, PBH122 (see Figure 4.11). Almost identical in composition, these three samples come from the same type of artefacts from the same location, namely stone-pointed spears from the Kimberley region. The similarities between these samples are more obvious by pulling out the m/z191 ion, as shown in Figure 4.11. The chromatographic profile of the resins in this group still appears to show a 'spinifex' type of resin, though they do not sit within any of the previous groups.

Sample PBH103 has some similarities with the group E spinifex resins, and PBH079, PBH088, PBH053 also show some similarities with the 'spinifex' type resins but do not fit well into any of the groups. Another two samples AM06 and AM11 have peaks in the same diterpenoid zone but do not fit in any of the groups and may originate from a different type of resin. The chromatograms for these samples can be found in Appendix K.

4.4.2 Samples with ironwood-type resin

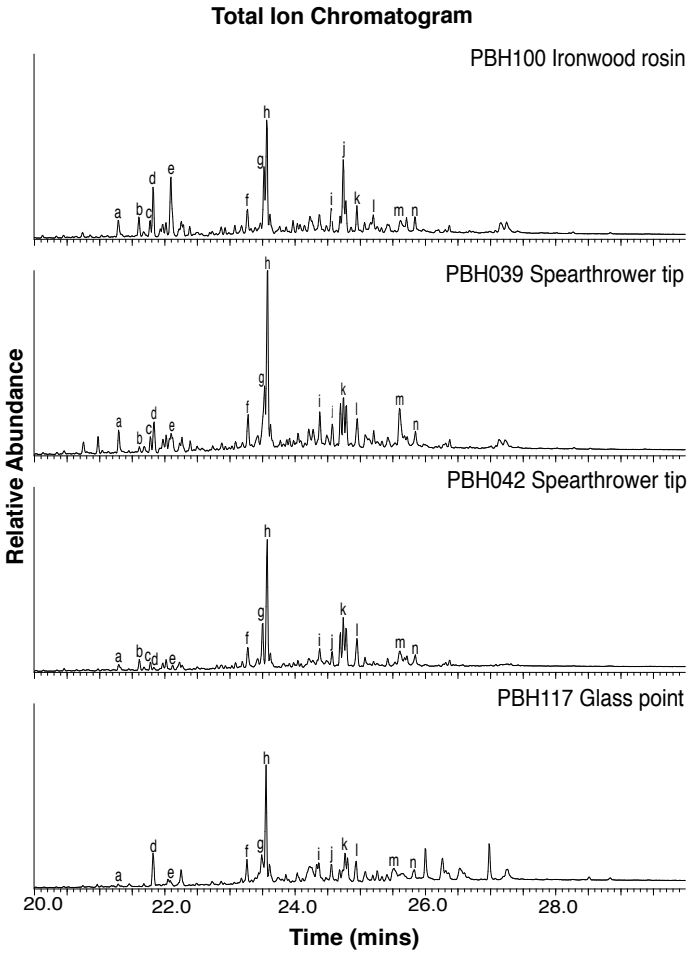


FIGURE 4.12: Ironwood Group

A further three samples that appear to also be in the non-conifer diterpenic resin category, but are significantly different to the presumed spinifex samples, are PBH039, PBH042 and PBH117. These samples are all consistent with PBH100 "ironwood rosin [*sic*]", and are cautiously identified as *Erythrophleum chlorostachys*, based on the presumed identity of the botanical source of this sample. The similarities of the three ethnographic samples with PBH100 are shown in Figure 4.12, with the corresponding mass spectral data as shown in Table 4.2.

The ironwood resins are distinct and can be identified with comparison of the peaks through the mass spectral data. The different types of 'spinifex' resin can be easily distinguished

by extracting the corresponding ion as presented above. A full characterisation of each individual resin has not been presented here as the focus was to find the similarities across the groups and provide a way to identify similar resins in further work. A more complete profile may be necessary to identify the resins if authenticated samples become available for comparison in the future.

4.5 Conclusion

This chapter has reviewed previous evidence for the identification of spinifex and ironwood resins in the archaeological and ethnographic record and presented the results of the GC-MS analysis of ethnographic resins with a similar diterpenoid composition, which is unlike the conifer resins.

The chemical analysis of putative spinifex and ironwood resins reported in this study has contributed much-needed knowledge towards their ethnographic and archaeological identification. The majority of compounds are unknown; future studies are needed to determine if they include any new diterpenoids of interest, including whether they are unique to specific botanical sources and suitable as biomarkers. However, the findings are not totally consistent with previous analyses. There was no evidence of communic, abietic or succinic acids in any of the spinifex-type resin samples in contradiction to findings by de Silva et al. (2009). The composition of the labelled *Triodia irritans* sample appears to be a mixture of at least two different resins (possibly contamination), none of which are consistent with any of the other labelled spinifex samples, also hypothesised to be sourced from *Triodia*. The chemical findings are not consistent with what appeared to be the description of the source of the resin.

There is a large amount of variation between the composition of different samples that look similar chromatographically, with only a few compounds appearing in more than one group. However, there is consistency within the groups A to E, and the 'ironwood' group. This variation is much larger than was expected, and may be due to different source species of *Triodia*, or from resins from genera other than *Triodia*.

Putative *Erythrophleum chlorostachys* resin, as assumed by the ethnographic label of "Ironwood rosin" appears to be distinctive, and recognisable in some unknown museum samples. However, none of the compounds were identifiable through the NIST11 mass spectral database, consequently the botanical source still needs to be confirmed by comparison with an authenticated sample of *Erythrophleum chlorostachys* resin.

Spinifex resin is clearly not one distinct resin used throughout Australia, and many different types of resin were being utilized. Whatever the source of these type of diterpenoid resins, there are distinct groups which have the potential to be differentiated in aged samples.

Chapter 5

Triterpenoid resins from the Angiosperms

5.1 Introduction

Triterpenoid resins are found throughout the Angiosperms (flowering plants) and include some of the most famous resins such as frankincense and myrrh. In Oceania, the most commonly used triterpenoid resins are the elemi-type resins from the same family as the botanical sources of frankincense (*Boswellia*) and myrrh (*Commiphora*), the Burseraceae family (Langenheim; 2003). Elemi is the trade name for resins mainly from specific species of the genus *Canarium*. Locally used resin, however, includes resin from several species of *Canarium*, and other parts of the *Canarium* tree also have a long and significant history of use in Oceania, particularly the nuts (Matthews and Gosden; 1997). Evidence of the use and cultivation of *Canarium* trees has been found archaeologically and is significant to the relationship of Oceanic peoples with this genus, which also relates to their use of the resin. This chapter reviews the archaeological record of *Canarium* and ethnographic

record of *Canarium* resin specifically, then introduces some other triterpenoid resins of ethnobotanical importance. This is followed by a review of previous work on the chemical characterisation of triterpenoid resins, focussing on those most relevant to Oceania, before reporting the results of both the reference triterpenoid resins and ethnographic museum samples analysed in this project.

5.2 Background to triterpenoid resins of ethnobotanical and archaeological significance in Oceania

Triterpenoid resins are produced by several species scattered throughout the Angiosperms (flowering plants) from a number of different families of broad-leaved trees, predominantly but not exclusively tropical in distribution (Mills and White; 1994, p. 105). Sources of triterpenoid resins are numerous in both the northern and southern hemispheres. Possibly the most ethnobotanically important source of triterpenoid resin in Oceania is the nut-bearing tree of the genus *Canarium* (Langenheim; 2003).

5.2.1 Sources of triterpenoid resins

The *Canarium* genus is in the family Burseraceae, which also contains the other important resin-producing genera: *Aucoumea, Boswellia, Bursera, Commiphora, Dacryodes*, and *Protium*. The Burseraceae is known as the 'torchwood' or 'incense' family, most likely due to containing the botanical sources of both frankincense (*Boswellia*) and myrrh (*Commiphora*). The family includes flowering trees and shrubs native to tropical regions of the Americas, Africa, Malaysia and parts of Oceania. *Canarium* occur naturally in Australia and across the western Pacific Islands, through East and Southeast Asia, and in India and

Africa. The other genera in the Burseraceae family occur mainly in Central and South America, and are not native to Oceania (Mathe et al.; 2009, p. 632-4).

The Burseraceae are recognised as a sister group to the Anacardiaceae family, which *Pistacia* resin comes from. *Pistacia* resin, also known as 'mastic' has been successfully recovered from archaeological contexts in the northern hemisphere, highlighting the potential for archaeological recovery of related triterpenoid resin such as *Canarium* resin. As well as local ethnobotanical use, the resin from *Canarium* spp. has a long history of being sold commercially under the name 'elemi'. Other types of triterpenoid resin also have a history of economic importance, like mastic (from *Pistacia* spp.), and dammar.

Dammar is a type of resin characterised by, and in some definitions restricted to, exudates from members of the Dipterocarpaceae family. The genera that contain resin-producing species are *Anisoptera, Dipterocarpus, Vatica, Hopea, Neobalanocarpus*, and *Shorea*. The Dipterocarpaceae are abundant in Southeast Asia, but are not present in either the extant flora or fossil record of Australia and New Zealand (Seyfullah et al.; 2015). The distribution of Dipterocarpaceae does not stretch into Oceania, and according to Bennett (2000, p. 7):

> Botanists believe that many tree species, such as the Dipterocarpaceae, failed to reach the Solomons from Malesia because of the sea distances between islands.

The distinct distributions of these different types of resin are significant for identifying trade activity if the resins can be recovered from archaeological contexts, and identified to botanical source.

Gardenia is a genus of shrub tree from the Rubiaceae family that is native to parts of Oceania, and has some resin-producing species. *Gardenia aubryi* Vieill. is native to New Caledonia and the exudate is reported as containing dammarane-type triterpenoids (Grougnet

et al.; 2011). The resin of *Gardenia resinifera* Roth has been recorded as being used by Indigenous groups in India for its medicinal properties. For example, the Gond tribe in the Bhandara district of Maharashtra use *G. resinifera* resin warmed in coconut oil applied to the forehead and throat to ease ailments (Gupta et al.; 2010, p. 715-6). It is also taken orally to act as an antihelminthic to treat parasitic infestations, and when mixed with *Semecarpus anacardium* L.f. (Anacardiaceae) and *Allium sativum* L. (garlic) and warmed in castor oil, they apply it to treat wounds and cuts (Gupta et al.; 2010, p. 715-6). There are no specific ethnobotanical references to the use of *Gardenia* resin in Oceania, however, that the author is aware of.

Artocarpus spp. from the Moraceae family have been reported to produce resin, however, "more chemical analysis is needed before definite conclusions can be made about the actual nature of these secretions" (Langenheim; 2003, p. 82). *Artocarpus altilis* (Parkinson ex F.A.Zorn) Fosberg is more commonly known as breadfruit, which is common throughout Oceania, not including Australia. Although known to be a valued and cultivated commodity in Oceania (Yen; 1996), there is not any documented use of breadfruit resin specifically, that the author is aware of.

5.2.2 *Canarium*

Canarium is a genus of resin-producing tree that is economically and culturally important across the Western Pacific, particularly in the Solomon Islands, where there is a long history of using different parts of *Canarium* trees for food, fuel, medicine and ceremonial purposes (McClatchey et al.; 2006, p. 214).

5.2.2.1 Species

The main *Canarium* species of interest for use in Oceania, based on their distribution and reference in the archaeological and ethnographic records are *C. indicum* and *C. salomonense*. *Canarium indicum* L. (syn. *C. commune*) (Canarium almond) occurs in Papua New Guinea, Indonesia including Java, the Pacific Islands including Vanuatu and the Solomon Islands, as well as South America and Africa. Known by the local names: uele (Ubili, West New Britain); galip (Pidgin, Kuanua, East New Britain); angal (Tarawe, Siassi Island); cây-tram-trang (Annamite name); and other English names: canarium nut; Molucca nut; Polynesian almond; Java almond; south-sea almond; nangai nut; kenari (Thomson and Evans; 2006; Regert et al.; 2008; Hill; 2001). *Canarium salomonense* B. L. Burtt. (syn. *C. solomonense*) is native and endemic to the geographic Solomon Islands including the Bougainville province of Papua New Guinea (McClatchey et al.; 2006; TPL; 2013).

There are several other species of *Canarium* currently occurring in Oceania. According to a review conducted by Mogana and Wiart (2011, p. 2482):

> The geographical centre of their genetic diversity is the Molucca Islands of eastern Indonesia, but their centre of cultivated diversity is undoubtedly western Melanesia.

Of the many *Canarium* species that are in the South Pacific, 21 species were found in Papua New Guinea, eight in the Solomon Islands and three or four in Vanuatu, plus about nine species in the Philippines (Mogana and Wiart; 2011).

5.2.2.2 Taxonomy

The taxonomy of *Canarium* is complex, and distinguishing between the different species is difficult. Several of the *Canarium* species are grouped with similar taxon, according to Yen (1996, p. 30). *C. indicum* is in a taxonomical grouping with *C. ovatum* and *C. vulgare*, which are distributed from eastern Indonesia to the eastern Solomons. *C. salomonense* is in a taxonomical grouping with *C. lamii* and *C. harvey* having a more limited distribution in the eastern Solomons, from eastern New Guinea to the Islands just east of the Solomons. Interestingly, Yen (1996, p. 40) points out that:

> As with most subsistence crops in Oceania, intra-specific variability is a characteristic of plantings. *Canarium* and other nut and fruit genera, whether planted in the margins of fields or as village trees, are 'varietally' mixed.

The long history of cultivation, and the associated effects including intra-specific variability, makes the taxonomy complicated. Thomson and Evans (2006, p. 2) conclude that:

> The existing taxonomy of *Canarium* is based almost exclusively upon the gross morphology of dried herbaria material. This taxonomy, particularly that of the cultivated taxa, is inaccurate, and is likely to be significantly changed once the taxa are subjected to thorough DNA analysis.

Resin analysis may also be able to shed more light on the relationship between the different types of *Canarium*, however, the uncertainty of the taxonomy certainly makes this task more complex.

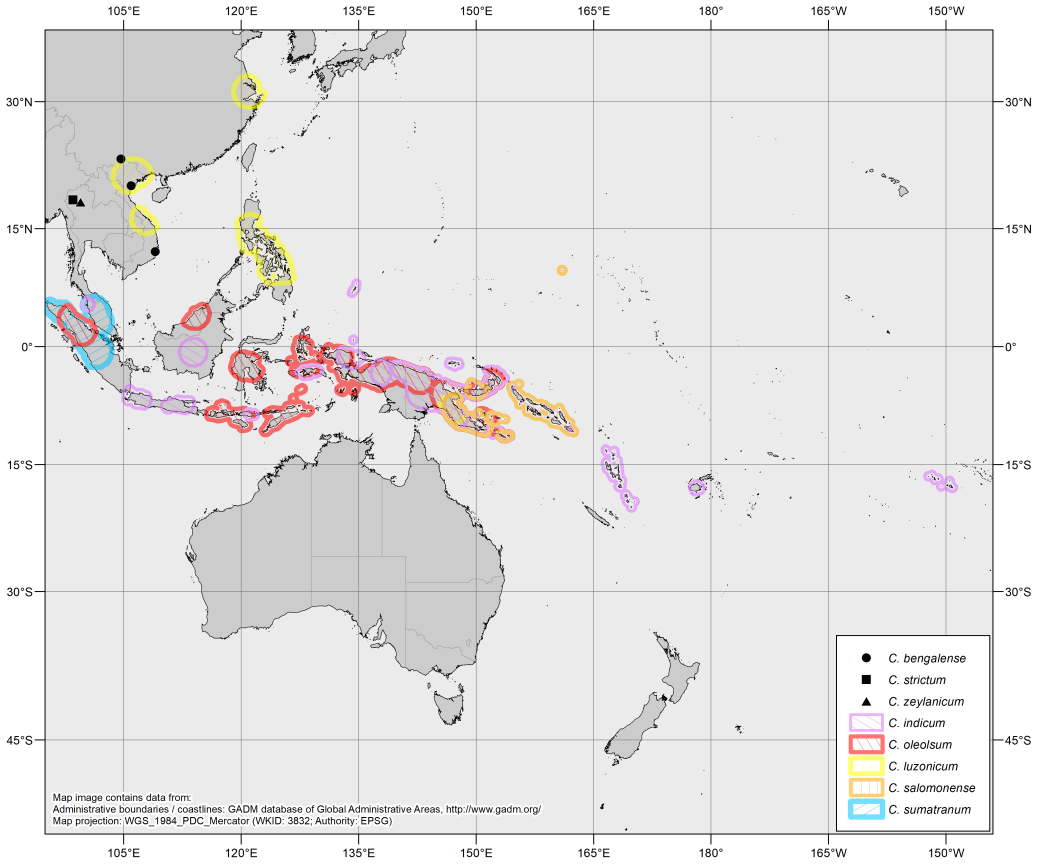


FIGURE 5.1: Map of the distribution of *Canarium* species in Oceania
Distribution data from ALA (2018); GBIF (2018)

5.2.2.3 Distribution

The distributions of some of the most ethnobotanically significant species of *Canarium* are shown in Figure 5.1.

5.2.3 Elemi and *Canarium* resin in the ethnographic record

Canarium resin has a long history of trade, and was sold commercially under the name elemi. The most important in terms of commercial export is Manila elemi, which is obtained mainly from *Canarium luzonicum* (Blume)A.Gray that grows in the Philippines, and specifically (strictly-speaking only) Manila (Mantell; 1950, p. 233). Other species of *Canarium* and various species from different genera but of the same family (Burseraceae)

are known to produce a similar type of oleoresin and have also been traded as elemi. Elemi is known to have been imported into Europe since the 15th century (de la Cruz-Cañizares et al.; 2005, p. 178). It became an important ingredient in varnishes in the 19th century and continues to be used in varnish for toys, furniture, musical instruments, and other applications (de la Cruz-Cañizares et al.; 2005, p. 178). Elemi and particularly Manila elemi has been especially important in the fine arts in its use as binding media and it is in this context that most chemical studies of the Burseraceae resins have been undertaken (de la Cruz-Cañizares et al.; 2005; White; 1978).

5.2.3.1 Indigenous use

Before this type of resin was discovered by Europeans, it was already being used by Indigenous communities local to where the resin-producing Burseraceae trees grow, in tropical and sub-tropical regions all across the world. Some species of *Canarium* are native to parts of Oceania, as well as near-by Southeast Asia. There are ethnographic accounts of Indigenous use of *Canarium* resins in Oceania but examples appear to be largely restricted to Melanesia, with very little mention of the use of *Canarium* in Australia or other parts of Oceania. There are, however, notably similar uses documented from the regions of Southeast Asia adjacent to Oceania.

The use of *Canarium* resin as canoe caulk, torch components, and traditional medicines are relatively well documented in Melanesia (Thomson and Evans; 2006, p. 9), and are similar to its uses in the nearby Philippines, Indonesia and Vietnam. For example, the resin was used as the principle combustable component in torches in the Solomon Islands (*C. salomonense* and *C. indicum* on Lauru Island) as described by McClatchey et al. (2006, p. 219-220). Similarly, an ethnographic account from the Philippines describes freshly gathered resin being mixed with dirt to make it stiff, rolled up and wrapped in a palm leaf to make a

torch that burns brightly and for a long time (Mantell; 1950, p. 234). In Vietnam, Viet (2010, p. 7) reports that ethnobotanical studies informed them of fresh *Canarium* resin being used for soaking a bunch of plant fibres, which were then used as a torch, and once hard, the resin coating the plant fibres burn longer, and are water-resistant. Soaking plant fibres in *Canarium* oleoresin wasalso recorded for binding a wooden handle onto stone waisted tools, a form of hafting (Viet; 2010, p. 7).

Another local traditional use has been documented in the coastal regions of Papua New Guinea, where recipes for red paint include the "bark sap" from *Canarium indicum* (also known as Polynesian almond), which turns red when mixed with an alkali such as lime (Hill; 2001, p. 56). Chemical analysis of the exudates in all these contexts would greatly enhance the knowledge around these traditional technologies.

There is very limited knowledge on the use of *Canarium* resin in Australia. In north Queensland, Roth reported that dry lumps of gum gathered from the brown cedar or the mackay cedar tree *Canarium australasicum*, were used for joining spear shafts (Maloney et al.; 2015, p. 37). Nugent (2015, p. 75) also notes a reference to *Canarium australasicum* being used as an alternative fixative, alongside ironwood gum, for hafting spears and bonding and sealing barb attachments, when grass tree gum (*Xanthorrhoea* resin) was not available.

5.2.3.2 Cultural and spiritual significance

Ethnographic research demonstrates that the *Canarium* tree is not only significant as a food resource in Melanesia, but has become central to traditional, customary life, and stories, songs, and dances relating to the tree have been recorded (McClatchey et al.; 2006, p. 214; Thomson and Evans; 2006, p. 2). In the Solomon Islands, the importance of the *Canarium*

tree is highlighted by the Marovo word *buruburu*, which is used for both the *Canarium* nut tree, and the time-span of a year, with the traditional calendar running from one *Canarium* harvest to the next (Hviding; 1996, p. 414; Lentfer et al.; 2013, p. 121). Seasonal markers such as the *mati buruburu* remain important socially, providing opportunities for group gatherings and affirmation of kin ties and other relationships, as well as other aspects of daily life in the New Georgia Islands of the Solomon Islands (Hviding; 1996, p. 53; Lentfer et al.; 2013, p. 121). Also in the Solomon Islands, the *Canarium* trees are known to have been used as tribal boundary markers on Lauru (Choiseul) Island, with social rules relating to harvesting the nuts, and logging (Thomson and Evans; 2006, p. 2; McClatchey et al.; 2006).

Canarium trees seem to have a certain spiritual or religious aspect associated with them, and different parts of the tree are often used in religious, cultural, healing, war, and ritual ceremonies (Tamalene et al.; 2016). There are also different rules for different species. McClatchey et al. (2006) conducted an ethnographic analysis of the importance of *Canarium* to the native people of Lauru (Choiseul) Island, part of the Solomon Islands, just south of Bougaineville. They found that logging of *Canarium* trees was common, and Malaysian and other foreign loggers left clearings in the *Canarium* forests, whereas local loggers left scatters of the single species *Canarium salomonense*. *C. indicum* trees were used for timber for canoes, houses, other wooden artefacts, and firewood, whereas *C. salomonense* were only used as a source of edible nuts and resin, "Lauru loggers left the trees because of their unique spiritual importance among all other forest trees" (McClatchey et al.; 2006, p. 212). Though very similar to *C. indicum* with only minor morphological differences, they found that *C. salomonense* was considered 'sacred' and a critical resource, whereas *C. indicum* could serve as a substitute in some but not all situations (McClatchey et al.; 2006, p. 223-4). The spiritual difference between the species is demonstrated, for example,

by a special tool 'kijalaku', which is a stone hammer used only for cracking *C. salomonense* fruits (McClatchey et al.; 2006, p. 223-4).

The report by (McClatchey et al.; 2006) addresses the need for more ethnographic research on domesticated trees of Melanesia, which is also highlighted by Matthews and Gosden (1997, p. 131). Thomson and Evans (2006, p. 2) note that "*Canarium* nut groves are often the only evidence left of pre-Christian inland villages and their associated taboo sites," making them a unique resource. However, the use of *Canarium* resin has survived Christianisation. In recent times, resin has been used on Lauru Island in the Catholic religion as incense during service and worship, and *Canarium* was preferred over alternatives because of its strong, pleasant, mint-like smell (McClatchey et al.; 2006, p. 220).

5.2.3.3 Medicinal significance

The Indigenous people of Melanesia have a "rich heritage of traditional knowledge in the uses of plants as medicines" (Holdsworth; 1980, p. 33-4). *Canarium* appears to have an important role in traditional medicine, for example, resin from the inner bark was an essential element in medicinal remedies in the Solomon Islands, which was both externally applied and ingested as tonic, where *C. salomonense* was more important for this but *C. indicum* was used just as often (McClatchey et al.; 2006, p. 220). Tonics were intended to provide strength and endurance, or as a blood enhancement, ingested as a water infusion along with other plant ingredients of family secret recipes. These tonics are known and commercially traded throughout the Solomon Islands as 'varuvare' or "Choiseul water" (McClatchey et al.; 2006, p. 220).

In the Philippines, the *Canarium* tree (both *C. luzonicum* and *C. ovatum* have been referenced) is known as "pili", the resin is called "brea", and the oleoresin is called "saheng"

(Mantell; 1950, p. 234; Lanting and Palaypayon; 2002, p. 18). According to Lanting and Palaypayon (2002, p. 18), saheng is used as a stimulant, a rubefacient (an external skin application causing redness of the skin), and an anti- rheumatic when applied externally. It is also used to form an ointment for applying to indolent (painless) ulcers, and the brea is used in poultices to apply to swellings of the legs Lanting and Palaypayon (2002, p. 18). According to Mogana and Wiart (2011, p. 2482), the resin of *C. tonkinense* Engl. is used for these same applications (locally to Vietnam) and *C. indicum* L. also has similar medical uses. In Indonesia, resin powder is given orally to treat rheumatism, epilepsy, syphilis, fever, bronchitis, asthma, cough, hernia, general stress and chronic skin disorders and also helps to improve dry, damaged or injured skin (Meena et al.; 2012; Tamalene et al.; 2016; Athar and Mahmood; 2005). The exudate from *Canarium* species (*C. schweinfurthii* in Camaroon) has even been referred to as a "panacea of witchcraft" (Jiofack et al.; 2009), suggesting either a universal remedy and magical cure-all, maybe an elixir of life, or perhaps rather a cure for evil and the unexplained.

5.2.4 *Canarium* in the archaeological record

Evidence for the use of *Canarium* has been recognised in the archaeological record of Oceania, through the nut shells, seeds, and other plant remains that have then been recovered at archaeological sites throughout Oceania.

5.2.4.1 *Canarium* nuts

Canarium trees have been particularly significant in Lapita studies, particularly in the study of the development of agriculture in Oceania and the discussion of an independent origin of agriculture in Papua New Guinea (Allen and Gosden; 1991; Spriggs; 1991; Matthews and

Gosden; 1997; Denham et al.; 2009; Bayliss-Smith et al.; 2003). The Lapita culture was the first substantial Austronesian colonisation and is seen in the archaeological record as moving into Melanesia and Polynesia from 3550 BP to 2450-1950 BP (Spriggs; 1991, p. 119). Significantly, *Canarium* nut exploitation represents a continuity of resource exploitation and management from pre-Lapita into the Lapita period (Wickler; 1995, p. 669; Bayliss-Smith et al.; 2003; Spriggs; 1991).

The first direct confirmation of Lapita-age use of nut-cracking tools comes from an artefact dated to approximately 2800 BP (mid-late Lapita) from the Makekur Lapita site on Arawe Island in West New Britain Province, Papua New Guinea. It has been interpreted as a nut-cracking anvil, with nutshell residue identified as "most likely *Canarium indicum* L." (Lentfer et al.; 2013, p. 5). A stone bark-cloth beater collected in the Kandrian area by Blackwood in 1937 (now in the Pitt Rivers Museum, Oxford: specimen registration number 1938.36.1229) is described in her catalogue as "also used as a nut cracker" (Lentfer et al.; 2013, p. 7). This is an example of why studying museum items is important, and how connecting information from different sources can contribute to the bigger picture.

5.2.4.2 Domestication

According to Yen (1996, p. 38), *C. ovatum*, *C. vulgare*, *C. indicum*, *C. decumanum*, *C. lamii*, *C. salomonense*, *C. harveyi* are all domesticated *Canarium* species occurring in the Western Pacific Islands, although the ability to identify domesticated varieties of *Canarium* is questioned (Fairbairn; 2005, p. 450). It has been suggested that the archaeological evidence supports the view that *C. indicum* is the oldest domesticated species in Melanesia, as indicated by its distribution, and that it played a significant role in the transition from hunting-gathering to horticulture, or at least resource management in the Pleistocene (Yen; 1996, p. 41; Wickler; 1995, p. 8; Spriggs; 1991, p. 122-3). *Canarium* plant material dated

to 17,000 BP in the middle Sepik area, 15,500 BP on Manus, 11,500 BP on Buka, and 9000 BP on New Ireland, can be seen to indicate a movement of the nut trees from the north coast of New Guinea through the Bismarck Archipelago to the Solomon Islands (Bourke; 2010, p. 13). It is likely that edible *Canarium* species were introduced to the Bismarcks and Solomons from mainland New Guinea as a managed food resource, by 10,000 BP, before the end of the Pleistocene (Wickler; 1995, p. 680; Bourke; 2010, p. 13; Spriggs; 1991, p. 122-3).

Fairbairn (2005, p. 494-5) argues that the "early long-distance transference in Near Oceania" may be more accurately described as a "local widening of the distribution of *Canarium* species." Re-dated early evidence suggests that large-fruited forms of *Canarium* may have been native to some of Papua New Guinea's islands (Fairbairn; 2005, p. 489). Landscape modification alongside exploitation of local resources continued through the early Holocene and mid- Holocene and as stated by Smith and Jones (2007, p. 29), was:

> [...]probably in association with the establishment of trade and exchange networks throughout the voyaging corridor of Island southeast Asia, New Guinea, the Bismarck Archipelago and the Solomon Islands.

Yen (1996, p. 40) highlights that other products "such as the resinous trunk exudates used in caulking of canoes" i.e. *Canarium* resins, need investigating as "possible products that might contribute to the value in the development of nut industries" highlighting the importance of resin analysis in archaeology.

5.2.4.3 Trade

In a discussion of the effects of European contact and the spice trade on the peoples of the Indonesian Archipelago, and particularly in the province of Maluku, Stark and Latinis

(1996, p. 63-4) claim that it is possible that *Canarium* nut processing played a much greater role in the early Maluku economy than previously thought. With *Canarium indicum* representing the dominant food species from 900 BP through to the 17th century at an archaeological site on the island of Ambon, Stark and Latinis (1996) compare the pattern to Lapita sites throughout Island Melanesia and New Guinea. The island of Ambon provides a good example of Indigenous peoples supplying local trade centres, as trade with New Guinea was extensive, particularly in the 17th century. Historical records from 1860 indicate a trade of prestige goods in return for commodities including dammar resins (Stark and Latinis; 1996, p. 57). Archaeological finds dating to 900 BP at the Batususu Rockshelter, on the island of Ambon, combined with a lack of the expected spice remains (clove and nutmeg) may indicate that the site was not used for supplying the spice trade, but used for the extraction and processing of forest resources such as *Canarium* nut and damar resin (Stark and Latinis; 1996, p. 63).

There is no mention of the origin of the dammar by Stark and Latinis (1996) but it is possible that the 'dammar' resin mentioned could also have been sourced from the *Canarium* trees. The word 'dammar' or 'damar' has a complex history and is known to have been used to refer to hard resin in general, rather than the specific type of dipterocarp resin for which the term is now generally reserved (Gianno; 1986). In reflection of this history, *C. strictum* is known locally in Thailand (and India) as 'black dammar.' This is another example where chemical analysis of archaeological resins could shed light on natural resource exploitation and trade systems.

Regarding the distribution of *Canarium*, there is a marked absence in New Caledonia, which along with breadfruit and kava, the absense of the canarium nut in the "traditional vegetational repertiore" is, as noted by Carson (2002, p. 35), curious. *Canarium* trees are capable of growing in New Caledonia, and Carson (2002, p. 35) conclude that their:

> [...]continued absence over ca. 3000 years of human occupation can be explained only by local cultural practices that effectively guarded against the introduction of these plants.

There may be a spiritual reason for this guarding, or an ecological one perhaps protecting local species that occupy similar habitats. In terms of archaeology, this hypothesis suggests that any finds of *Canarium* in New Caledonia will either have implications for the trade of artefacts or raw resin materials, otherwise it is unlikely that *Canarium*-like resins used here are actually from *Canarium*, and may indicate a different genus that produces a similar type of resin.

5.2.5 Previous identification of archaeological *Canarium* resin

Though *Canarium* resin has not been identified specifically in archaeological contexts in Oceania so far, elsewhere in the world, ancient *Canarium* resin has been tentatively identified. Traces of *Canarium*-like resin were found on stone waisted tools excavated in the rock-shelter Du Sang (Hoa Binh, Vietnam) (Viet; 2010, p. 7), possibly representing a similar technique of hafting as was ethnographically documented (section 5.2.3). Plant remains of *Canarium* (*C. album, C. indicum* and *C. tramchim* (wild)) have been found at similar sites in Vietnam dated to 11,000 BP or after, during the Holocene, later than they have been found in Melanesia (Viet; 2010, p. 2). This indicates that *Canarium* resin may have been used for hafting, and chemical analysis of finds such as these could provide a much more detailed picture of hafting practices and the use of *Canarium* resin in different localities.

Possible evidence that the Nabataeans used African elemi in their techniques to prepare dead bodies during their funeral practices comes from GC-MS analysis of four Nabataean samples of textile fragments from monumental tombs of Madâ'in Sâlih, ancient Hegra, in

Saudi Arabia (Mathe et al.; 2009, p. 635). Archaeological samples of textiles that are either covered with a black layer or bound together with some black amorphous substance are thought to possibly contain *Canarium* resin based on the presence of ursa-9(11),12-dien-3-ol,ursa-9(11),12-dien-3-one, olean-9(11),12-dien-3β-ol, β-amyrone, β-amyrin, α-amyrone, α-amyrin and lupeol detected along with some fatty acids (Mathe et al.; 2009, p. 635). The abundance of these triterpenic compounds indicates that the resin is an elemi-type resin of the Burseraceae family.

Mastic, or *Pistacia* resin, has been identified in archaeological finds, due to the survival of characteristic triterpenoids. Four different species: *Pistacia atlantica, P. khinjuk, P. lentiscus*, and *P. terebinthus*, may have been available in the Mediterranean for the production of resin. However, Pollard et al. (2007, p. 155) explain that it is not possible to distinguish the species, even in fresh samples, based on triterpenoid composition. The same may be true for the other types of triterpenoid resins under the same conditions, though research has not yet been extensive enough to draw this conclusion for elemi, or *Canarium* resin.

5.2.6 Previous work on the characterisation of triterpenoid resins

5.2.6.1 Chemistry of triterpenoid resins

The majority of chemical study on triterpenoid resins has focussed on those that were commercially available in Europe and used for varnish or binding media in artwork throughout the 17th-19th centuries. Dammar (resin from Dipterocarpaceae) and mastic (resin from *Pistacia* from the Anacardiaceae family) are the main types of resin to have been traded and used as varnishes, and thus have received the largest amount of chemical analysis. The use of mastic is mostly confined to the northern hemisphere with the natural distribution

of *Pistacia* spp. Dammar has important local uses in Southeast Asia, but not as far as Oceania (section 5.2.1).

Elemi (discussed earlier), dammar and mastic all have a triterpenoid based chemistry and can therefore appear very similar chemically. However, the triterpenoids in each of the types of resin are quite different.

Oleanane- and ursane-type triterpenoids

Oleanane derivatives are present in almost all triterpenoid resins and are therefore alone not suitable as markers beyond that categorisation (Burger et al.; 2011, p. 191).

Most of the elemis contain substantial amounts of the pentacyclic alcohols α- and β-amyrin, which are ursane- and oleanane-derived respectively. The amyrins occur in many plant families but are present in considerable abundance in the Burseraceae family (Lampert; 2003). α-Amyrin is not found in mastic or dammar resins and is therefore suggested as a reasonable biomarker for Burseraceae resin (de la Cruz-Cañizares et al.; 2005). Rhourrhi-Frih et al. (2012) found that *Canarium madagascariensis* resin contained pentacyclic triterpenes, a lanostane-type alcohol, and a triterpenic dialcohol, and appeared to be very distinct in composition compared to *Boswellia* and *Commiphora* (Frankincense and Myrrh) also of the Burseraceae family. Biomarkers for *Boswellia* and markers for heating treatment in these types of resins have been published elsewhere (Ménager et al.; 2014, Table 2).

Lucero-Gómez et al. (2014) provide an example of the identification of the botanical sources of resin to species using GC-MS, for Mexican species of *Bursera*. In their analysis of the variability of the triterpenic molecular composition of resins from Mexican *Bursera* spp. Lucero-Gómez et al. (2014, p. 682) found that there was a clear distinction among the different species studied except two that share an identical triterpenic fraction: *B. bipinnata* and *B. stenophylla*. This work indicates that identification to species is possible for some

resins within the Burseraceae family, therefore it may also be possible for resins of other genera of the same family to also be identified to species of botanical source, though there is clearly difficulty in distinguishing some species.

Both oleanane- and ursane-type molecules, including α- and β-amyrin, have a similar fragmentation pathway during electron ionisation mass spectrometry, resulting in abundant ions at m/z 189, 203 and 218 (Modugno et al.; 2006). For example, α- and β-amyrin (urs-12-en-3-ol and olean-12-en-3-ol respectively) have very similar mass spectrometric signatures, but they have different retention times, also β-amyrin has a higher melting point than α-amyrin (Vázquez et al.; 2012). Nuclear magnetic resonance (NMR) is suggested as the best way to distinguish between the different pentacyclic triterpenoids of the ursane and oleanane type (Vázquez et al.; 2012).

Euphane-type triterpenoids

In addition to the amryins, Manila elemi has been found to contains the 'elemi acids' of the euphane series, which are thus thought to be indicators of the species *Canarium luzonicum*, but the group of resins as a whole has not been systematically studied (Mills and White; 1977, p. 22; Mills and White; 1994, p. 108; de la Cruz-Cañizares et al.; 2005).

Lupane-type triterpenoids

Some triterpenoid resins consist of compounds with a lupane-structure. Betulinic acid is a pentacyclic lupane-type triterpenoid which is found in birch bark tar (Pollard and Heron; 1996, p. 252). Betulinic acid is derived from betulin, and betulin is present in the bark of the birch tree *Betula* spp. (Betulaceae) (Kommera et al.; 2010, p. 3346). *Betula* spp. is an introduced species in New Zealand (Spellerberg et al.; 2006).

In mass spectrometry triterpenoids with a lupane-structure are recognised by the fragment ion m/z189 (Modugno et al.; 2006). However it can be difficult to see chromatographically as, according to Peters et al. (2005, p. 580), lupane co-elutes with oleanane on typical apolar chromatographic columns, and also has a similar spectrum to oleanane, producing a strong m/z 191 ion fragment. A prominent m/z 369 fragment resulting from loss of an isopropyl group (m/z 43) acts as a distinguishing characteristic for lupane, while oleanane lacks an isopropyl group and thus yields no m/z 369 fragment, but gas chromatography-tandem mass spectrometry (GC-MS/MS) is recommended for the best way to quantify lupane (Peters et al.; 2005, p. 580). This co-elusion is important to note, but other lupane-type triterpenoids may be more easily identifiable by GC-MS.

Dammarane-type triterpenoids

The definition of dammar is ambiguous, however, as it originally referred to resins of a particular type with particular characteristics, even if from different sources. However, with the development of the scientific taxonomic system, dammar has been re-defined to refer to resin specifically from the Dipterocarpaceae family, to which the most common dammar producing species belong (Lampert; 2003). Dammarane-structure triterpenoids represent, and are indicative of the dammars, of the Dipterocarpaceae family. It has been generally thought that the combined presence of of dammarane, oleanane and ursane derivatives is an indicator for dammar and can be used to identify the presence of the resin even in a mixture (Burger et al.; 2011, p. 191). Burger et al. (2011) have had positive results in differentiating dammar resins at species level in fresh resins, and going on to positively identify degraded dammar resin from a shipwreck to source species.

5.2.6.2 Degradation of triterpenoid resins

Archaeologically, several triterpenoid resins have been recognised in aged samples, for example, mastic (*Pistacia*) found in amphorae (Stern et al.; 2003), and identified in the balm of Egyptian mummies (Colombini, Modugno, Giannarelli and Fuoco; 2000). This has been achieved through the use of biomarkers, however, degradation can make identification of resin more complex.

Regert et al. (2008, p. 692) suggests that Frankincense (*Boswellia*) may be more prone to degradation than diterpenoid resins which readily polymerise. This hypothesis can be extended to all the resins from the Burseraceae family, as the triterpenoids found in resins are of a non-polymerising but easily oxidisable nature (Mills and White; 1994, p. 105). The amyrins oxidise with age, with a decrease of the β-/α- amyrin ratio, suggesting the processes may affect β-amyrin to a greater extent than α-amyrin (at least in Manila elemi). Oxidation products that may become visibile are α- and β-amyrone and a-neooleana-3(5),12-diene (de la Cruz-Cañizares et al.; 2005). Importantly however, α- and β-amyrin have been found in significant amounts in fossil resins dated to many millions of years old, suggesting that these compounds are stable over long periods of time and are suitable as biomarkers (de la Cruz-Cañizares et al.; 2005; Mills and White; 1977; Langenheim; 1990).

Previous work on birch bark tar (betulin and lupeol with low amounts of lupenone, betulone and betulinic acid) provides information on the degradation pathways of lupane type molecules, notably betulin is partly transformed into lupa-2,20(29)-dien-28-ol by dehydration, and lupeol leads to formation of the triterpenoid hydrocarbon lupa-2,20(29)-diene (Modugno and Ribechini; 2009, p. 223). Both of these molecules are indicative of thermal treatment and their proportion changes depending on the duration and the intensity of the hard-heating treatment (Modugno and Ribechini; 2009, p. 223).

5.2.6.3 Previous work on *Canarium* resin

There is not very much in the literature specifically on the chemical analysis of *Canarium* resin, but individual triterpenes have been isolated from various plant parts of several species of *Canarium* for medical research. Isolation and structure elucidations of secondary metabolites in *Canarium*, including from the resin as well as the fruit, has been carried out since the 1950s (Mogana and Wiart; 2011, p. 2482). A review in 2011 by Mogana and Wiart (2011) reported collective data from the literature of about 99 isolated compounds (including 58 terpenoids) from 9 species of *Canarium: C. schweinfurthii, C. madagascariense* (syn. *C. boivinii*); *C. odontophyllum, C. denticulatum* (syn. *C. manii*); *C. album, C. zeylanicum, C. indicum* (syn. *C. commune), C. muellerii*; and *C. bengalense*. The review highlighted that at that time, only a small percentage of the extant species of *Canarium* had been studied chemically so far, which, even with some new studies is still true considering there are now 94 accepted species according to The Plant List (2013).

According to He and Xia (2008) *Canarium album* (Lour.)DC. fruit contains the phenolic compounds gallic acid, ellagic acid, corilagin, quercetin-3-galactoside (hyperin), and kaempferol-3-glucopyranoside. In the analysis of the resin, however, Tamai et al. (1989) found seven triterpenes, including what they identified as urs-12-ene-3α,16β-diol and olean-12-ene-3α,16β-diol. This indicates the chemical composition of *Canarium* resin is not necessarily related to that of other parts of the tree, and the resin needs to be studied in isolation. The most widely studied of the *Canarium* resins is unsurprisingly *C. luzonicum*, the main source of Manila elemi (Villanueva et al.; 1993; Sawadogo et al.; 1985; de la Cruz-Cañizares et al.; 2005). Lampert (2003) analysed *C. luzonicum* resin, and reported the mass spectral data, describing the chromatogram as two main peaks of β- and α-amyrin, followed by five minor peaks. A recent study of *Canarium ovatum* Engl. resin reported

that the methanol extract contained the fourteen known triterpenoids, α-amyrin, 3-epi-α-amyrin, brein, 3-epibrein, uvaol, β-amyrin, 3-epi-β-amyrin, maniladiol, 3- epimaniladiol, lupeol, 3-oxotirucallic acid, 3α-hydroxytirucallic acid, 3β-hydroxytirucallic acid, and 3α-hydroxytirucalla-7,24-dien- 21-oic acid, as well as some sesquiterpenes (Ragasa et al.; 2015, p. 94).

Canarene was identified in *C. schweinfurthii* and described by Kamdem et al. (2011), noted as having a unique carbon skeleton and representing a new class of triterpenoids to be called canarane. The terpenoids 3α-hydroxyurs-12-en-11-one, 3α-hydroxyolean-12-en-11-one, olean-12-en-3,11-dione, urs-12-en-3,11-dione, α- and β-amyrin, α- and α-amyrenone, were identified in the oleoresin, bark and timber of *Canarium zeylanicum* (Retz.) Blume (Ceylon elemi), along with taraxerol, sitosterol, canaric acid, elemene, elemol, α-pinene, α- and β-phellandrene, limonene, terpineol and carvone (Bandaranayake; 1980).

In summary, the previous work on the terpenoid components of *Canarium* resin shows different compositions in different species, indicating that although the main components, α- and β-amyrin are the same in several species, there is likely to be enough variation in the other terpenoids to distinguish between certain species. This hypothesis is supported by the species level identification possible in the Mexican *Bursera* as previously discussed, which is a closely related genus, although difficulties distinguishing between certain other species were also noted.

It is also noted that only certain species across the Burseraceae family produce elemi-type resins, characterised by the large proportions of α- and β-amyrin, including several species of *Canarium*. Therefore, it is reasonable to hypothesise that there may be non-elemi-type resins produced by other species in *Canarium*, as there are across the family, such as *Boswellia* and *Commiphora* (Frankincense and Myrrh).

5.3 Results from GC-MS analysis of reference triterpenoid resins

5.3.1 *Canarium* samples

Resin samples from ten different species of the genus *Canarium* L. have been successfully analysed by GC-MS after methylation. This is the first report of chemical data from the resin of several species of *Canarium*, with some replicates, that have been analysed together and compared. The source species of the resin samples are shown in Table 5.1. The natural distributions of these species are shown in Figure 5.1.

TABLE 5.1: Samples of resins from *Canarium* species analysed

Species name	Common name	Sample numbers
Canarium bengalense Roxb.	East Indian copal	K081
Canarium indicum L. [syn. *C. commune*]	Molucca nut	K018, K083, K084
Canarium luzonicum (Blume)A.Gray	Elemi canary tree, Manila elemi	K019, K020
Canarium paniculatum (Lam.)Benth.ex Engl.	-	K082
Canarium salomonense B.L.Burtt.	Canarium almond	K021
Canarium schweinfurthii Engl.	Bush candle tree	K087, K088, K101
Canarium similajau [unrecognised name]	-	SWF10
Canarium strictum Roxb.	Dhup tree, Black dammar	K092, K093, K094
Canarium sumatranum Boerl. and Koord.	-	K095
Canarium zeylanicum (Retz.)Blume	Ceylon elemi	K096

All the resin samples from *Canarium* are consistent in displaying a characteristically high proportion of both α- and β-amyrin (Figure 5.2).

The main components of these resins, congruent with previous reports, are the amyrins and related oleanane- and ursane- derivatives. These related compounds are very difficult to distinguish between using GC-MS alone, in some cases more difficult due to such low abundances. The oleanane- and ursane-type compounds are characterised by an abundance of the fragment ion m/z 218 and can be seen more clearly on the chromatogram by extracting

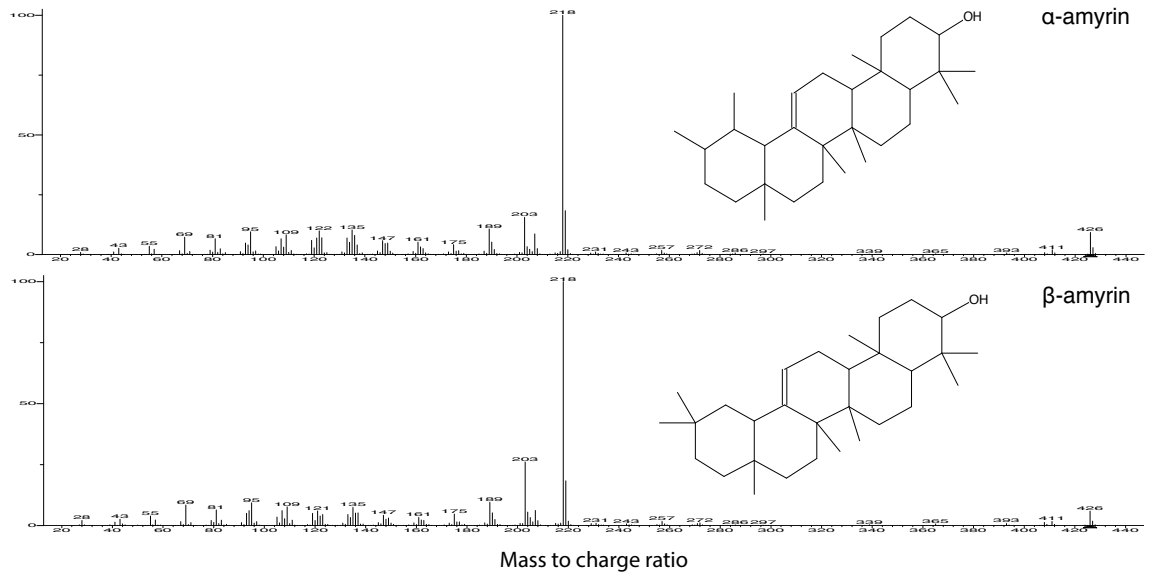


FIGURE 5.2: Mass spectra and structures of α-amyrin (above) and β-amyrin (below)

this ion. Extracting the m/z 424 molecular ion can assist in observing the peaks other than the dominant α- and β-amyrin, which has a molecular ion of m/z 426.

5.3.1.1 Species characterisation

From the analysis of resin from several species of *Canarium*, it is apparent that there are only subtle differences between the various species, in some cases no apparent differences as can be differentiated by GC-MS alone. The most significant findings are presented here, with α- and β-amyrin represented by 'A' and 'B' respectively, and the full mass spectral data for all the triterpenoid samples analysed are presented in Appendix F.

The two *C. luzonicum* samples, K019 and K020, which are consistent with each other in the triterpenoid component, as shown in Figure 5.3, were compared to the mass spectral data presented by Lampert (2003) in her analysis of *C. luzonicum* from the same source as K019 (Kew EBC Cat. No. 63270). The main amyrin peaks were apparent in both analyses, though five small unidentified peaks, described by Lampert (2003), occurring after the main amyrin peaks, were not clearly detected in the analysis for this project. The absence of

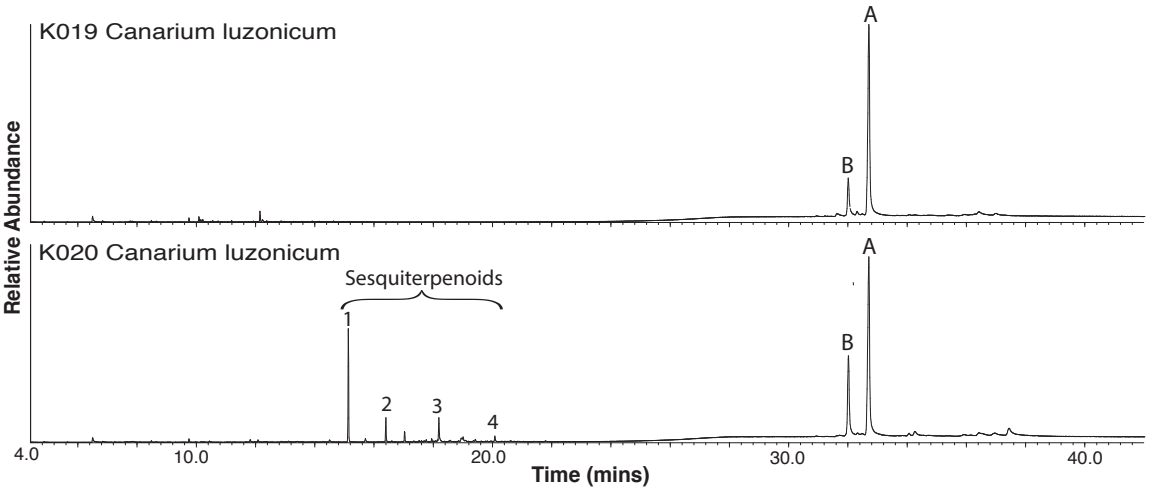


FIGURE 5.3: Chromatograms showing the main components in two samples of *Canarium luzonicum* resin (B = β-amyrin, A = α-amyrin)

these smaller peaks may reflect further degradation of the sample, or else differing factors in the analytical process, including the different methylation method used.

There was no evidence of euphane-type triterpenoids detected in either analysis. Sample K020 did however contain some sesquiterpenoids including eudismol, which is known to occur in Manila elemi, suggesting the sample is less degraded as the more volatile sesquiterpenes are still present.

The two *C. indicum* samples, K018 and K084, are consistent with other. These samples are very similar in composition to *C. luzonicum*, to the point where is not possible to tell the resins apart by this type of analysis. The amyrin content is seen clearly by extracting the m/z 218 ion, and is almost identical in the resin samples from these two species, as shown in Figure 5.4. In this case, extracting the m/z 424 ion did not produce any peaks for either of the two resins.

The composition of *C. salomonense* resin, however, appears to be significantly different to *C. indicum* and *C. luzonicum* (Figure 5.5). *C. salomonense* has more main components in addition to the α- and β-amyrin, all strongly related to the amyrins, but displaying clearly as at least four seperate peaks on the chromatogram. The *C. strictum* and *C.*

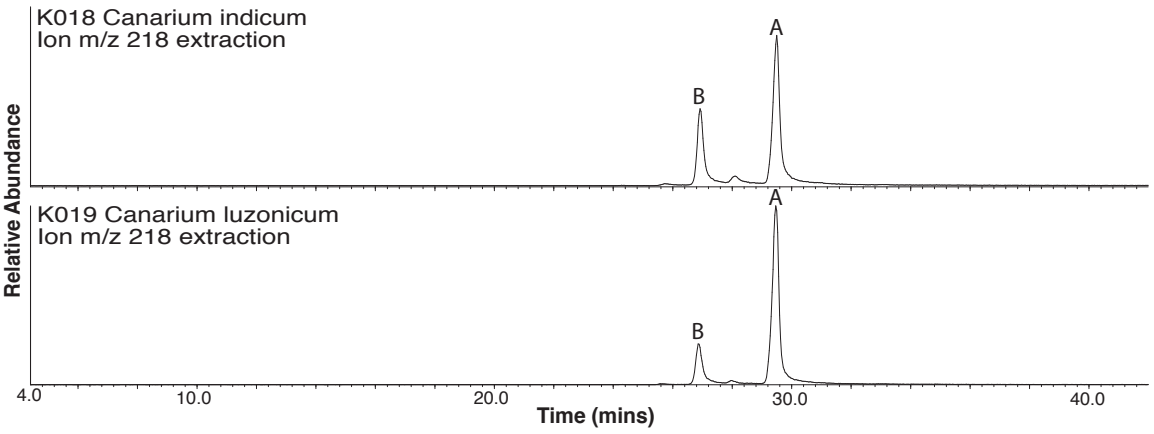


FIGURE 5.4: Partial chromatograms comparing the main components in samples of *Canarium indicum* and *C. luzonicum* resins (B = β-amyrin, A = α-amyrin)

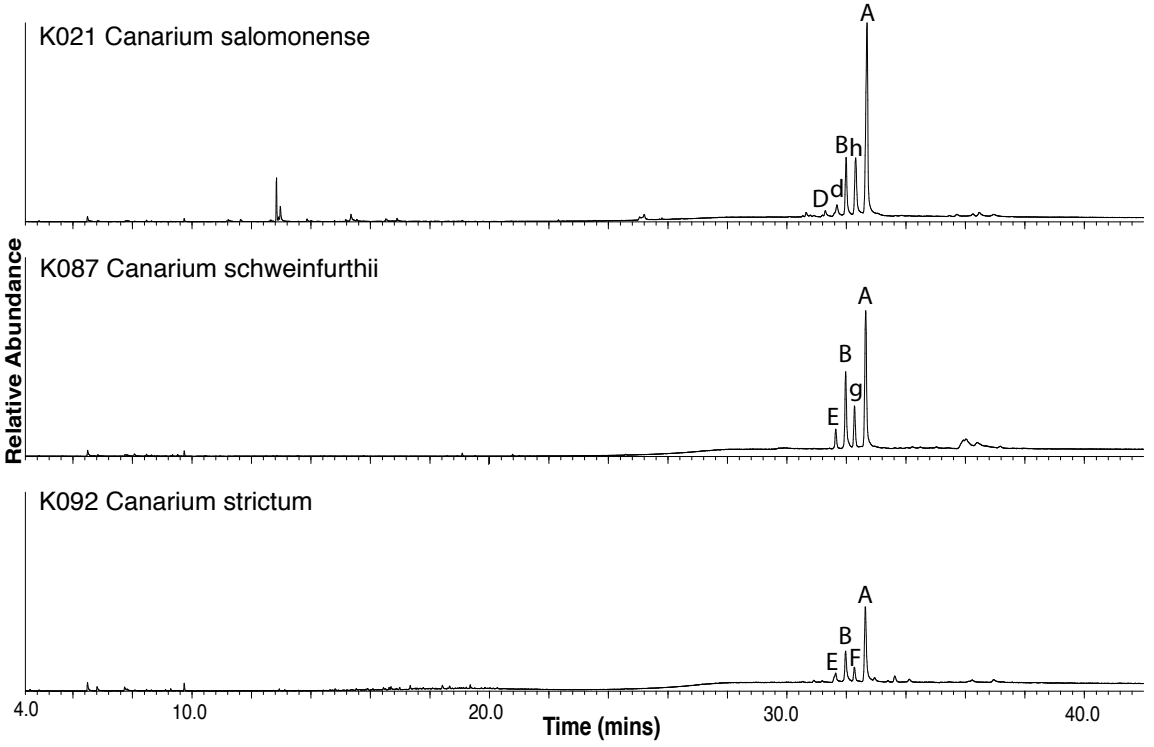


FIGURE 5.5: Chromatograms of *Canarium salomonense*, *C. schweinfurthii* and *C. strictum* reference resins
(D = ursa-9(11),12-dien-3-ol, d = oleanane-type compound, E = β-amyrone, B = β-amyrin, F = α-amyrone, g and h = unknown compounds, A = α-amyrin, full mass spectral data in Appendix F)

schweinfurthii resin samples produce similar chromatograms to *C. salomonense* in that there are four distinct peaks, but there is some variation on the smaller peaks of each species as demonstrated in Figure 5.5. Additionally, the geographical distributions of these species are very different, and it can be assumed that examples from Oceania are more likely to be from *C. salomonense* than the African species.

In terms of inter-species variation as seen in the chromatograms, where two or more samples were available, there is some variation in relative abundance of compounds within the same species. However, the mass spectral data for the compounds themselves appear to be largely consistent, even when occurring in low abundances. This is demonstrated by the analysis of three samples of *C. schweinfurthii* resin and three samples of *C. strictum* resin, as shown in Figure 5.6 (K094 may be showing coelution with a dammarane compound from contamination or a dammar resin within the sample[1]).

The resins from *C. salomonense*, *C. schweinfurthii* and *C. strictum* are all different in composition to those of *C. luzonicum* (Manila elemi) and *C. indicum*, and are also distinguishable from each other. However, comparison of the chromatograms from several more species of *Canarium* resin show the extent of similarities across the genus. The mass spectral data of even the smaller peaks appear conistent across all five species shown in Figure 5.7.

This chemical similarity suggests that species level identification may not be possible for most species of *Canarium* via resin analysis by GC-MS. However, it does appear that there are two distinct groups, the elemi-like resins with two main amyrin peaks and only trace levels of related compounds, such as *C. luzonicum* and *C. indicum*, and the non-elemi resins

[1]Sample K094 presents a peak identified as a dammarane-type compound where we expect to see α-amyrin. This is very strange as the Kew EBC specimen was labelled as *C. strictum* and the accompanying peaks match those in the other *C. strictum* samples. It may, however, represent a mixture of two resins, where the two compounds have co-eluted, forming the large peak together. It is possible that the resin specimen was contaminated with an unknown dammar resin.

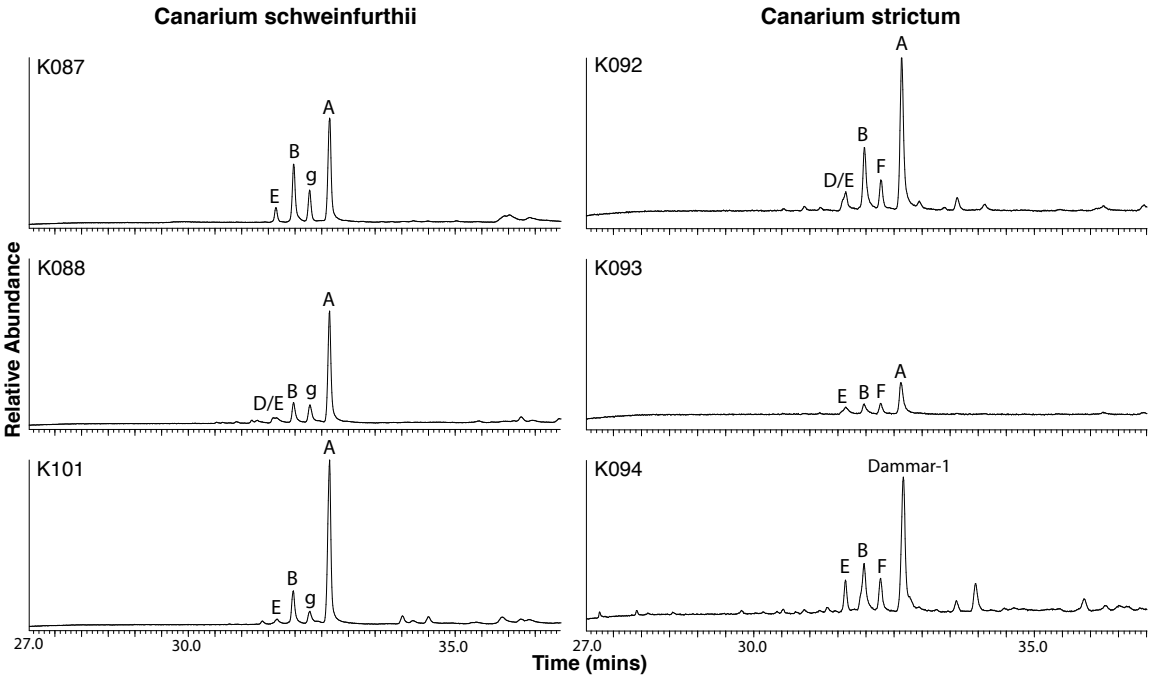


FIGURE 5.6: Partial chromatograms comparing the main components in multiple samples of *C. schweinfurthii* and *C. strictum*
(D = ursa-9(11),12-dien-3-ol, E = β-amyrone, B = β-amyrin, F = α-amyrone, g = unknown compound, A = α-amyrin, full mass spectral data in Appendix F)

with four or five main peaks such as *C. salomonense*. Cautiously using relative abundance of the amyrin peaks compared to the additional peaks of these further species, a closer look assigns *C. paniculatum* and *C. zeylanicum* resins to the elemi-like two-peak group, and *C. similajau, C. sumatranum* and *C. bengalense* resins to the non-elemi four-peak group (chromatograms shown in Figure 5.7).

5.3.1.2 *Canarium* resins of unknown species

Four resin samples of unknown species of *Canarium* clearly fall into either the two- or four-peak groups (Figure 5.8). Sample K090 peaks match with the *C. salomonense* reference resin, plus it was collected from the Solomon Islands and therefore identification as resin coming from *C. salomonense* is highly plausible. Interestingly, sample K102 is recorded as coming from a torch, but it has no associated geographical information. It does, however,

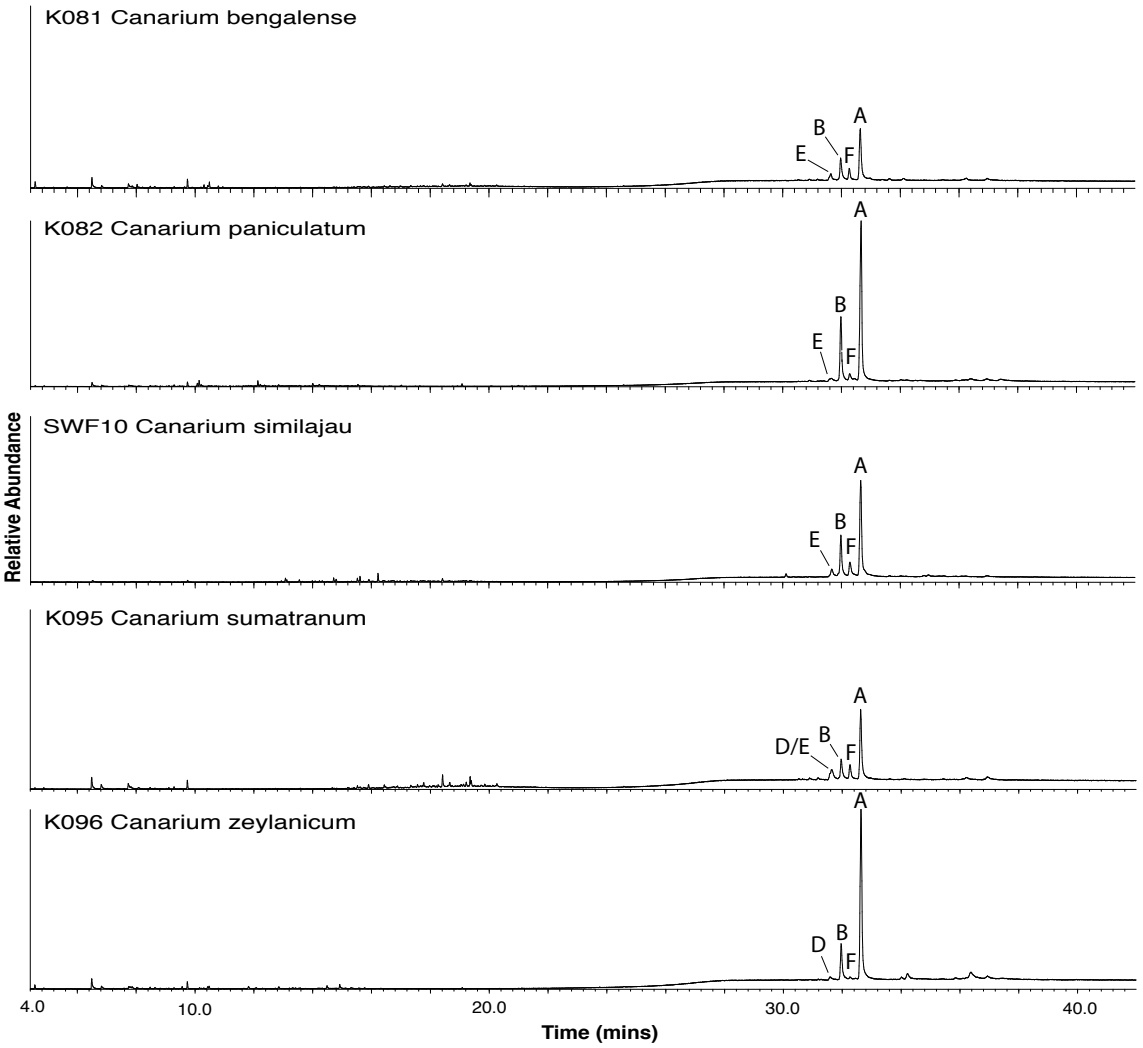


FIGURE 5.7: Chromatograms of *C. bengalense, C. paniculatum, C.similajau, C. sumatranum* and *C. zeylanicum* reference resins
(D = ursa-9(11),12-dien-3-ol, E = β-amyrone, B = β-amyrin, F = α-amyrone, A = α-amyrin, full mass spectral data in Appendix F)

have a very high consistency with the *C. salomonense* reference resin, and so is hypothesised to be the same.

Sample K089 is from Malaya and is clearly also a four-peak resin, similar to the *C. strictum, C. bengalense* and other resins in the four-peak group with peaks E,B,F and A. More research into the local Malayan species would be required for a confident identification.

Sample K091 is in the two-peak group, and is therefore categorised here as an elemi-type resin. This sample is from New Guinea, according to the herbarium notes, so could plausibly

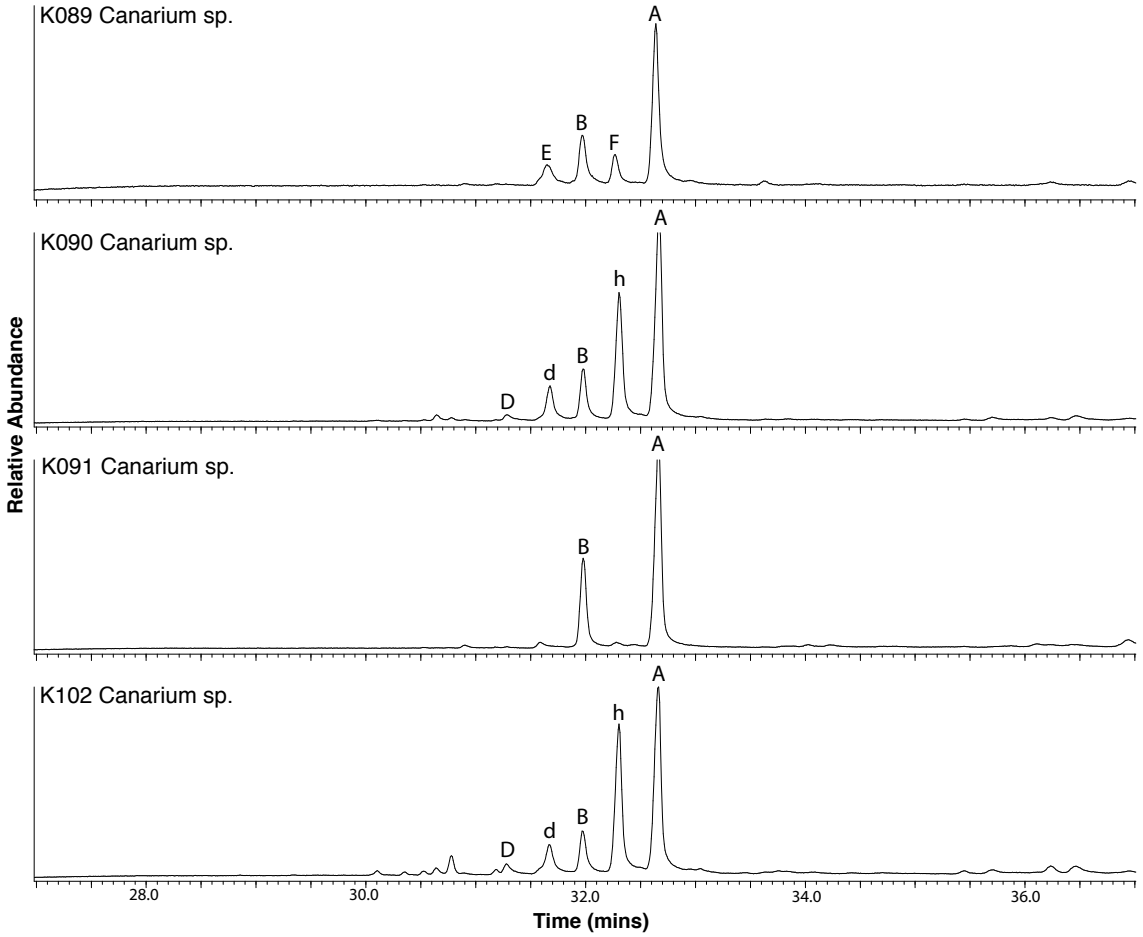


FIGURE 5.8: Chromatograms of resin samples from four unknown species of *Canarium* (B = β-amyrin, A = α-amyrin, details of other peaks in Appendix F)

be resin from *C. indicum, C. luzonicum*, or potentially *C. oleolsum*, for which a reference sample would be needed for comparison.

Further research into the analysis of resins from *Canarium* would be required to see a more complete picture of the relationship between the composition of resin produced by different species and within the same species. As some of the species are so well geographically defined, geographical distributions can be used alongside the chemical analysis to deduce probable species identity.

5.3.2 Other Burseraceae samples

The chemical profile of resins from *Canarium* spp. are also similar to those of the non-*Canarium* Burseraceae resins included in the reference collection. The resin samples from non-*Canarium* species in the family Burseraceae Kunth that are included in this project are shown in Table 5.2.

TABLE 5.2: Samples of resins from other Burseraceae species analysed

Species name	Distribution	Sample numbers
Protium guianense (Aubl.)Marchand	Southern America (*Protium* spp: Indonesia)	EB06
Bursera simaruba (L.)Sarg.	America	EB08
Aucoumea klaineana Pierre	Africa	K080
Dacryodes edulis (G.Don)H.J.Lam	Africa (*Dacryodes* spp.: New Guinea, Indonesia, Malaya, Philippines)	K085

The main compounds in *Canarium* resin, α- and β-amyrin, that are characteristic when in large quantities, are also present in similar quantities in resins from these related genera as shown in the respective chromatograms in Figure 5.9.

Protium guianense (Aubl.) Marchand is native to Southern America, but there are some species of *Protium* Burm.f. in Indonesia. *Bursera simaruba* (L.) Sarg. is native to Southern and Northern America. There are no species of *Bursera Jacq.* ex L. native to Oceania. *Aucoumea klaineana* Pierre is native to Africa and is only species in the genus *Aucoumea* Pierre. *Dacryodes edulis* (G.Don) H.J.Lam is native to Africa, but there are some species of *Dacryodes* Vahl in New Guinea, Indonesia, Malaya, and the Philippines. Despite the large geographic and taxonomic seperation between some of these species, the chemical composition of the resin is remarkably similar, as shown in Figure 5.9.

It appears as though the resin from certain species of *Canarium*, namely *C. indicum*, and *C. luzonicum*, are more similar to these non-*Canarium* Burseraceae resins than they are to the

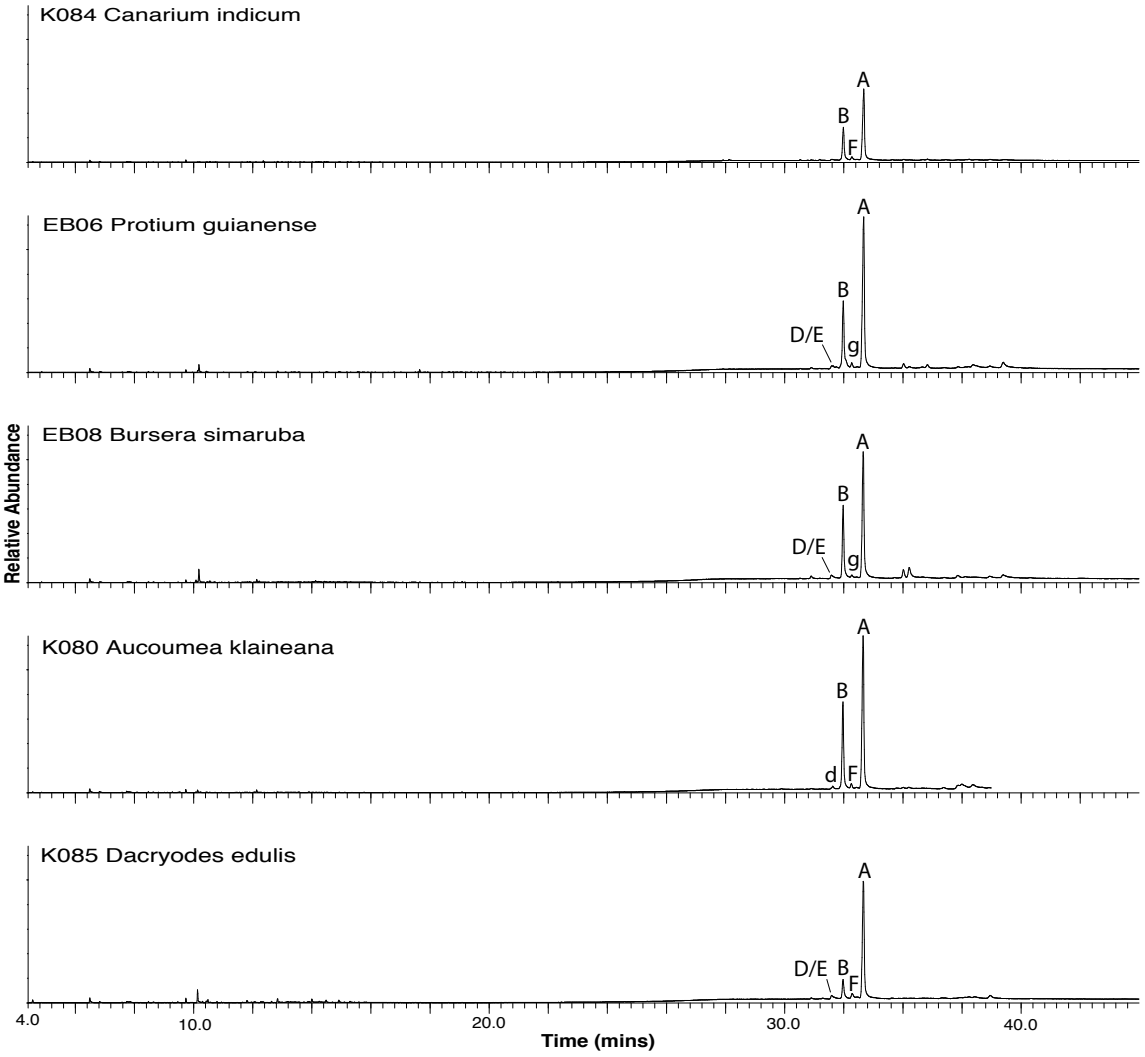


FIGURE 5.9: Partial chromatograms showing the main components in the resin from several genera of the Burseraceae family (A = α-amyrin, B = β-amyrin, details of other peaks in Appendix F)

species of *Canarium* that are in the four peak group (Figure 5.7). It is concluded that the 'elemi' type resins, that is the resin from species that produce a similar resin to *Canarium luzonicum*, characterised by just two peaks: α- and β-amyrin, are scattered throughout the Burseraceae family.

The dominance of the α- and β-amyrins make finding the differences in the less abundant compounds very difficult, but there does appear to be subtle variations in the composition of the 'elemi' type resins, as shown in Figure 5.9. The relationship between the resins from different genera in the Burseraceae family, and the different species within the *Canarium*

genus, needs to be investigated in order to better distinguish the different resins. This further work may require a complementary technique to GC-MS, such as NMR, to more easily differentiate and gain confidence in the identifications of these various elemi-like resins.

5.3.3 Dipterocarpaceae samples

TABLE 5.3: Samples of resins from Dipterocarpaceae species analysed

Species name	Distribution	Sample numbers
Anisoptera grossivenia V.Sloot.	Borneo	SWF08
Anisoptera marginata Korth.	Borneo, Malaya, Sumatera	SWF09
Anisoptera thurifera (Blanco)Blume	Philippines, Indonesia	K054
Dipterocarpus globosus Vesque	Borneo	SWF02
Dipterocarpus sarawakensis Slooten	Borneo, Malaya	SWF01
Shorea lunduensis P.S.Ashton (unresolved)	Borneo	SWF04
Shorea scabrida Symington (unresolved)	Borneo	SWF05
Shorea sp.	India, SE Asia	SWF03
Vatica mangachapoi Blanco	Hainan, Malaya, Philippines	SWF12
Vatica rassak Blume	Maluku, New Guinea, Sulawesi	K055, K057
Vatica sp.	India, China SE, SE Asia, New Guinea	EB02

Reference resin samples from a range of Dipterocarpaceae species were also analysed, and are listed in Table 5.3. The Dipterocarpaceae resin samples were all found to contain low levels of α-amyrin and compounds related to both α- and β-amyrin (ursane- and oleane-type).

Anisoptera

All three *Anisoptera* samples eluted α-gurgujene, an unknown compound, olean-12-en-28-oic acid, 3-oxo, methyl ester, and urs/olean-12-en-3-one, listed in retention order.

Dipterocarpus

Sample SWF01 had previously been analysed and hypothesised to have been wrongly classified in belonging to the *Dipterocarpus* genus due to its inconsistencies with the composition of the other dipterocarp resins (Bradshaw; 2009), but has not as yet been otherwise re-classified. The chromatograms for these Dipterocarpaceae samples can be found in Appendix J.

Vatica

Four resin samples from species of *Vatica* were analysed and are shown in Figure 5.10. The label for sample K055 was unclear but interpreted as *Vatica papuana*, which is an unresolved name and a synonym of *Vatica rassak* Blume according to GBIF (2018). The consistency in chemical composition of K055 with the other *V. rassak* resin sample (K057) supports this assignment (Figure 5.10).

The sample from *Vatica mangachapoi* is slightly different. Sample EB02 of unknown species appears chemically consistent with the two *V. rassak* resin samples and is therefore cautiously identified as *Vatica rassak*, although the inter-species variability of *Vatica* resins will require more research to whether species can be determined in this way.

5.3.4 Other triterpenoid resin samples

Artocarpus altilis

The Moraceae species *Artocarpus altilis* (breadfruit) (K053) produces a triterpenoid resin of the ursane/oleanane type like *Canarium* spp. resin, but with no α- or β-amyrin, as shown in Figure 5.11.

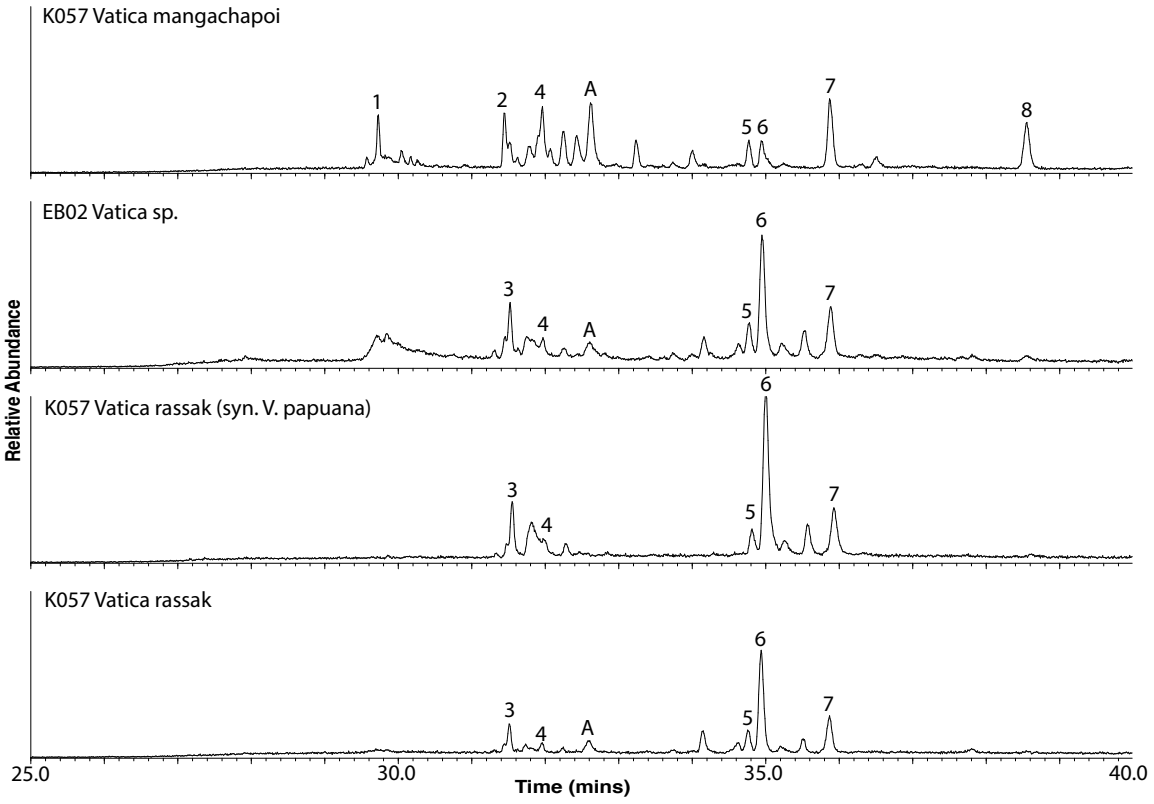


FIGURE 5.10: Partial chromatograms of samples SWF12, K055, K057 and EB02 (A = α-amyrin, peaks 1-8 = unidentified (possibly dammarane) triterpenoids)

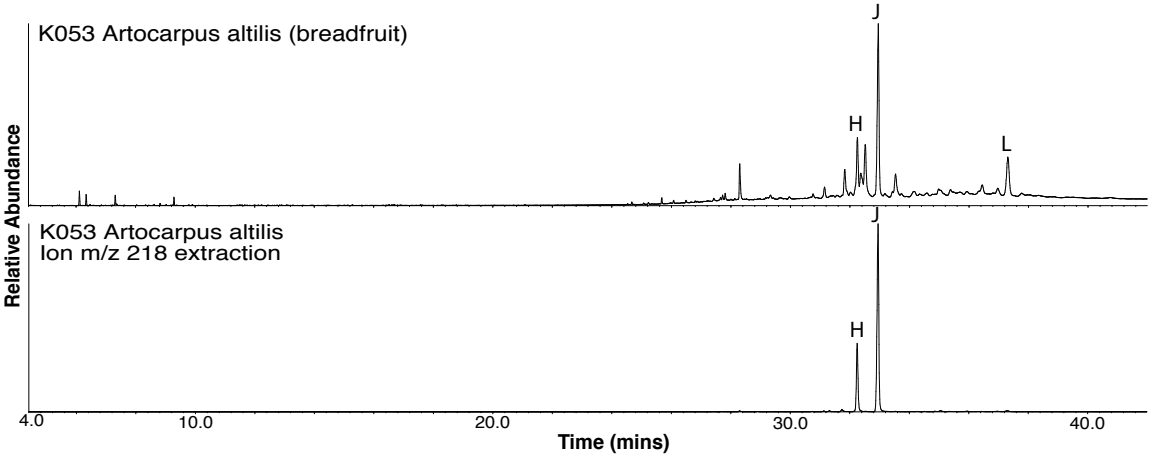


FIGURE 5.11: Chromatograms of *Artocarpus altilis* resin sample (above) and the m/z 218 ion extraction (below)
(H=12-oleanen-3-yl acetate, J=urs-12-en-24-oic acid, 3-oxo, methyl ester, L=11-Oxoolean-12-en-3-yl acetate)

Gardenia aubryi

A sample of *Gardenia aubryi* (EB15), a species of the Rubiaceae family native to New Caledonia was found to contain lup-20(29)-en-3-one (peak N) and some unknown triterpenoids. The chromatogram is shown in Figure 5.12.

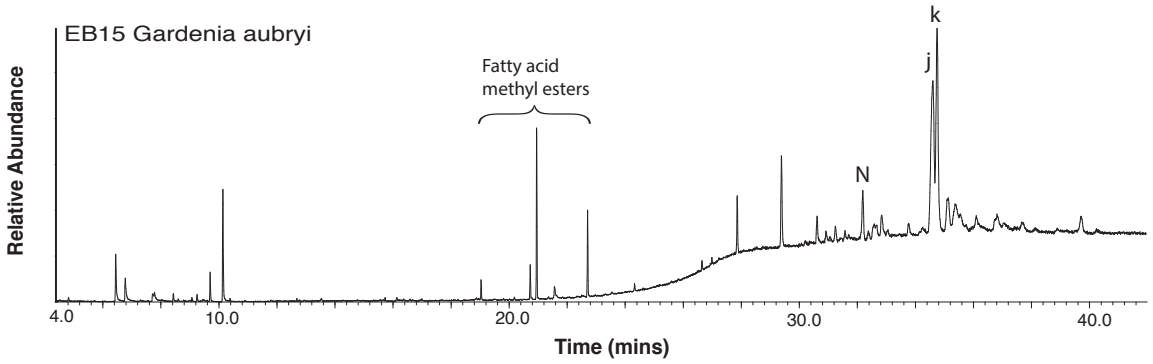


FIGURE 5.12: Chromatogram of *Gardenia aubryi* resin sample (N = lup-20(29)-en-3-one, peaks j-k = unidentified triterpenoids)

Further samples

Further triterpenoid resin samples (Appendix A) included in the reference data were found to have the following notable characteristics: Anacardiaceae, Clusiaceae and Myoporaceae resins do not contain α- or β-amyrin. The four *Calophyllum* samples (K097, K098, K099 and SWF11) do not have any significant peaks in the di- or triterpenoid region of the chromatogram. The two *Myoporum platycarpum* samples (K047 and K048) are consistent and have one main peak of cembra-2,7,11-trien-4,5-diol. None of the ethnographic samples resembled any of these reference materials.

5.4 Results from GC-MS analysis of ethnographic museum artefacts with triterpenoid resins

Triterpenoids were identified in several of the resin samples from the ethnographic museum artefacts. The majority of these samples contained triterpenoids of the oleanane- and ursane-type that are known to occur in Burseraceae resins. Many of these samples included α- and β-amyrin, which are characteristic of the Burseraceae, and particularly the 'elemi' type of resin. The presence of these and related compounds were not always obvious and extraction of the ion m/z 218 was used to more clearly identify the oleanane-/ursane-type compounds present in the resin samples. Dammarane- and lupane-type triterpenoids were identified in some of the other resin samples. The mass spectral data can be found in Appendix F.

5.4.1 Oleanane- and ursane-type triterpenoid resins

5.4.1.1 *Canarium salomonense* resin

Three samples, PBH040, PBH060, and PRM29 are consistent with the more distinguishable four-peak *Canarium* resins, and with consideration of the geographical distributions, are cautiously identified as resin from the species *Canarium salomonense*. The chromatograms are shown in Figure 5.13. Based on the results of this project (section 5.3), the identification of *C. salomonense* at species level is plausible, however, a more comprehensive study of resins from all the different *Canarium*, and non-*Canarium* Burseraceae species would be necessary to strengthen this identification.

5.4.1.2 Elemi-type Burseraceae and other possible *Canarium* resins

Two samples, AM18 and PRM27 produced chromatograms that are very similar to the 'elemi' resins of the Burseraceae family, as shown in Figure 5.14. The amyrins (peaks B and A) are far more prominent than any other compounds. This is consistent with the resin samples from *Canarium luzonicum*, *C. indicum* and the other samples with the elemi-type composition from throughout the Burseraceae family. Two more samples PRM28 and PBH029 also have the dominant amyrin peaks, but look more like the 4-peak *Canarium* resins. These four ethnographic samples are therefore identified as Burseraceae resins, and as three of the four are from artefacts originating in Papua New Guinea (PBH029 is of unknown Oceanian origin), the source species of the resins are reasonably likely to be *Canarium* spp.

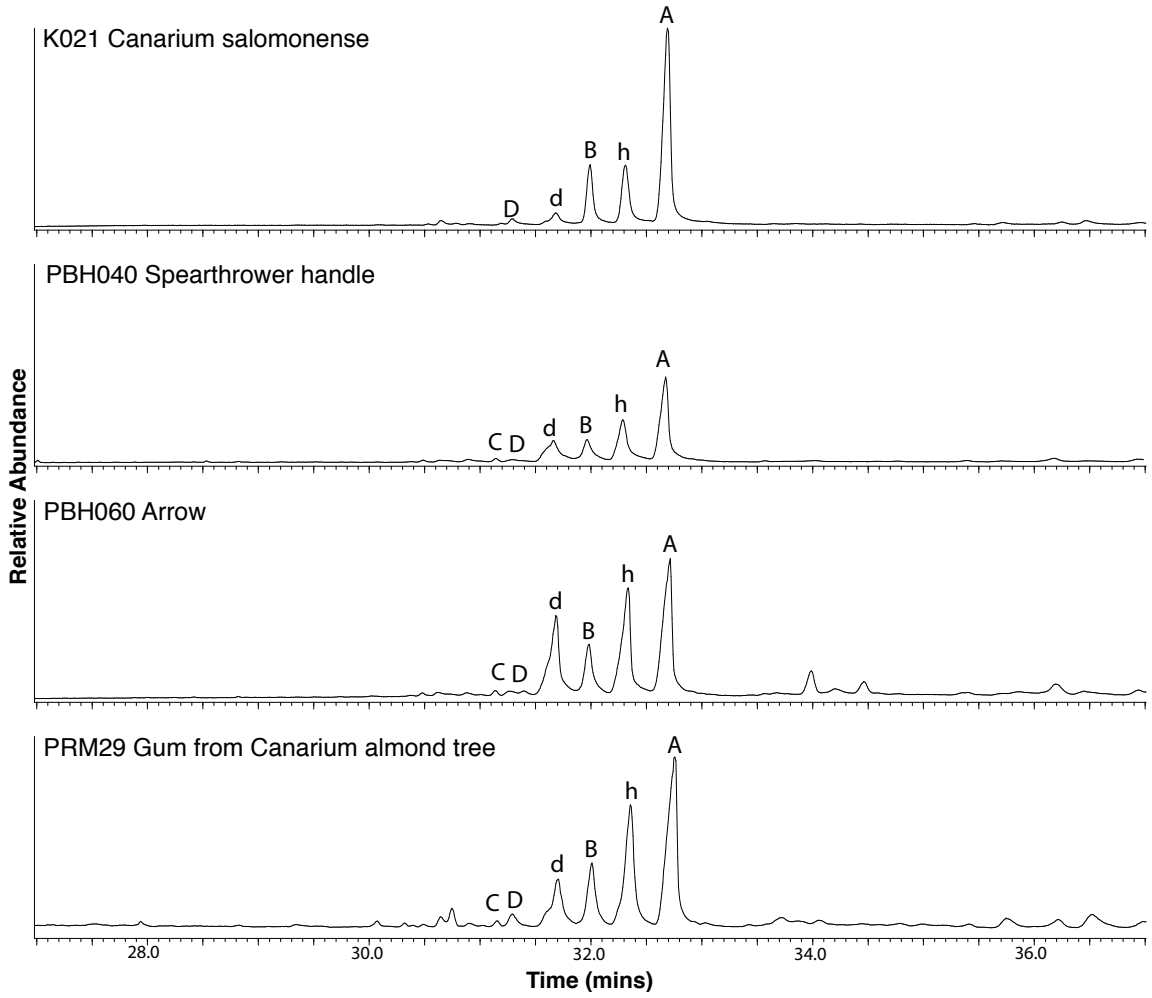


FIGURE 5.13: Partial chromatograms of K021 *C. salomonense* and samples PBH040, PBH060 and PRM029
(A=α-amyrin, B=β-amyrin, C=ursa-9(11),12-dien-3-one, D=ursa-9(11),12-dien-ol, lower case letters=unknown compounds (mass spectral data can be found in Appendix F))

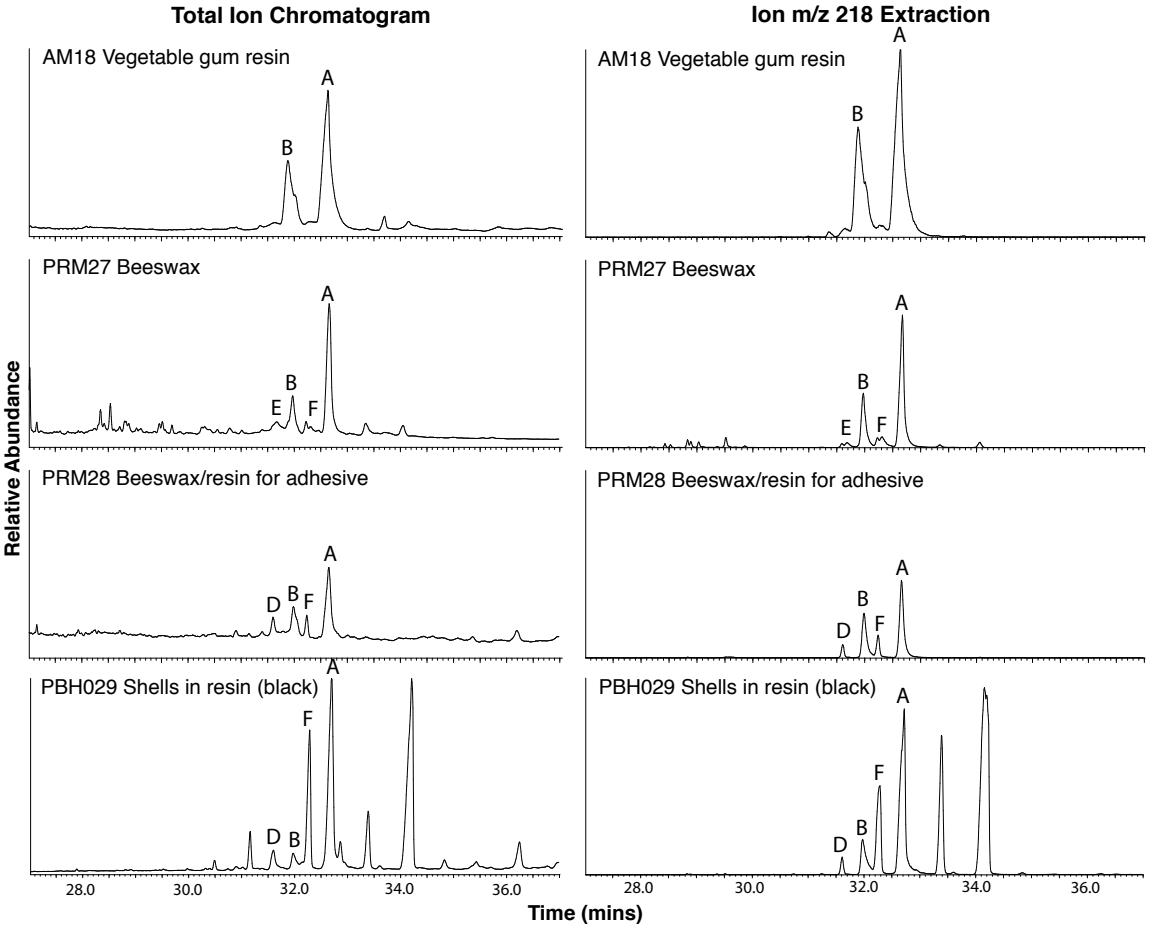


FIGURE 5.14: Partial chromatograms of amaryn-dominant samples AM18, PRM27, PRM28 and PBH029 showing total ion chromatogram and m/z 218 ion extractions (A = α-amyrin, B = β-amyrin, details of other peaks in Appendix F)

5.4.1.3 Non-elemi-type Burseraceae resins

Samples PBH037, PBH038, PBH096, PBH098 and AM01 are chromatographically similar to each other (Figure 5.15). The amyrins are present in these samples but are less prominent than in the elemi-type Burseraceae and other *Canarium* samples.

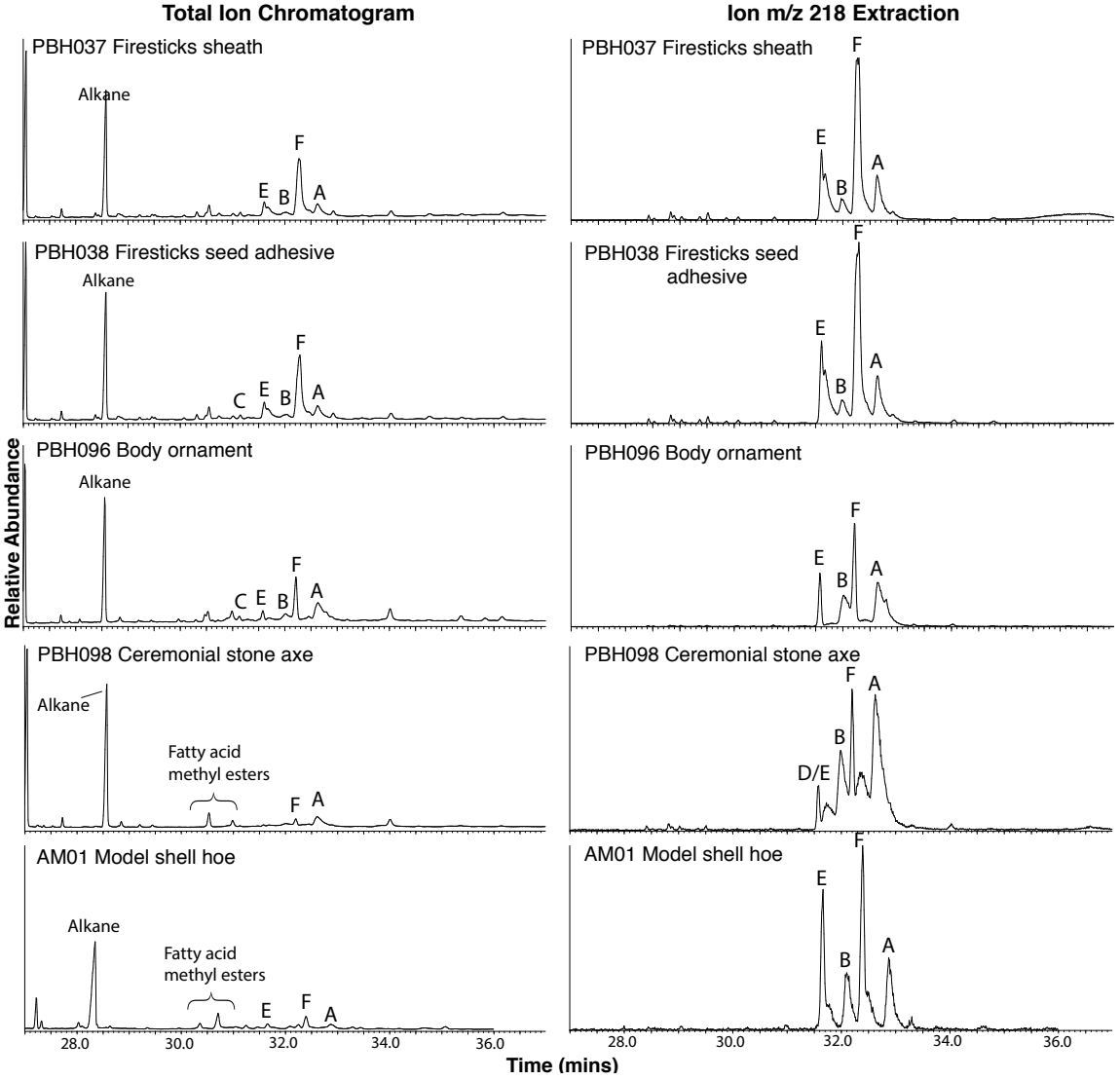


FIGURE 5.15: Partial chromatograms of PBH037, PBH038, PBH096, PBH098 and AM01 showing total ion chromatograms and ion m/z 218 extractions (A = α-amyrin, B = β-amyrin, details of other peaks in Appendix F)

Instead, the amyrin-related compounds, the amyrones are relatively more abundant. There may be some degree of degradation affecting the ratios of these compounds, particularly as the amounts of the triterpenoids detected in the sample are low in general. However,

the low abundance of the amyrins compared to the amyrones, shown more clearly by the ion extraction, is likely to reflect the original composition of the resin. These ethnographic samples do not represent the elemi-type Burseraceae resins sampled in this project, but are likely to originate from other sources within the Burseraceae or related family, and possibly even within the *Canarium* genus. These samples all come from artefacts that originated in the far north of Australia, mostly far north Queensland, and AM01 from the Torres Strait.

The finding of *Canarium*-like resins found on artefacts from Australia is interesting as there is not much reference to the use of *Canarium* in the ethnographic literature on resin use in Australia. The presence of *Canarium* resin on artefacts such as these from Far North Queensland could indicate either that the resin and/or complete artefacts have been traded in from Papua New Guinea or the Solomons, or the resin could have been obtained from the locally growing species. *Canarium australianum*, *C. australasicum*, *C. vitiense*, *C. muellerii*, and *C. acutifolium* are the only currently known native species of Burseraceae to Australia, occurring across the tropical north and east of Australia. The only references found in the literature to *Canarium* species from Australia are for *C. australasicum* used for hafting for example by Nugent (2015, p. 75).

Based on the geographical origin of the items and corresponding species distribution, it is possible that the resins originate from *Canarium australasicum*, or else a non-*Canarium* source of triterpenoid resin. More research is required to find the source of these resins.

5.4.1.4 Non-Burseraceae resins

The amyrins were not detected in significant quantities in samples AM02, AM12 and PBH082, with α-amyrin only detectable in the latter (Figure 5.16). The oleanane- and ursane-derived amyrones are however, clearly present.

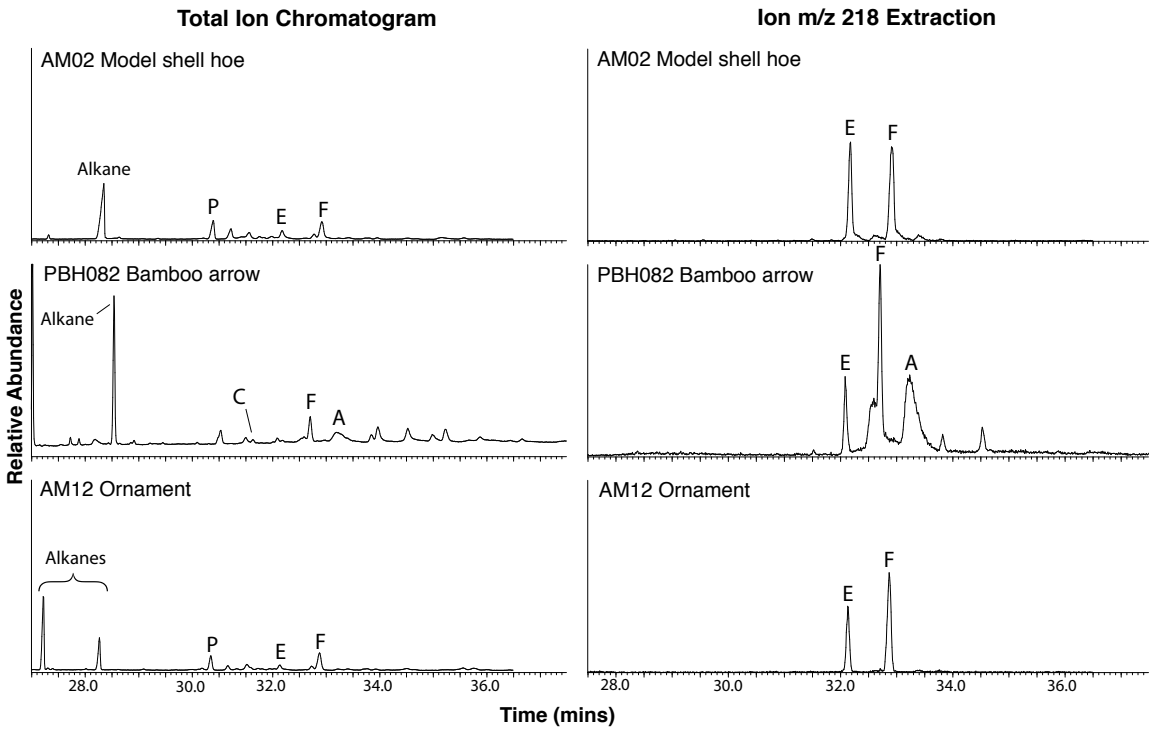


FIGURE 5.16: Partial chromatograms of AM02, PBH082 and AM12 showing total ion chromatograms and ion m/z 218 extractions (A = α-amyrin, F = α-amyrone, details of other peaks in Appendix F)

These ethnographic samples do not resemble the elemi-type resins. Sample PBH082, with the presence of α-amyrin and ursadienone (peak C), may possibly come from a Burseraceae resin, however the presence of lanostadienone (peak P) in AM02 and AM12 suggest a different source to the Burseraceae. The low abundance of triterpenoids in the samples make the characterisation difficult, but these samples may represent the same, or two different unknown triterpenoid resins, most likely not from the Burseraceae family.

Sample PBH078 also shows a trace amounts of α-amyrin and other urseane and oleanane-type compounds. Two samples from another item, AM09 and AM10, show trace amounts of α-amyrin and possibly a lupane-type triterpenoid. Sample PBH076 has trace levels of a triterpenoid resin without α- or β-amyrins, but with ursane/oleanane- type compounds. The resins on these samples are also unlikely to have come from the Bursearaceae family. The chromatograms for these samples can be found in Appendix L.

5.4.1.5 *Artocarpus altilis* resin

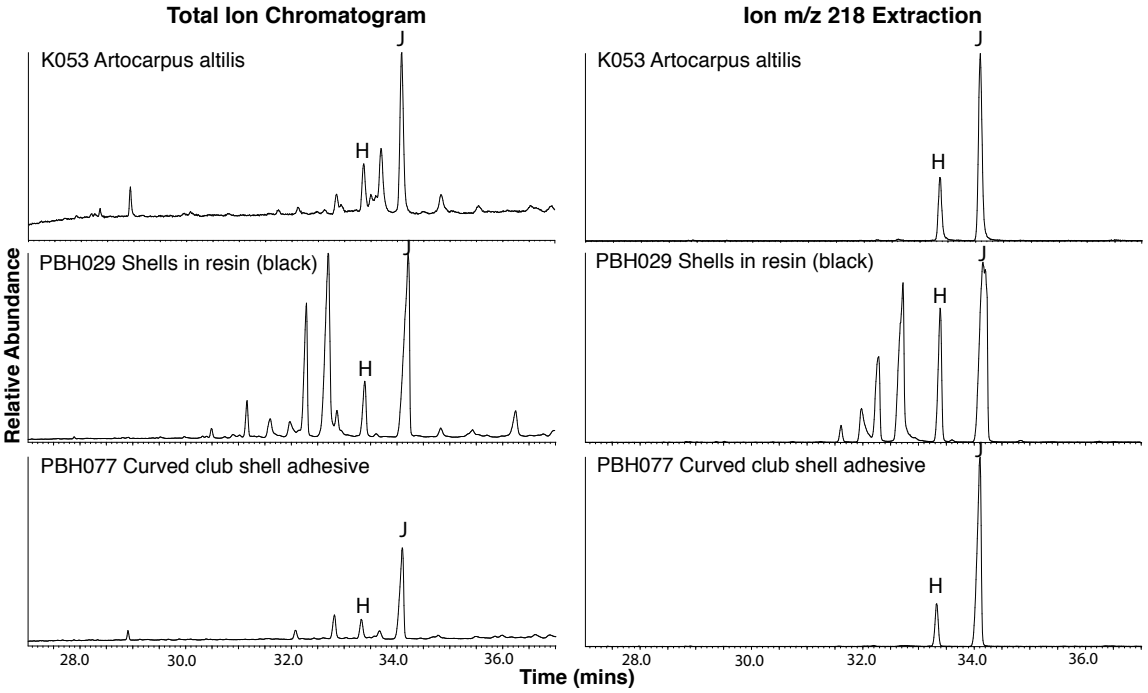


FIGURE 5.17: Partial chromatograms of K053 with PBH029 and PBH077 showing total ion chromatograms and ion m/z 218 extractions (H = 12-oleanen-3-yl acetate, J = urs-12-en-24-oic acid, 3-oxo-, methyl ester)

Two samples, PBH029 and PBH077 produced two peaks on the chromatograms that are oleanane- and ursane-related, respectively (Figure 5.17). These peaks match very well with those produced by reference sample K053 *Artocarpus altilis* (breadfruit) resin, however research on this resin is currently very limited. This consistency suggests the presence of *A. altilis* resin in the two ethnographic samples. Sample PBH029 looks to therefore consist of a mixture of possible *A. altilis* resin and a non-elemi 4-peak Burseraceae resin (see Figure 5.14).

5.4.2 Lupane-type triterpenoid resins

Some triterpenoids resins from the ethnographic samples contain predominantly lupane-type triterpenoids, rather than the oleanane/ursane type. AM08, AM04, PBH081 and PBH015 indicate the presence of lupane-type triterpenoids. The chromatograms for these

samples can be found in Appendix L. A discussion on the sources of these resins is outside the scope of this project.

5.4.3 Dammarane-type triterpenoid resins

Samples in which dammarane-type triterpenoids were detected are PBH036, PBH067, PBH018 and AM13. As expected, the dammar-type resins are reasonably similar to each other and significantly different to the elemi-type resins. The chromatograms for these samples can be found in Appendix L. A discussion on the sources of these resins is outside the scope of this project.

5.5 Conclusions

From the analysis of the reference resins, it is apparent that there are two main groups of *Canarium* resins, those presenting two main amyrin peaks, and the other presenting at least four distinct amyrin-related peaks.

The two-peak group includes Manila elemi (*Canarium luzonicum*), which is indistinguishable from other elemi-like resins such as *C. indicum*. Elemi-type resins also appear throughout the Burseraceae family and show very little variation when analysed by GC-MS. Nuclear magnetic resonance (NMR) may be able to be used to differentiate these samples further, based on the ability to distinguish between the different oleanane- and ursan-type triterpenoids (Vázquez et al.; 2012). The four-peak group includes *Canarium salomonense*, which appears to be distinguishable at species level, though more research is needed for a more robust method of identification. In general, amongst the non-elemi type *Canarium* resins, there is some variation in the composition between some of the species, however, more research is needed to assess whether they are different enough to be indentified in unknown samples. The ability to identify some species, but not others where the triterpenic fraction is too similar, reflects what what was found by Lucero-Gómez et al. (2014) in the study of Mexican species of *Bursera*.

Of the ethnographic samples, 17 samples have been found to include triterpenoid resins, mostly of the oleanane- and ursane-type. The remaining samples contain lupane-type, or dammarane-type triterpenoids.

The botanical source of five unknown samples has been identified as the species *Canarium salomonense*, for which the chemical profile is significantly different to that of the resins from other *Canarium* species native to Oceania. The combination of both chemical and geographic parameters, allows some confidence in this identification. Four samples have been

identified as 'elemi-like' by the presence of both α- and β-amyrin in abundance producing just two dominant peaks, which is indicative of resins from the Burseraceae family. Another five triterpenoid resins have been hypothesised to be from *Canarium australasicum*, which will need further research. Three more samples contain resin of the oleanae- and ursane-type but do not resemble the Burseraceae resins. *Artocarpus altilis* (Breadfruit) resin was also cautiously identified in two samples, one in a mixture with a Burseraceae resin.

The results show there is a much wider range of triterpenoid resins used in Oceania than just those from *Canarium* species. The mixing of different types of resin, as well as mixtures of resin with non-resin materials is also apparent. The context of these results in relation to the artefacts the resins have been sampled from, will be discussed in Chapters 7 and 8.

The peaks labelled as E, B, F and A are consistent across many of the ethnographic triterpenoid samples and may be products of certain degradation pathways, rather than directly associated with source species. The degradation of these resins requires further research.

Chapter 6

Phenolic resins from the Angiosperms

6.1 Introduction

A further category of resin is not terpenoid based but is composed of phenolic compounds. The only known source of this type of resin in Australia is the genus *Xanthorrhoea*. This chapter discusses the history of use of this resin, as well as the history of its chemical analysis, followed by the results from the analysis of phenolic resins in the project.

6.2 Background to the genus *Xanthorrhoea* (grasstree)

Xanthorrhoea is a genus of perennial trees with a grass-like appearance, and thus the common name 'grasstree'. The genus *Xanthorrhoea* was previously regarded as belonging to the Liliaceae family, as it appeared to be related to the lilies, and thought to be similarly related to the aloes and dragons blood (Seth; 2003, p. 361). It is now placed in a separate

monogenetic family, Xanthorrhoeaceae. This native Australian plant produces one of the two most important sources of resin for Indigenous use in Australia, alongside spinifex from the genus *Triodia* (Chapter 4).

Like *Triodia, Xanthorrhoea* is endemic to Australia, including Tasmania and other associated islands. However, *Xanthorrhoea* occur in a variety of soil, terrain and vegetation types in coastal heaths, as well as wet and dry forests (Borsboom; 2005, p. 27), occupying a very different habitat to *Triodia*, which thrive in the arid hinterland. It is sometimes mistakenly thought that the *Xanthorrhoea* genus is characteristic of the drier Australian regions (Ghisalberti and Godfrey; 1998, p. 221), but they are actually only found in the tropical, sub-tropical and temperate regions, generally with more than 250mm rainfall (Clifford; 1998, p. 469).

The *Xanthorrhoea* are slow-growing trees living for hundreds of years, and like *Triodia*, they are well-equipped to withstand bush fires. The plant itself is semi-fire-resistant, due to a high internal moisture content, and a protective outer covering of the trunk, built of the "resin-cemented leafbases," on which fire cannot usually burn long enough to kill the plant (Borsboom; 2005, p. 57). The resin, secreted from the stem and leaf bases (Clifford; 1998, p. 469), melts in the heat of fire and forms globules that drip down onto the old leafbases. Sometimes the *Xanthorrhoea* don't flower for years at a time, but they often flower in the next season following a bush fire, in response to the heat (Borsboom; 2005, p. 12).

Most species of *Xanthorrhoea* produce a deep reddish brown resin, apart from the type species (species typica) first described by J. Smith in 1798, which produces a yellow resin (Duewell; 1997, p. 717). The genus is named after the resin of the type species: *xanthas* meaning 'yellow' in Greek, and *rhoea* meaning 'flowing' (Langenheim; 2003, p. 70).

The resin from *Xanthorrhoea* has been used by Aboriginal Australians for thousands of years, particularly for hafting composite tools. According to Powell et al. (2013, p. 220) in parts of Queensland in north-eastern Australia, below the tropic of capricorn where *Triodia* (spinifex) are rare, current Aboriginal knowledge recognises only the tree exudates from *Xanthorrhoea johnsonii*, and *Erythrophleum chlorostachys* (northern ironwood) (see Chapter 4) as suitable for hafting. Additionally, Pitman (2010, p. 95) notes that *Xanthorrhoea* resin was generally used in southern Australia where *Triodia* does not occur, as grasstree resin was considered inferior in strength and malleability to spinifex resin. However, despite this there are records of *Xanthorrhoea* resin being used occasionally in the spinifex-dominated desert areas (Pitman; 2010, p. 95).

6.2.1 Species distribution

There are at least 28 species of *Xanthorrhoea* according to The Plant List (TPL; 2013), all of which produce resin, but not all in copious amounts. The genus is generally restricted to the east coast with a small concentration of a few species in the far southwest of Australia (GBIF; 2018). The majority of *Xanthorrhoea* species have distinct distribution patterns around the east coast of Australia, occuring naturally across the south and east of South Australia, continuing to Tasmania, and extending all along the coastline up to the far north of Queensland, but not continuing up on the Torres Strait Islands.

Eight species, which are highlighted in the ethnographic accounts as some of the most ethnobotanically significant species for resin collection and use, have been selected for this study. These are:

1. *X. arborea* R.Br. (Broad-leaved grasstree (Clarke; 2012))

2. *X. australis* R.Br. (Austral grasstree (Clarke; 2012))

3. *X. johnsonii* A.T.Lee (Northern grasstree (Clarke; 2012))

4. *X. media* R.Br. (Forest grasstree (State of New South Wales and Department of Planning Industry and Environment; 2018))

5. *X. preissii* Endl. (Balga grasstree (Clarke; 2012))

6. *X. quadrangulata* F.Muell. (Square-leaved grasstree (Clarke; 2012))

7. *X. resinosa* Pers. (syn. *X. hastilis, X. resinifera*) (Dwarf grasstree (Clarke; 2012))

8. *X. semiplana* subsp. *tateana* (F.Muell.) (Kangaroo Island grasstree (Nelson and Bedford; 1993))

The distributions for these species of *Xanthorrhoea* are shown in the map in Figure 6.1.

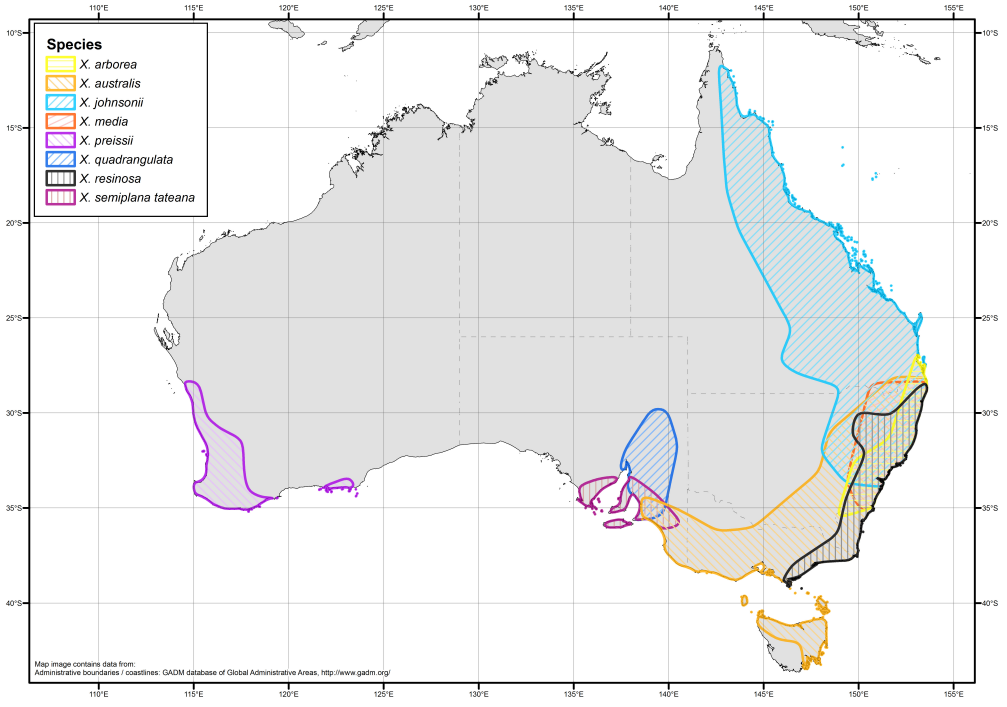


FIGURE 6.1: Map showing geographical distribution of eight resinous *Xanthorrhoea* species.
Distribution data from ALA (2018); GBIF (2018).

Distinguishing different species of *Xanthorrhoea* botanically is difficult, and according to Borsboom (2005, p. 27) "Species can rarely be identified on one or two characteristics alone,

identification usually requiring the use of many characteristics." Duewell (1997, p. 718) highlights that, at least until recently, many species have been morphologically poorly defined, and as grass-trees go without flowering for years, the more distinctive fertile parts of the plant cannot always be used to identify the species. To confuse matters, hybridisation does occur between some species, including *X. resinifera* and *X. johnsonii*, although hybridisation appears to be restricted to *Xanthorrhoea* species in habitats on quaternary sand deposits along the east coast of Australia where two species meet on the ecocline (e.g. between wet and dry habitats) (Borsboom; 2005, p. 27).

Difficulties in distinguishing between different *Xanthorrhoea* species botanically makes identifying their resins more difficult, but ultimately more important.

6.2.2 Commercially exported resin

As is typical for resins with a long history of commercial use, different names for *Xanthorrhoea* resin took a while to be reconciled. The resin was sold commercially under the name 'acaroid,' 'accroid', or 'acroide' , or 'Botany Bay resin'. In 1881, 'gum acroides', which had been announced at a pharmaceutical meeting as a new Australian product, were reported as the resin from species of *Xanthorrhoea* by Maisch (1881). Maisch (1881, p. 10) had found that "the appellation acroides is a corruption of acaroides, and that the resin is identical with Botany Bay resin", from the genus *Xanthorrhoea*, of which a quantity had been kept in a store in New York for a "quarter of a century" and fully stocked for ten years. Maisch (1881) continues with a description of the appearance, composition, and uses of *Xanthorrhoea* resin, recognising that the acaroid resin was first noticed for commercial potential in 1789 by Governor Phillips in a Voyage to Botany Bay. Maisch (1881) also noted that *Acaroides resinifera* is a synonym of *X. resinosa*, thus explaning the link with the name acaroid used in commerce.

The resin from *Xanthorrhoea* is also referred to as 'yacka' or 'blackboy gum'. 'Blackboy' is an antiquated name that was undoubtedly only used by European explorers and settlers, rather than the native peoples, as it reflects the "settler-era likening of the plant to the distant image of an Aboriginal person" (Ryan; 2014, p. 24). The current preferred generic name is 'grasstree' resin.

There are also inconsistencies in the description of the commercial resins and their sources. Maisch (1881, p. 11) describes the *Xanthorrhoea* resins as one yellow, one brown and one red, with suggestions of the source species being *Xanthorrhoea resinosa, X. arborea*, and *X. australis*. According to Cribb and Cribb (1981, p. 89), the species most commonly collected for commercial purposes were: *X. resinosa* (yellow resin) from NSW, Vic; *X. preissii* from WA; and *X. semiplana subsp. tateana* (syn. *X. tateana*) from Kangaroo island. The species mentioned by Seth (2003, p. 364) as the acaroid or grass-tree resins, however, are again slightly different: *X. resinosa* (syn. *X. hastilis*), *X. semiplana* subsp. *tateana* (syn *X. tateana*), and *X. australis*. Mantell (1950, p. 219) explains that "While all the known species of *Xanthorrhoea* contribute to the supply of accroides gum collected, there is not any commercial distinction made in the resin obtained from the various species other than recognising yellow and red varieties." All species of this genus exude resin, but according to Howes (1949, p. 158) and Mantell (1950, p. 212) only the following five species are regarded as economically important sources of resin: *X. arborea* (NSW, Qld), *X. australis* (NSW, Vic, Tas), *X. resinosa (X. hastilis)* (east and southeast Australia), *X. tateana* (South Australia including Tasmania) and *X.presissii* (South western Australia). Interestingly, as reported by Borsboom (2005, p. 37) Kangaroo Island in South Australia is the only place significant amounts of *Xanthorrhoea* resin harvesting still occurs in Australia.

6.2.3 *Xanthorrhoea* resin in the ethnographic record

Different parts of the *Xanthorrhoea* plant have many uses including as food, making fire, forming all or parts of tools and weapons including fire-drills and spear-shafts, and significantly the resin can be used as an adhesive. These uses have a long history and many still continue in Aboriginal communities.

Ethnographic accounts suggest that the collection and preparation of resin from the grass tree is similar to that of spinifex, "The raw resin powder was collected either by beating the leaf bases or by searching for hardened globules on the trunk" (Clarke; 2012, p. 137), and heated carefully to soften (Cribb and Cribb; 1981, p. 89). As *Xanthorrhoea* resin can be brittle, it was often altered to make it more suitable for use, particularly for hafting axes and such like, as Cribb and Cribb (1981, p. 89) explain, "For this purpose it was sometime mixed with native beeswax or with fine sand and dust." Different methods of preparation were used for different intended purposes of the resin, and the methods varied geographically. This is discussed in more detail in Chapter 7. Cribb and Cribb (1981, p. 89) also note that *Xanthorrhoea* resin was traded with tribes who did not have access to the plants, which implies a preference of *Xanthorrhoea* over locally available resins on these occasions.

There are several references to the use of *Xanthorrhoea* resin in the ethnographic literature for Australia. However, there are many different names for *Xanthorrhoea* resins in both commerce (section 6.2.2), and local Aboriginal communities, and matching these names with taxonomic identities can be problematic. References to specific *Xanthorrhoea* resins used in Western Australia and Queensland are highlighted in the following paragraphs.

Western Australia

Many localised Indigenous communities have their own names for grasstree resins and different names for the particular species the resin was collected from. The names that have been documented as used by the Nyungar people in southwest Western Australia have been gathered and published by Clarke (2012).

Clarke (2012, p. 137) reports that 'balga' is the Nyungar word for *X. preissii* as was noted by George Moore[1] in 1884. The Aboriginal use of *X. preissii* resin, also referred to as "blackboy gum", was also recorded by Hassell (1936 cited in Clarke; 2012, p. 137) and said to be difficult to use, as the "wet loosens and destroys it." As researched by Clarke (2012, p. 316), 'piring' is the Nyungar word for the resin from the 'balga' grasstree.

The resin from another grasstree species that the Nyungar called 'barro' was considered to be superior (Clarke; 2012, p. 137). The species identity of the 'barro' grasstree is unclear, but was described by Moore as growing "generally in high and dry situations", rather than the "low and rather damp soils" preferred by the 'balga' (*X. preissii*) (Clarke; 2012, p. 136). As researched by Clarke (2012, p. 316), 'kadjo' was the name for the resin from the 'barro' grasstree, which is also a type of 'native hammer', described by Moore as being double headed, with a short wooden handle. Similarly, Tindale referred to a 'kodja' in 1974, also in southwest Western Australia, which was hafted with *Xanthorrhoea* resin, but onto a 'climbing stick' (Clarke; 2012, p. 316).

According to Moore, the tough-topped grasstree exuded the strongest resin, which was used for fastening on the heads of their stone hammers (Clarke; 2012, p. 137). A testiment to this was made by Chauncy in 1878, and quoted by Clarke (2012, p. 137):

[1]He originally incorrectly identified 'balga' as the word for *Xanthorrhoea arborea*, however *X. arborea* is an east coast species (Clarke; 2012, p. 137).

> The strength of this gum [tough-topped grasstree] is extraordinary, for I have seen a native use his Kadjo [hatchet] to cut large limbs off gum-trees without at all loosening the stones.

Additional Nyungar words, in various dialects, were thought to refer to other species of *Xanthorrhoea*, as noted by Moore: 'ballok', 'golgoyl', 'mimidi', 'tdud-tin' and 'yango.' However, Von Brandenstein (1988) (cited in Clarke (2012, p. 316)) treated 'ballak' and 'balga' as different words for *Xanthorrhoea preissii*, suggesting that 'ballok' may also refer to *X. preissii* resin. Prepared grasstree resin was termed 'tadibi' (Clarke; 2012, p. 316).

It is clear from Clarke's 2012 research that the resin from at least two species of *Xanthorrhoea*: *X. preissii* ('piring', from the 'balga' grasstree); another unknown species ('kadjo', from the 'barro' or 'tough-topped grasstree'); and likely more, were exploited in the south-west of Western Australia for hafting.

In Worms' (1954, p. 1073) ethnographic report of prehistoric petroglyphs of the Upper Yule River, North-Western Australia, he postulates that the stone implement used for hammering the cave engravings is likely to have been similar to previous tool descriptions by A. K. Richardson and C. F. Armstrong[2]:

> [...]a flint was fastened at the end of a wooden handle or to the butt of a throwing stick or *miro*, with the resin of spinifex grass in the northern parts, and with that of the "blackboy" (*Xanthorrhoea*) in the south-western parts of Western Australia.
>
> Worms; 1954, p. 1073

[2]Referenced by Worms as E. M. Curr, The Australian Race, Melbourne 1886, Vol. I, pp. 297 and 329.

This statement suggests that *Xanthorrhorea* resin may have been used as a direct equivalent of spinifex resin in this region.

Queensland

In northeast Queensland, Khan (2004, p. 32) describes raw resin in the Roth collection as grasstree resin found in lumps among the roots, and only needing heating before use. Roth's notes include that the Kokoyimidir people of Cooktown and Cape Bedford called this resin 'pungga', whereas the notes in the Australian Museum's anthropology register records the names 'tun-ja' and 'kannojo-ol'.

Xanthorrhoea johnsonii resin is also known to have been used during the 19th and 20th centuries in various parts of Australia to fix objects onto wooden shafts or handles, such as spears and spear throwers (David et al.; 2007, p. 467).

Ghisalberti and Godfrey (1998, p. 221) suggest that the resin from all species are known to have been used as adhesives by Aboriginals for fixing spear or axe heads to wooden shafts, but some species are definitely mentioned more often than others.

6.2.3.1 *Xanthorrhoea* resin in museum collections

Lampert and Konecny (1989) describe five spears that are in the Australian Museum, as having shafts made from the flower-stalk of *Xanthorrhoea resinosa* and barbs attached with "grass-tree" resin (residues on spear E.31764 identified by Dr R. Fullagar), presumably meaning resin from *Xanthorrhoea*, and thus potentially also from *X. resinosa*. They have attributed the spears to coming from the area around Sydney based on the use of the grass tree, which was most common in New South Wales. They have also used one of the museum items for comparison with archaeological finds from Durras North, comprising 200

unipoints thought to be the tips or barbs of multi-pronged fishing spears. The comparison reinforces their interpretation because "both sets of points are of split bird bone, are partly coated with grass-tree resin, and fall into the same size range" (Lampert and Konecny; 1989, p. 141). This study demonstrates the value of museum items for aiding interpretation of archaeological finds. Chemical analysis to confirm the source of the resin on these artefacts would be interesting for both the museum collections and the archaeology.

Probably the most well known collection of well-documented Aboriginal items is the Roth collection, which includes several references to the use of *Xanthorrhoea* resins. This collection of artefacts gathered by the First Protector of Aboriginals in north Queensland, Dr Walter Edmund Roth between 1898 and 1904, comprises some 2000 artefacts (from Queensland, the Northern Territory, New South Wales, Victoria and Tasmania) and associated photographs and other material (Khan; 2004). Khan (2004) provides an excellent overview of the Roth collection from Cape York Peninsula, north Queensland, and any ethnographic resources related to the items in it, and the collection includes some particular items referring to *Xanthorrhoea* resin. An account by H. G. Smith of some resin thought to be grasstree resin includes the description:

> "This cement is in irregular lumps, having a purplish-brown colour in the fracture, but almost black externally... In alcohol the whole of the resin was dissolved, having a deep red colour: the organic matter is then left behind... It seems probable that this organic material is added to the resin to overcome the brittleness; but the quality of the cement would be improved if inorganic constituents were present also."
>
> Khan (2004, p. 84)

A round lump of reddish brown resin from the Starcke River was collected by Roth in 1898. The Australian Museum's Anthropology register dated 1905 includes "*Xanthorrhoea arborea* as carried about on a piece of stick ready for use. Reddish, typical of the northern specimens", which "in 1904 Mr Henry G. Smith, F.C.S. of the then Museum of Technology, Sydney, identified the resin for Roth as coming from the grass tree, *Xanthorrhoea arborea*, now known as *Xanthorrhoea johnsonii*" (Khan; 2004, p. 84). *Xanthorrhoea johnsonii* grows naturally in far north Queensland, therefore this identification is likely to be accurate. It is beneficial to be able to connect such rich descriptions of the resin to a particular species.

Megaw (1993) describes the examination of surviving pre-circa 1820 Aboriginal ethnographic material claimed to be from the Botany Bay-Port Jackson area, in the light of a number of recent surveys of the art, archaeology and ethnography of the Sydney district at the beginning of the period of European settlement. This material includes four items with reference to "grass-tree gum". Firstly, a woomera or spear-thrower of wood with wooden peg at one end and shell adze at other, both fixed with probable grass-tree gum from New South Wales (UMAA 1922.994) which Megaw (1993, p. 28) links to a number of descriptions and depictions. Additionally but with no reference to grass-tree gum, "A shell adze of this general form made from the Sydney cockle (Anadara trapezia) was in fact recovered in the 1970 excavations at Captain Cook's Landing Place, Botany Bay" (Megaw; 1993, p. 28). Similarly to the first item, a second woomera with wooden peg set in probable grass-tree gum is mentioned, from "New Holland" an old name for Australia (Cuming Museum, London Borough of Southwark C3502) (Megaw; 1993, p. 33). Thirdly, an edge-ground stone axe set in probable grass-tree gum with split sapling handle and two-ply vegetable cord (probably kurrajong bark) binding, also from "New Holland" (UMAA 1922.995), and lastly a boomerang with traces of probable grass-tree resin from Port Jackson (MAE 736-186) are described (Megaw; 1993, p. 31,35).

The chemical analysis of the resin in all these cases would add a more precise description of the artefacts, whilst providing information on the source of the material, which may have other implications for the study of these artefacts and how and where they were made.

6.2.4 *Xanthorrhoea* resin in the archaeological record

There are a few published cases of *Xanthorrhoea* resin from the archaeological record, usually as hafting residues that have survived adhered to the stone points of composite tools and weapons. The ability to confidently identify residues on archaeological artefacts as *Xanthorrhoea* resin, and furthermore identify the source species, would offer an extra level of insight to the technology behind these stone points, and help to avoid assumptions about past human behaviour at archaeological sites. Some examples are discussed here, demonstrating how chemical identification of these resins would be, or has been, beneficial.

Western Australia

Smith (2011, p. 17) describes evidence of resin used for hafting on adzes, including small tula-shaped adzes and a partially backed flake, from the archaeological record from the Esperance area of southwestern Australia, historically belonging to the Nyungar speakers. According to Smith (2011, p. 23), the resin on all stone tools with hafting residue from this area, including many small flakes where the position of the residue indicates that they had been hafted either in a taap (knife) or spear, appears to be from *Xanthorrhoea* sp. However, there is no mention of any detailed analysis of the residue so it is likely that this conclusion was reached only by visual analysis along with the geographically-based premise that *Xanthorrhoea* resin is the more common choice of hafting cement in the South-West (Smith; 2011, p. 25). It is notable that knowledge of the range of hafting residues appears limited as only *Triodia* sp. and beeswax are mentioned as alternative materials used ‘elsewhere in

the state'. Research by Clarke (2012) on the ethnographic accounts of the *Xanthorrhoea* species used in southwest Western Australia, suggests that the Nyungar people used *X. preissii*, and at least one other unknown species of *Xanthorrhoea*. Analysis of the archaeological hafting residues from the Esperance area would be particularly interesting to find if *Xanthorrhoea* was the source of the hafting resin, if one or more than one species was used, and if any other materials were used in the manufacture of the hafting cement.

New South Wales

Lampert and Steele (1993) report "blobs of resin" thought to be *Xanthorrhoea resinosa* amongst the archaeological findings at Bomaderry Creek, New South Wales. The resin, along with other macroscopic plant remains may be attributed to Aboriginal occupation of the large rock-shelter, which was briefly inhabited by hunter-gatherers at about 1900 years BP and about 1400 years BP (Lampert and Steele; 1993). The resin resembled the residue preserved on the backs of some eloueras (backed stone points) and was therefore presumed to be used for hafting. According to Lampert and Steele (1993, p. 60) the local grass tree is *Xanthorrhoea resinosa* (syn. *X. resinosa* subsp. *resinosa*) and is therefore the most likely source of this material. To confirm by chemical analysis if this hypothesised identification is correct or not would be interesting either way.

European contact

More recent finds can also be interesting in terms of trade and relationships between Aboriginal Australians and European settlers, and a positive chemical identification of *Xanthorrhoea* resin in the following case has interesting implications, demonstrating the importance of resin analysis on archaeological finds. Traces of a resinous material, likely to be the remains of a hafting cement, were found on a ground stone hatchet head, found amongst a collection of items that were raised from a shipwreck near Norfolk Island (Mcbryde and

Watchman; 1993). The HMS *Sirius*, the flagship of the First Fleet of 1786-1790, which set out from Portsmouth, England for Botany Bay, New South Wales in 1787, and was wrecked off Norfolk Island in 1790 during a supply run. The hatchet head was concluded to be of probable Nepean/Hawkesbury (NSW) Australian Aboriginal form, made of spotted pelitic hornfels from the cobble beds of the Nepean River between Emu Plains and Richmond Hill (Mcbryde and Watchman; 1993; Anderson et al.; 1997). In the words of Mcbryde and Watchman (1993, p. 139) "It is an unexpected and intriguing find from an 18th century naval wreck", which they concluded to have been part of a collection of "curiosities" belonging to an officer on the *Sirius*.

The find indicates a contact of exchange between the officers of the First Fleet and the Aboriginal Australians, symbolising the importance of artefacts, services and food to both parties (Mcbryde and Watchman; 1993, p. 139). This find also has implications regarding the local trade if it was acquired from a Sydney District Aborigine and not directly from the Aborigines of the Nepean/Hawkesbury, suggesting an exchange between members of Eora clans of Port Jackson and the Dharug of the Cumberland Plain (Mcbryde and Watchman; 1993, p. 139). As reported by Ghisalberti and Godfrey (1998), NMR was used to identify the coating on the surface as coming from a vegetable or microbiological origin. Further to that, a small irregular lump of resinous material was also found at the wreck site, amongst the ship's stores, and was found by NMR analysis to be a resin that is not terpenoid based, and most closely resembling *Xanthorrhoea* due to the presence of cinnamyl esters, chalcone, flavanone aglycones and glyosides (Ghisalberti and Godfrey; 1998, p. 221). This identification of *Xanthorrhoea* resin on the hatchet head is important as it corroborates a provenance of New South Wales, an Aboriginal origin, and the material being a hafting residue reflecting traditional patterns of technology.

6.2.5 Previous work on *Xanthorrhoea* resin identification

6.2.5.1 History of *Xanthorrhoea* resin characterisation

In his description of *Xanthorrhoea* (acaroid) resin, Maisch (1881, p. 11) notes that the resin hardens on exposure, is often broken into irregular pieces on account of its brittleness, and when fractured has a speckled or granitic character, also that it is intermixed with portions of wood, stalks, earth, etc. He concludes that resin from different species, "undoubtedly differs in appearance and also in composition" after previous accounts distinguishes three different *Xanthorrhoea* resins: one yellow, one brown and one red, the latter which contains some benzoic acids which have previously been obtained from benzoin, and thus more than just yellow and red. Birch and Salahuddin (1964, p. 1623) found that the basic constituents of *Xanthorrhoea* resins are acids, free or partly in the form of esters (benzoic, cinnamic, p-coumaric), and aldehydes (vanillin, p-hydroxybenzaldehyde), but had difficulties in identifying different species of 'red' resin *Xanthorrhoea*. The yellow resin has long been known to have significant differences to the other resin, including an absence of xanthorrheol, that has been found in the red resin (Duewell; 1997, p. 718).

Early chemical analysis of *Xanthorrhoea* resins in 1920 (Finlayson; 1926) provides a description of the phenolic and non-phenolic fractions of *X. resinosa* (*X. hastilis*) resin from New South Wales and *X. preissii* (then known as *X. reflexa* resin, which they found to be chemically very similar to that of *X. preissii*, and which is now an accepted synonym of *X. preissii* (TPL; 2013). Since then, much more research into the chemical composition of *Xanthorrhoea* resins has been published, which is summarised by Duewell (1997). It was then suggested that once it was apparent that the chromatographic patterns of the resins were species-specific, a contribution towards clarifying the complex taxonomy of *Xanthorrhoea* could be made (Duewell; 1997, p. 718).

Through the 1980s and 1990s, a number of chromatographic and other methods were employed in characterising *Xanthorrhoea* resin. Gas chromatography on fresh *Xanthorrhoea* resin (Reynolds and Bowden; 1980; Bowden and Reynolds; 1982), thin layer chromatography (Rosenfeld et al.; 1981), solubility testing in organic solvents (Bootle; 1985, p. 10), identification of *Xanthorrhoea* resins by general appearance of the raw material, using four to five physical attributes, as well as paper chromatography (Boot; 1993), and high-pressure liquid chromatography (HPLC) (Welch; 1997).

Parr (2002) successfully found starch grains with unique morphological features to different species of *Xanthorrhoea*, with attributes specific enough to "provide at least some assistance in the identification of resin samples" (Parr; 2002, p. 266). There is potential for this to be used as a complimentary technique to chemical methods, but it also requires a reference collection. This does sidestep many of the issues with chemical analysis, including the additional other materials such as beeswax that complicate interpretation of chromatographic methods, as well as chemical changes such as the effect of taphonomic processes, and anthropogenic alterations of the resin itself (Parr; 2002, p. 261).

Chromatographic techniques have progressed over the past few decades, and GC-MS has become a standard and effective way for analysing plant resins, alongside other methods including NMR, FTIR and Py-GC-MS. However, there has still been very limited work on the characterisation of fresh *Xanthorrhoea* resin, particularly compared to some of the other types of resin. These methods have the potential to identify *Xanthorrhoea* resins in unknown samples from ethnographic museum artefacts. Some of the components of *Xanthorrhoea* resin have been isolated, and the general chemical composition of *Xanthorrhoea* resin is discussed in the next section.

6.2.5.2 Chemistry of *Xanthorrhoea* resin

Dissimilar to most other plant resins, *Xanthorrhoea* species produce non-terpenoid resin. Ghisalberti and Godfrey (1998, p. 222) describe the major components of *Xanthorrhoea* resins as aromatic pigments, Matheson and McCollum (2014, p. 120) describe them as being dominated by phenolic and aromatic hydrocarbons, and Duewell (1997, p. 718) describes them as entirely phenolic polyflavanoid material. In Langenheim's (2003, p. 24) definition of plant resin, she describes the material as consisting primarily of secondary metabolites that are either terpenic or phenolic, and refers to resins as being either terpenoid or phenolic. *Xanthorrhoea* resin is therefore categorised as a phenolic resin for this study. This type of phenolic resin is composed of naturally occurring phenols (phenolic compounds have an aromatic hydrocarbon ring with a hydroxyl group bonded directly to it) and related compounds, and is not the same as synthetic phenol-formaldehyde resin, also sometimes called phenolic resin.

Duewell (1997, p. 718) found that *Xanthorrhoea* resin is composed of mainly flavonoids, with chalcones and flavanones, and varying amounts of free acids, essentially p-coumaric and cinnamic acids. He also found that resins from different species of grass trees shows a wide variation in composition (Duewell; 1997, p. 730). There is some consistency across the group, however, and Duewell (1997, p. 718) reports that with the exception of the resin produced by one species, all samples studied contained naringenin, isosakuranetin and sakuranetin. Duewell (1997, p. 718) deduced that chromatography of *Xanthorrhoea* resin can be used to distinguish different species and has used 18 distinctly different chromatographic patterns to form the basis of a chemotaxonomic key, setting a precedent for the ability to be able to distinguish resins from different species of *Xanthorrhoea*.

Some other significant compounds have been individually identified, namely the flavonoids

5,7,4'-tri-OMe-flavone, xanthorrhone, and 14-hydroxyxanthorrhone, which were all isolated from *X. preissii* (after methylation) (Saini and Ghosal; 1984). The compound (2S)-3',5'-dihydroxy-7,4'-dimethoxyflavanone was isolated from *X. resinosa* and noted to have allergy preventive activity (Veitch et al.; 2011).

Some early research reports 2', 4'-dihydroxy-4-methoxychalcone, as being isolated from, and forming the major pigment constituent of *X. australis* resin (Duewell; 1954). The presence of a class of compounds so far not found in any other plant family, the dihydronaphtho[1,8-b,c] pyrans, is also notable (Duewell; 1965; Duewell and Haig; 1968; Duewell; 1997; Birch and Dahl; 1974), and may be important as family specific biomarkers.

Langenheim (2003, p. 70, 391) refers to *Xanthorrhoea* as a phenolic acaroid resin with appreciable quantities of free benzoic and cinnamic acids and thus similar to the balsams, benzoe and storax. Benzoe (from the genus *Styrax*) and storax (from the genus *Liquidambar*) are balsams, slightly more viscous than the oleo-resins, containing cinnamic acid, benzoic acid, and cinnamyl alcohol as major compounds. Modugno and Ribechini (2009, p. 229) report benzoe as containing 4-hydroxybenzaldehyde, vanillin, 3-hydroxybenzoic acid, 4-hydroxybenzoic acid, and vanillic acid, and storax as containing 4-hydroxy-benzenepropanol, p-hydroxycinnamic acid, 3-phenyl-2-propanol, triterpenoid acid (oleanonic and oleanolic). Storax is particularly interesting as it both phenolic and terpenic.

As mentioned above, Reeves et al. (2013), for their study of indigenous Australian paint binders, used pyrolysis gas chromatography mass spectrometry (py-GC-MS) to analyse *Xanthorrhoea tateana semiplana* (two seperate samples from Kangaroo Island, and west of Clarendon in WA), which tentatively identified 1-(2-hydroxy-4-methoxyphenyl)-ethanone, 1,2-dimethoxy-4-(2-methoxyethenyl)benzene, 2',4'-dimethoxyacetophenone, 3-(4-methoxyphenyl)-2-propenoic acid methyl ester, 2,4,6-trimethoxyacetophenone, and 3,4,5-trimethoxy-benzamide

as components of both resin samples.

6.2.5.3 Conservation of traditional Aboriginal artwork

Alcock (2014, p. 73) highlights the importance of resin identification when working with art to address difficulties surrounding the conservation of traditional binders as illustrated by the use of *Xanthorrhoea* resin by three Australian Aboriginal artists. Alcock (2014, p. 73) calls for more research in this area, explaining that accurate description of materials is required to prevent ambiguity and misunderstanding. Alcock (2014, p. 73) explains that the botanical source should be properly identified by specialists, and a reliable method of identifying small samples of traditional binders and of differentiating them from each other is needed with information specifically relating to the stability and ageing characteristics of these resins.

The benefit of studying contemporary materials is that cultural and practical questions can be addressed by discussions with artists about their techniques, by monitoring their paintings over time and by research on the physical and ageing characteristics of samples. Questions have been proposed by Alcock (2014, p. 73) such as did the act of painting have a cultural significance which would be affected by a particular type of treatment? Alcock (2014, p. 73) concludes that to increase their knowledge conservators need to engage not only with artists and curators, but also with scientists studying the plants and resins from which binders are obtained.

There are a few studies that address the identification of traditional binders, which often include plant resin as an ingredient. Hill's (2001) study on traditional paint binders in Papua New Guinea reports *Canarium indicum* mixed with lime or another alkali to create a red paint. FTIR analysis of pigments and binders on stone knives found spinifex resin

was used in Australia (Blee et al.; 2010). Reeves et al. (2013) have contributed to the study of Indigenous paint binders including Yacca gum (*Xanthorrhoea*) alongside several other commonly used paint binders, by using Py-GC-MS to analyse raw samples, including *X. tateana*[3], *X. tateana* is a subspecies of *X. semiplana* from Kangaroo Island, and *X. semiplana* from West of Clarendon, South Australia. These studies all call for more research on the resins used in binders, reinforcing Alcock's (2014) concern about the need for better understanding of the deterioration of plant resins in the context of traditional artwork.

6.2.5.4 Chemical alterations in *Xanthorrhoea* resin

According to Duewell (1997, p. 730), *Xanthorrhoea* resins are light-sensitive and subject to oxidation, which seems to induce polymerisation that appears to increase proportionally with the age of the resin. Duewell (1997, p. 718) suggests that reports of the isolation of more complex compounds, the xanthorrhones and 4-styrylflavans may indicate possible structural types for the polymer or condensation product. He also suggests that the polymerised material is responsible for the brown colour of the resins: "It is interesting to note that all red resins are in fact yellow, once the polymer phase is removed" (Duewell; 1997, p. 717). This calls in to question the ability to identify the botanical sources of *Xanthorrhoea* resin based on colour. More research on this area is required.

Duewell (1954, p. 2563) found that chrysophanic acid (1:8-dihydroxy-3-methylanthraquinone), isolated from *Xanthorrhoea* resin, was only present in a sample that had been charred or burnt by bush-fire. The connection between the compound and fire was confirmed experimentally when *X. australis* and *X. resinosa* resin was ignited and the chrysophanic acid was produced (Duewell; 1954). This study therefore infers that chrysophanic acid could be a chemical marker for burning in *Xanthorrhoea* resin.

[3]According to IPNI; 2018

6.3 Results from GC-MS analysis of *Xanthorrhoea* resins from the reference collection

6.3.1 Characterisation of *Xanthorrhoea* resins

The resin from each of eight known species, plus a few specimens of unconfirmed species of *Xanthorrhoea* have been sampled. The resin samples are either fresh (collected from the tree in 2014), or ethnobotanical (collected in the past, up to 150 years ago). A total of 20 samples of *Xanthorrrhoea* resins have been analysed by GC-MS and the key mass spectral data is provided in Appendix G.

The geographical occurrences of these eight resinous species of *Xanthorrhoea*, according to the Global Biodiversity Information Facility (GBIF; 2018) and Atlas of Living (ALA; 2018) Australia, show that each species has a distinct geographical distribution, where some species overlap and others do not. This indicates there is geographical significance to the identity of *Xanthorrhoea* resins to species level, particularly when associated with ethnographic or archaeological artefacts. The geographical distributions of the eight resinous *Xanthorrhoea* species included in this study are shown in the map (Figure 6.1) in section 6.2.1. Table 6.1 shows the reference samples analysed in this study.

Table 6.1: *Xanthorrhoea* resin samples analysed

Species name	Common name	Sample numbers
X. arborea R.Br.	Broad-leaved grasstree	K022, K023
X. australis R.Br.	Austral grasstree	K024, K025
X. johnsonii A.T.Lee	Northern grasstree	S06
X. media R.Br.	Forest grasstree	S03
X. preissii Endl.	Balga grasstree	K027, K028
X. quadrangulata F.Muell.	Square-leaved grasstree	K033, K034
X. resinosa Pers. (syn. *X. hastilis*)	Dwarf grasstree	K026, K029, K030
X. semiplana subsp. *tateana* (F.Muell.)	Kangaroo Island grasstree	K031, K032
Xanthorrhoea spp.	Unknown species	K066, K067, K068 NSW1, WA1

The results from the analysis of the reference resins from members of the *Xanthorrhoea* genus (grass trees) confirmed them to be phenolic rather than terpenic in composition. Phenols and phenolic compounds have been found to be dominant in all of the *Xanthorrhoea* resin samples, particularly flavanones (type of flavonoid, which are plant secondary metabolites), aldehydes, ketones, chalcones, and esters plus a range of other known, and unrecognised compounds, in varying combinations and abundances.

All the *Xanthorrhoea* resin samples have been found to contain a respectively large quantity of the flavanone sakuranetin (4',5-dihydroxy-7-methoxyflavanone). The mass spectrum of sakuranetin is shown in Figure 6.2 and its presence is demonstrated by a large peak at approximately 26.4 minutes on the chromatograms. This has been consistently detected (or else the O-glucoside of sakuranetin 'sakuranin', the mass spectra are very similar) in all *Xanthorrhoea* samples, fresh and aged, including the ethnographic samples (see section 6.4). As this compound appears to be stable over a moderate amount of time, and to occur in abundance, it is a strong indicator for the presence of *Xanthorrhoea* resin within a sample.

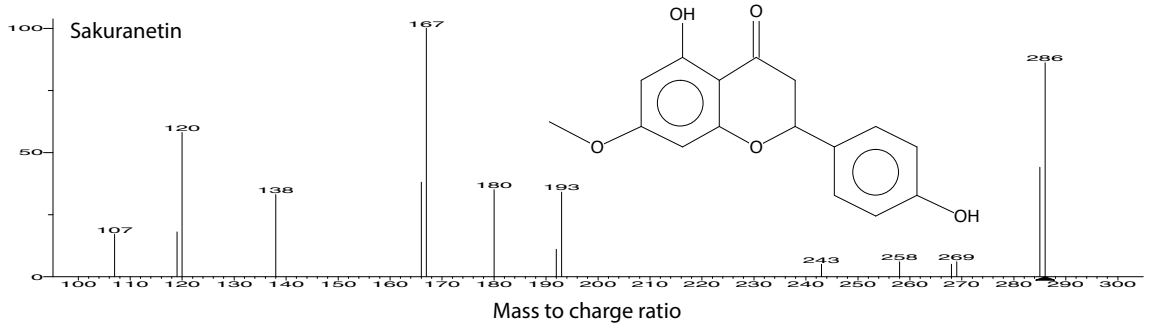


FIGURE 6.2: Mass Spectrum of Sakuranetin

A *Xanthorrhoea* specimen of unknown species (K068) was confirmed as *Xanthorrhoea* resin by the presence of sakuranetin as well as another phenolic compound, 4-hydroxycinnamic acid methyl ester, however the chromatogram was too poor to identify the specimen source to species. The rest of the samples produced high quality chromatograms.

6.3.2 Species differentiation

Analysis of the reference *Xanthorrhoea* resins by GC-MS has produced chromatograms and corresponding mass spectral data for each sample. There is a visual difference in the chromatography of the resin from each of the species (Figure 6.3) and a distinct difference in their chemical composition as identified by the mass spectral data. These differences indicate that the resin from each of the species included in this study, in most cases is distinguishable from others and therefore have the potential to be identifiable to species when found in an unknown context. Each of the eight species of *Xanthorrhoea* have been characterised chemically (see Appendix G for m/z values).

The only species' of *Xanthorrhoea* that produce resin that appear via GC-MS analysis to have exactly the same chemical composition, are *X. arborea* and *X. resinosa*. The visual difference in colour, however, of red and yellow resin respectively, conveniently distinguish one from the other.

GC-MS data from the reference samples known to be *Xanthorrhoea* but of unknown species have been compared the known species and have been identified in most cases.

6.3.2.1 *Xanthorrhoea resinosa*

Three specimens of *Xanthorrhoea resinosa* Pers. resin were sampled as K029, K030, and K026 labelled as "*X. hastilis*", which is now considered to be a synonym of *X. resinosa*. The three samples were all found to be consistent in composition. Two more samples from the Kew EBC, K066 and K067, were labelled as unknown species of *Xanthorrhoea*. These samples are chromatographically consistent with the *X. resinosa* samples, and are concluded to also be *X. resinosa* resin.

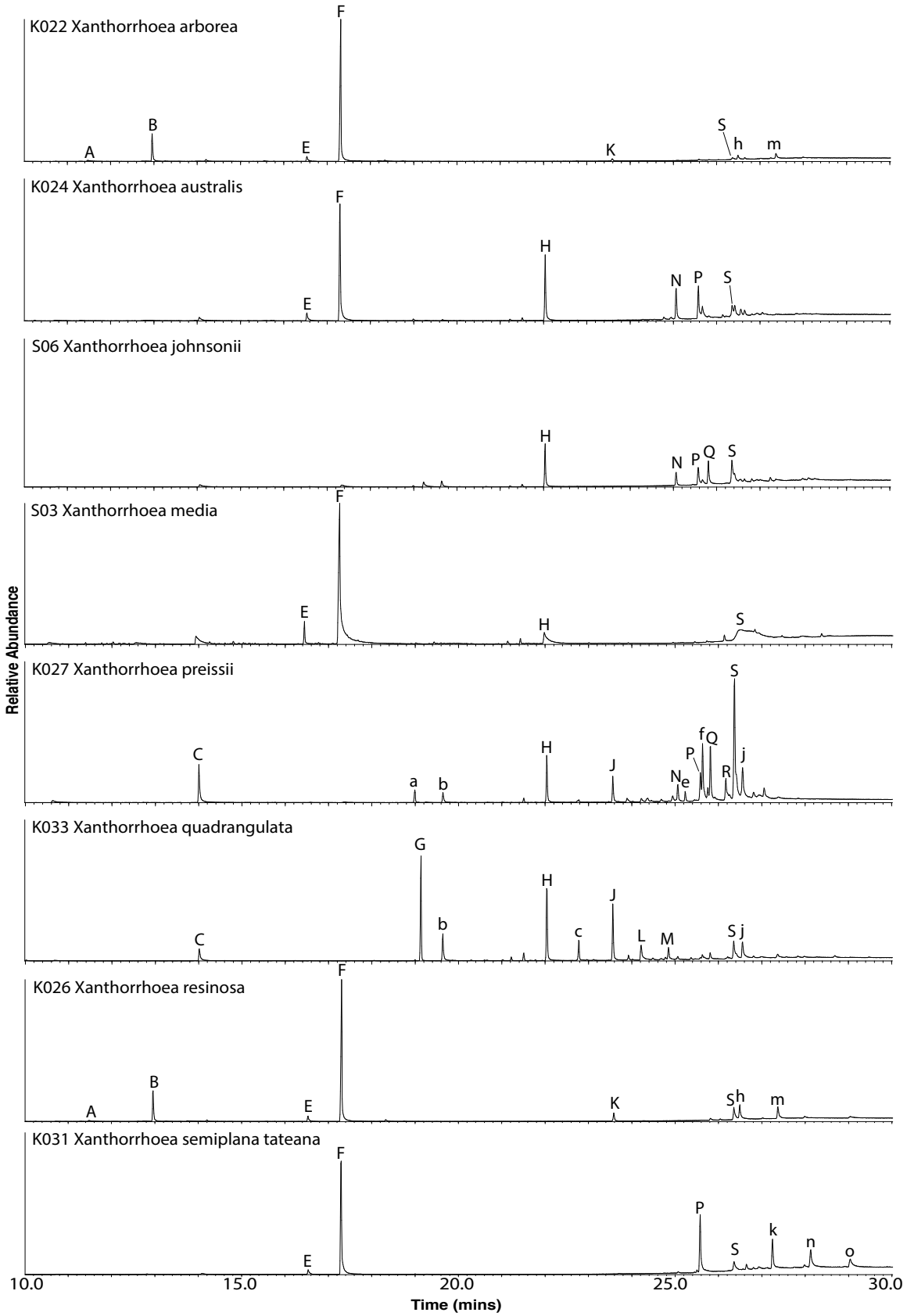


FIGURE 6.3: Partial chromatograms of samples K022, K024, S06, S03, K027, K033, K029 and K031 comparing resin composition from each of the eight *Xanthorrhoea* species. Mass spectral data for all peaks can be found in Appendix G

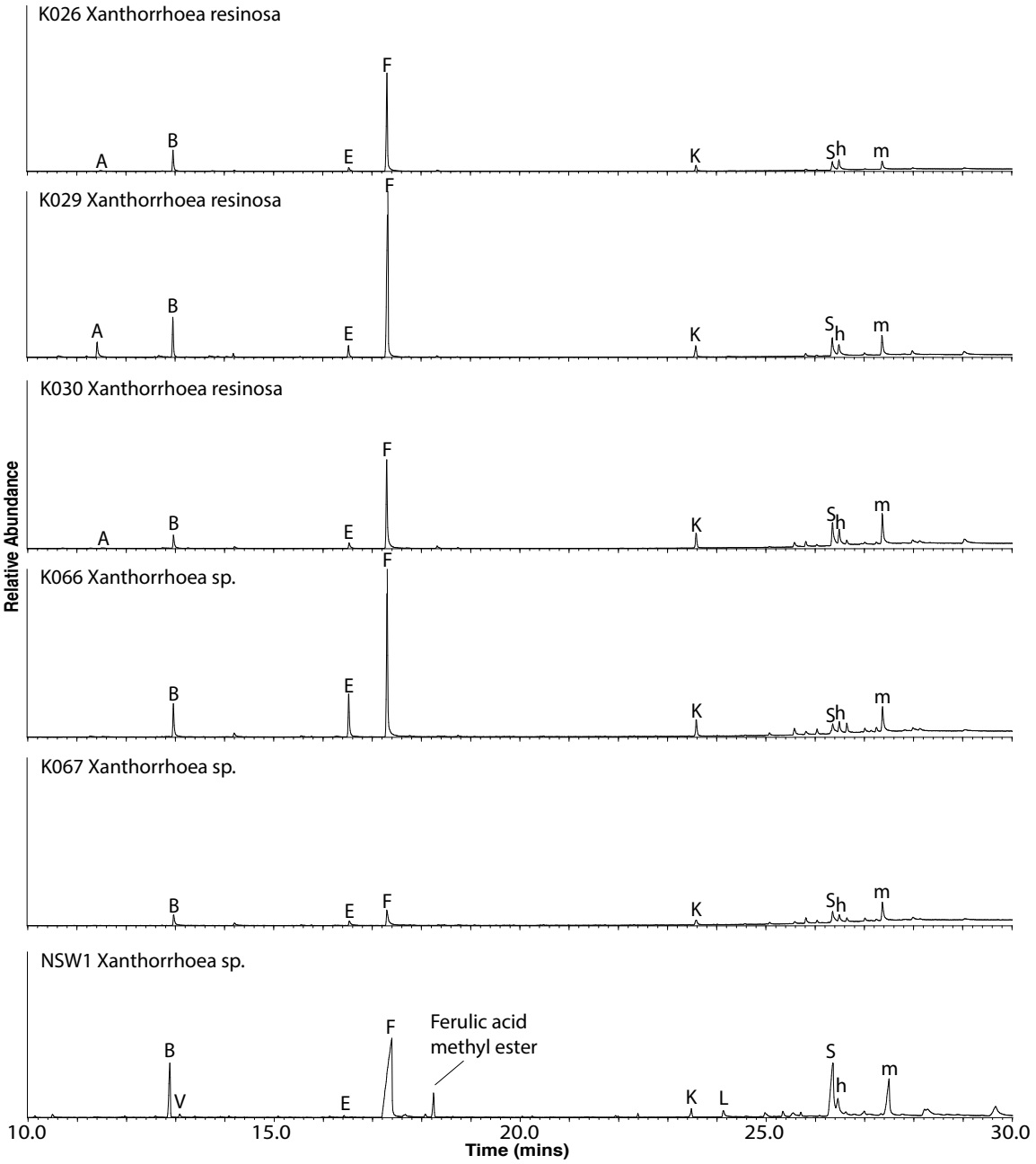


FIGURE 6.4: Partial chromatograms of samples K026, K029, K030, K066, K067and NSW1 confirmed as *X. resinosa*
F=4-hydroxycinnamic acid, methyl ester, S=sakuranetin, mass spectral data for all peaks can be found in Appendix G

Sample NSW1 is a yellow resin collected directly from a grasstree on 16/12/12, just off West Head Road in Ku-Ring-Gai Chase National Park, to the north of Sydney in New South Wales. This resin was hypothesised to be from *X. resinosa* due to the yellow colour it had when collected, and *X. resinosa* being the only known species to produce yellow resin. The location of sampling corresponds with known areas of *X. resinosa* in the park. The composition of NSW1 is consistent with the composition of the *X. resinosa* samples from the Kew EBC, confirming the identity of the resin sample as coming from *X. resinosa*.

The chromatograms from the resins known to be, and those identified as *Xanthorrhoea resinosa* are shown in Figure 6.4. Three additional compounds, vanillin (peak V), ferulic acid methyl ester (labelled), and 5,7-dihydroxyflavanone (peak L), were present in sample NSW1, the freshest sample, and were only just detectable in some of the other samples but not in a significant enough quantity to be useful in identification. Cinnamaldehyde (peak A) was also only present in a significant amount in three of the samples. Some of these compounds may be products of degradation but more work on the degradation pathways of *Xanthorrhoea* resins would be needed to ascertain this hypothesis.

6.3.2.2 *Xanthorrhoea preissii*

Two specimens of *Xanthorrhoea preissii* Endl. resin, K027 and K028, were analysed and found to be consistent in composition, with a characteristic cluster of compounds around a large sakuranetin peak.

Sample WA1, resin from an unknown species of *Xanthorrhoea* collected in the bush in Western Australia, has a composition consistent with that of the known *X. preissii* resin samples. This botanic source makes sense geographically as *X. preissii* naturally occurs in Western Australia. There is no further information on the location of the collection of

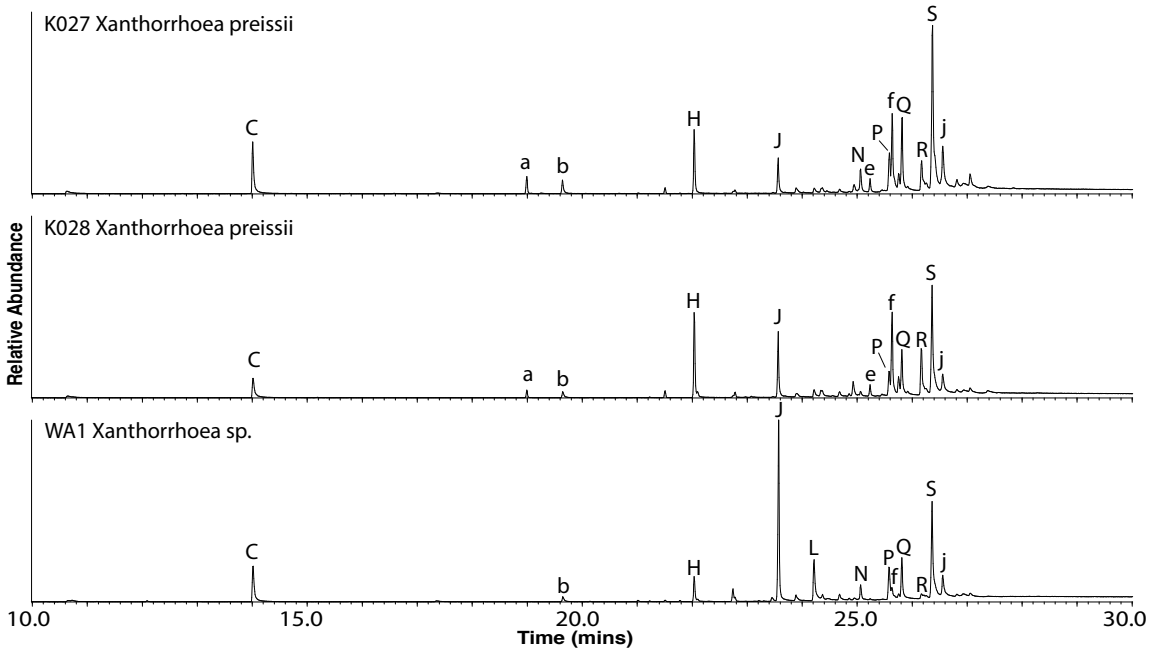


FIGURE 6.5: Partial chromatograms of K027, K028 and WA1 confimed as *X. preissii* resin R=naringenin, S=sakuranetin, mass spectral data for all peaks can be found in Appendix G

sample WA1, and there is the possibility that it could have come from a different species which has not been analysed as part of this project, for example *X. thorntonii*, which also occurs in Western Australia, though more inland, than *X. preissii*. Until further research on a wider range of species can be done, it can be presumed that the close chemical match to the *X. preissii* samples indicates the identity of *X. preissii* as the botanical source of WA1.

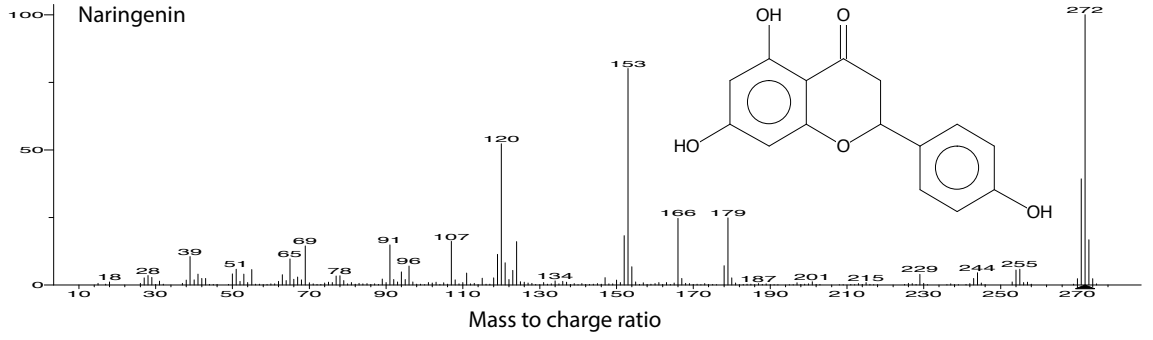


FIGURE 6.6: Mass spectra of naringenin, a potential species biomarker for *X. preissii* resin

The flavenoid naringenin (Figure 6.6), eluting just before sakuranetin, appears to occur

only in *X. preissii* and may be a suitable biomarker for this species, though it occurs in varying abundances. There are also two unknown compounds, denoted as peaks e and f in Figure 6.5, that appear to only occur in *X. preissii*, however these are less prominent in the fresher sample (WA1) and may be degradation products. Peak L (5,7-dihydroxyflavanone) was only present in WA1, suggesting it may be prone to degradation. These compounds would need to be researched more in the resins of various *Xanthorrhoea* species, particularly in relation to degradation.

6.3.2.3 *Xanthorrhoea quadrangulata*

Two specimens of *Xanthorrhoea quadrangulata* F.Muell. resin, K033 and K034, were analysed and the chromatograms are shown in Figure 6.7.

The variation in the presence of specific compounds separates *X. quadrangulata* from *X. resinosa* and *X. preissii*, including the presence of unknown compound c, benzeneacetic acid, 2-phenylethyl ester (peak G), and 5,7-dimethoxyflavanone (peak M), which appear to be unique to *X. quadrangulata*.

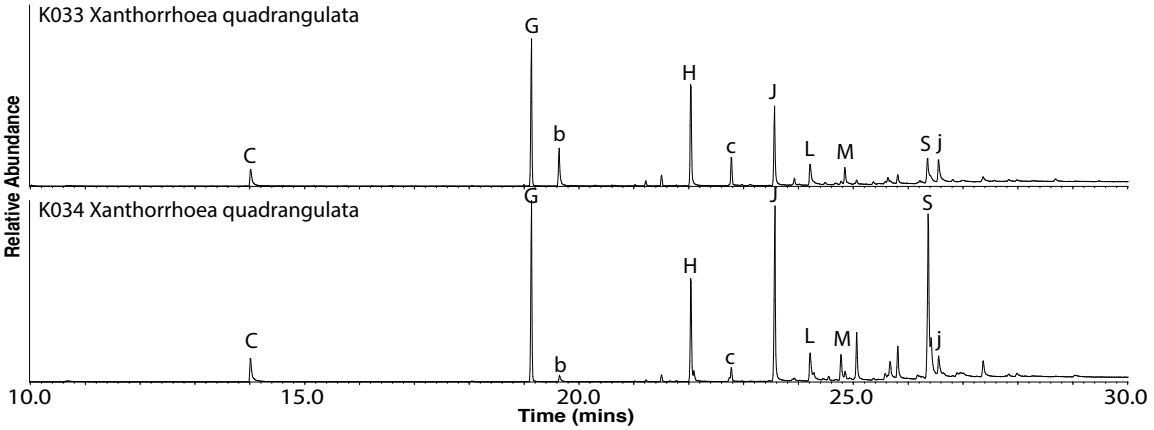


FIGURE 6.7: Partial chromatograms of the *X. quadrangulata* resin samples K033 and K034 G=Benzeneacetic acid, 2-phenylethyl ester, M=5,7-dimethoxyflavanone, S=sakuranetin, mass spectral data for all peaks can be found in Appendix G

The resins from these three species of *Xanthorrhoea*, in particular, are easily identifiable in fresh samples. Importantly the species with a West coast habitat, *X. preissii*, is clearly distinguishable from the East coast species.

6.4 Results from GC-MS analysis of ethnographic phenolic resins

Pictures and chromatograms for the ethnographic samples are presented in the adjoining catalogue. The significant mass spectral data for the ethnographic samples containing phenolic resins are presented in Appendix G. The results of the findings are summarised here.

6.4.1 *Xanthorrhoea* resins

Several of the ethnographic resin samples, analysed by GC-MS after methylation, produced chromatograms that resembled those of the known *Xanthorrhoea* resins. A few of these were identifiable to species level.

6.4.1.1 Species-level identification

***X. resinosa* resin**

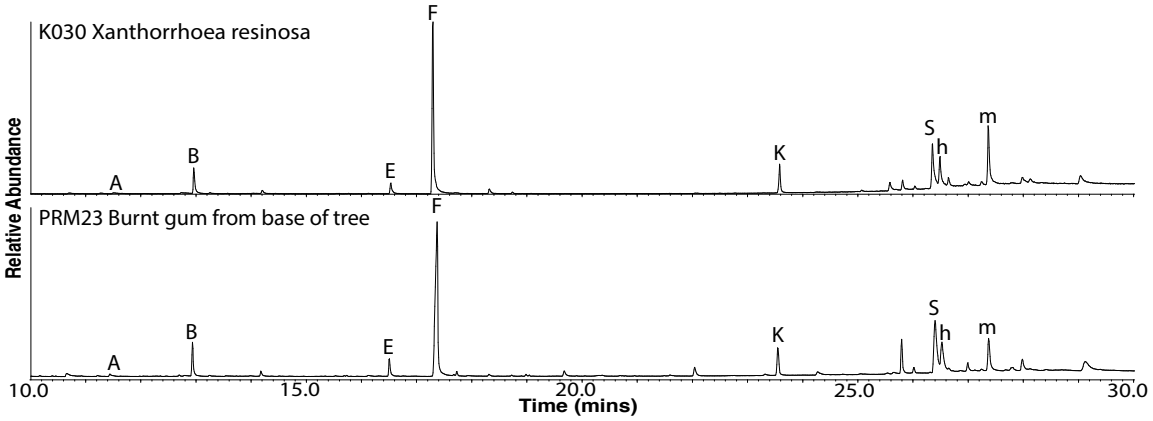


FIGURE 6.8: Partial chromatograms of PRM23 and *X. resinosa*
F=4-hydroxycinnamic acid, methyl ester, S=sakuranetin, mass spectral data for all peaks can be found in Appendix G

Sample PRM23 had been previously analysed and identified as *Xanthorrhoea resinosa* (Bradshaw; 2013). The similarity of chemical composition of sample PRM23 with that of the *X. resinosa* samples suggests a match (Figure 6.8). However, with further investigation, it is apparent that the chemical composition of *X. arborea* resin is also similar to that of PRM23, and the *X. resinosa* samples. The yellow colour of the PRM23 sample when extracted in solvent, compared to the red solvent extract of the *X. arborea* resin, alongside the chemical match, reaffirms the identification of PRM23 as resin from *X. resinosa*.

X. preissii resin

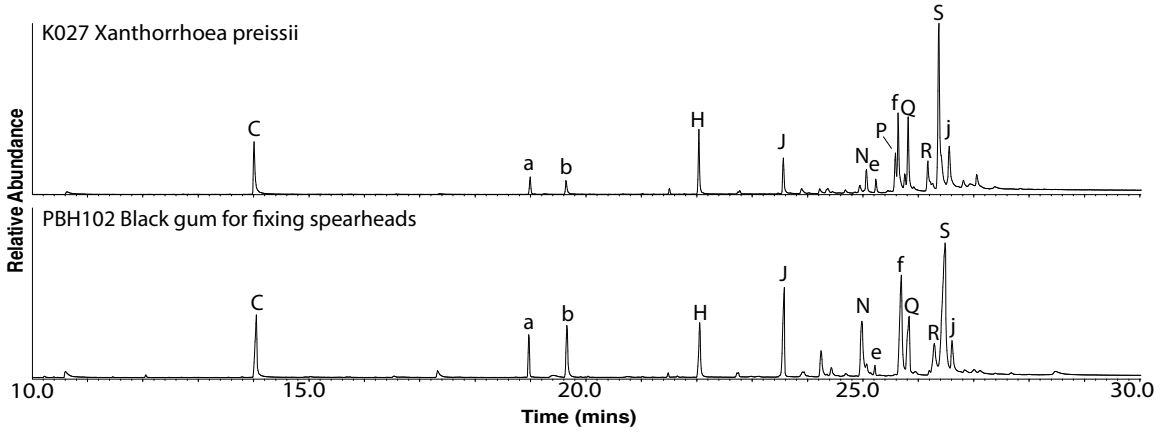


FIGURE 6.9: Partial chromatograms of PRM102 and *X. preissii*, R=naringenin, S=sakuranetin, mass spectral data for all peaks can be found in Appendix G

Another sample, PBH102, has been identified as coming from a specific species of *Xanthorrhoea*. The chemical composition of PBH102 is consistent with that of the *X. preissii* specimens, apart from the absence of 2-hydroxy-α-(p-hydroxybenzylidene)-4-methoxyacetophenone (peak P), which is an aromatic ketone. PBH102 is otherwise a match with *X. preissii* and dissimilar to samples from other species, and is therefore identified as *X. preissii* resin

(Figure 6.9). The loss of an aromatic ketone is feasible as a minor degradation alteration, but more research on this is needed.

X. quadrangulata resin

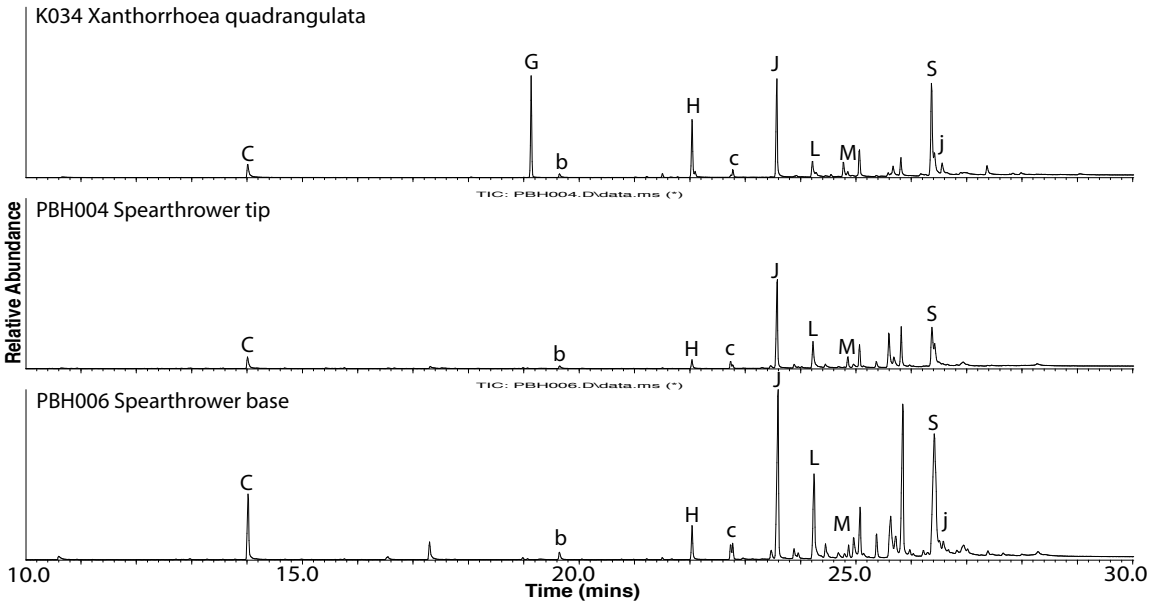


FIGURE 6.10: Partial chromatograms of PBH006, PBH004 and *X. quadrangulata* G=Benzeneacetic acid, 2-phenylethyl ester, M=5,7-dimethoxyflavanone, S=sakuranetin, mass spectral data for all peaks can be found in Appendix G

Samples PBH004 and PBH006 (Figure 6.10), produced chromatograms that were consistent with each other. The GC-MS data show similarities with both the *X. preissii* and *X. quadrangulata* samples, but not an exact match with either. Neither of the proposed species specific markers of naringenin for *X. preissii*, and benzeneacetic acid, 2-phenylethyl ester for *X. quadrangulata* were detected in either sample. However the stability of the latter is not known, whereas naringenin has been seen to survive in the aged sample PBH102 (peak R in Figure 6.9). The resin in these two samples are therefore cautiously identified as resin from *X. quadrangulata*.

6.4.1.2 Other *Xanthorrhoea* resins

Seven further samples of unknown resin from ethnographic samples produced chromatograms similar in appearance to that of the *Xanthorrhoea* samples, and all contain sakuranetin indicating they are most likely *Xanthorrhoea* resin, but of unknown species. These samples form two seperate groups, possibly representing two different species.

Group one

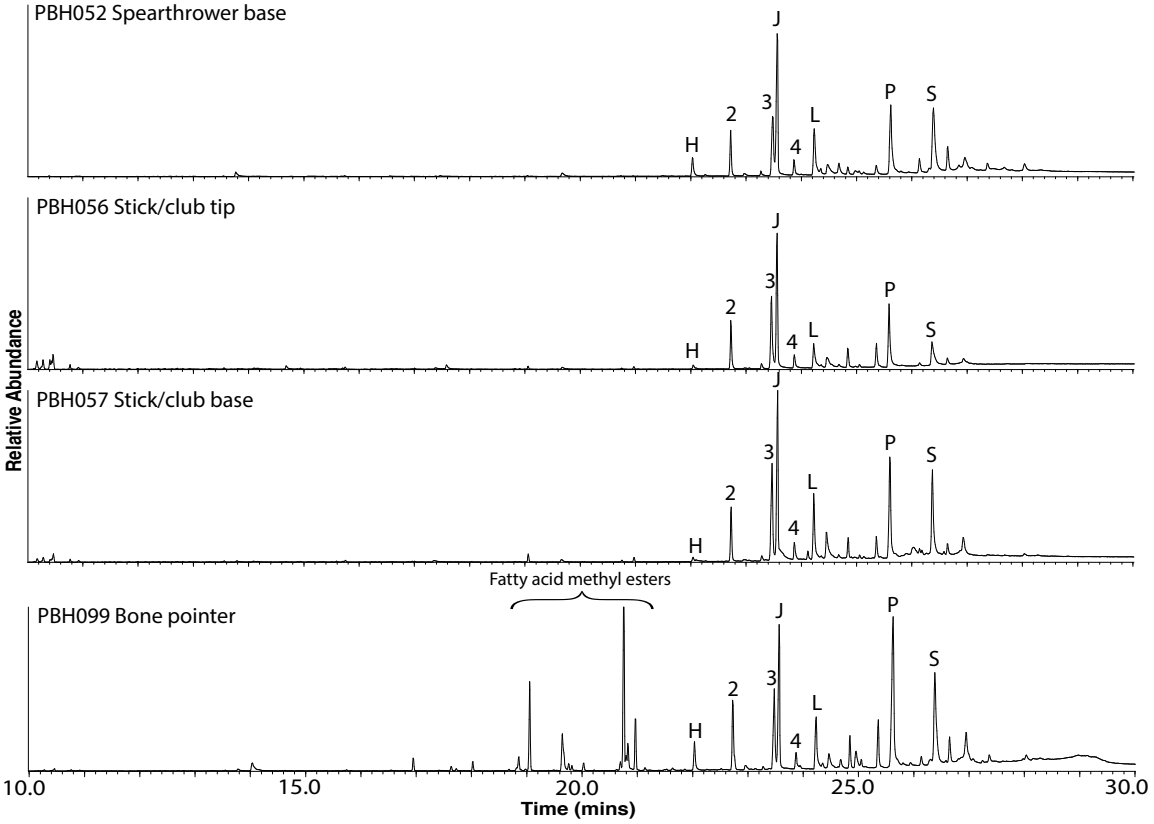


FIGURE 6.11: Partial chromatograms of group one *Xanthorrhoea* sp. samples: PBH052, PBH056, PBH057 and PBH099.
Mass spectral data for all peaks can be found in Appendix G

Samples PBH056 and PBH057 appear to be the same resin as each other and are very similar to samples PBH052 and PBH099, together forming the first of two groups of unknown *Xanthorrhoea* resins (Figure 6.11). The chemical composition of all four resin samples

have similarities with that of *X. preissii*, but also some differences, including an absence of several peaks including naringenin, and the additional presence of peak L. The composition also seems similar to *X. quadrangulata*, which has peak L, or *X. australis* which has peaks N, P and S without the extras of *X. preissii*. However, there is not an exact match with any of the reference resins, and the latter two are unlikely identities for these samples as PBH052, PBH056 and PBH057 were from items originating in Western Australia. It is more likely that the resin comes from a different species of *Xanthorrhoea*, such as *X. thorntonii*, which occurs throughout inland Western Australia, including Laverton where the artefact associated with sample PBH052 originated.

Further analysis of resins from more *Xanthorrhoea* species including *X. thorntonii* plus more research on the degradation pathways of the *Xanthorrhoea* resins is required to be able to identify the source species in aged resin samples such as these.

Group two

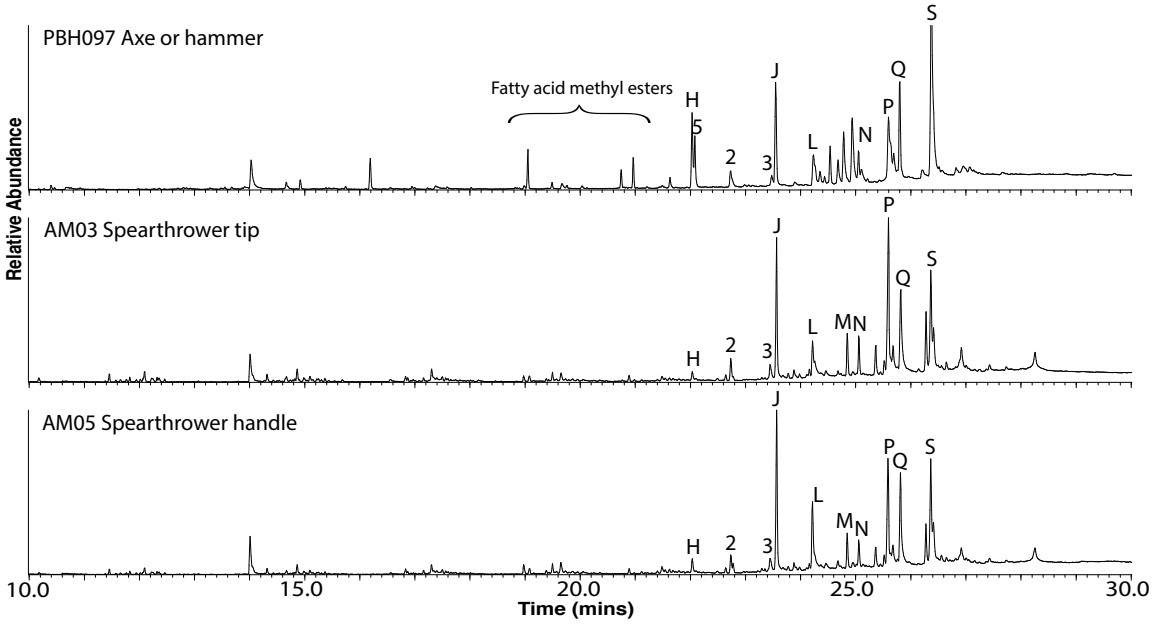


FIGURE 6.12: Partial chromatograms of group two *Xanthorrhoea* sp: samples PBH097, AM03 and AM05
Mass spectral data for all peaks can be found in Appendix G

The two samples AM03 and AM05 are highly consistent and indicate that they contain the same resin. PBH097 mostly has compounds in common with AM03 and AM05, forming group two (Figure 6.12). All three samples contain components that are consistent with *Xanthorrhoea johnsonii*, which makes most sense geographically for the two samples from Torres Strait (AM03 and AM05), as that would represent the shortest trade troute to the islands. However, PBH097 originates from south-west Western Australia. The components in these three samples are also present in *X. preissii*, which occurs in south-west WA, though several more compounds present in *X. preissii* are not present in the group two samples. There are also a few components in the samples that are not present in the resin from either of the species discussed, indicating a mixture of at least two resins, or else a different unknown species of *Xanthorrhoea*. Either way, it is interesting that resin samples from items that originate at opposite ends of the country are so similar in composition, most likely representing trade in some form.

6.4.2 Non-*Xanthorrhoea* phenolic resins

Samples PBH033 and PBH034 are highly similar to each other, but are not similar to any of the reference resins. They both contain a significant amount of sakuranetin, but demonstrate a very different type of chromatographic response to the *Xanthorrhoea* resin samples. PBH101 also contains sakuranetin and similar compounds to PBH033 and PBH034 (Figure 6.13). Not matching any of the reference *Xanthorrhoea* spp. resin samples, none of these samples are thought to be from *Xanthorrhoea*, and therefore represent an unknown type of phenolic resin or kino.

Sample PBH070 contains sakuranetin (peak S) and pinostrobin chalcone (peak J), along with vanillic acid, methyl ester (VA) and some other phenolic compounds including peaks 6 and 8 that are in PBH101, PBH033 and PBH034 (Figure 6.14). Again the chromatogram

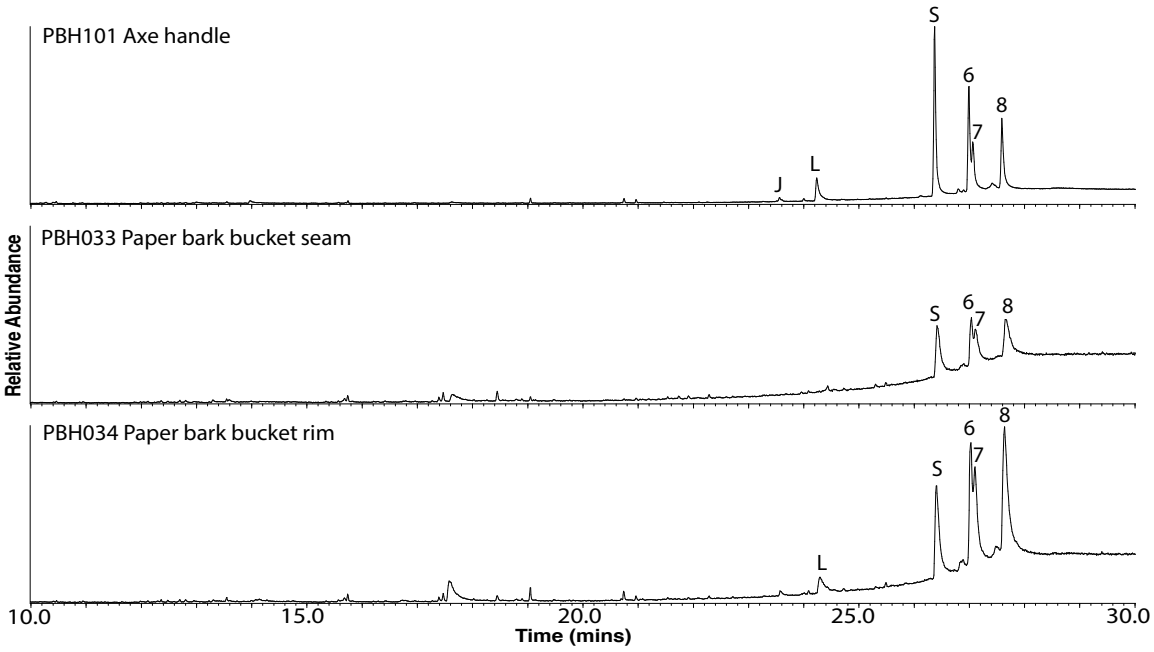


FIGURE 6.13: Partial chromatograms of samples PBH033, PBH034 and PBH101
S = sakuranetin, mass spectral data for all peaks can be found in Appendix G

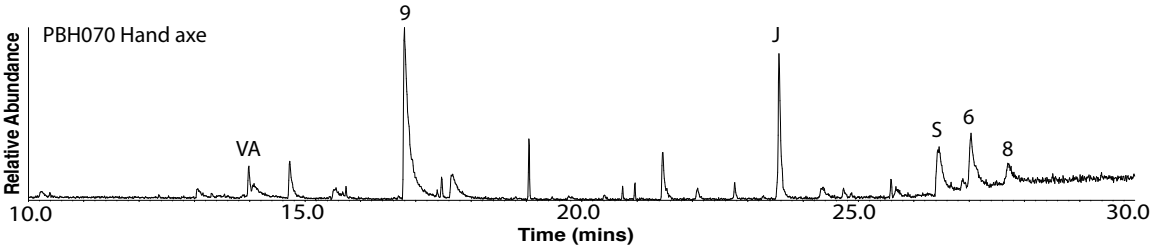


FIGURE 6.14: Partial chromatogram of sample PBH070.
Mass spectral data for all peaks can be found in Appendix G

does not match any of the reference *Xanthorrhoea* samples but does indicate a phenolic resin, possibly the same or similar to PBH101, PBH033 and PBH034.

Sample PBH055 also contains sakuranetin, but not many of the other peaks from the known *Xanthorrhoea* samples, only peak J (Figure 6.15). PBH055 is a sample from an item from south-west WA, and is unique in this study in that it also shows a presence of diterpenic compounds, including a compound that is possibly callitrisic acid, which would indicate the presence of *Callitris* resin (see Chapter 3).

The majority of the other peaks in sample PBH055 have not been identified, but it is clear that the material is a mixture of at least two resins, a phenolic and a diterpenoid resin, as

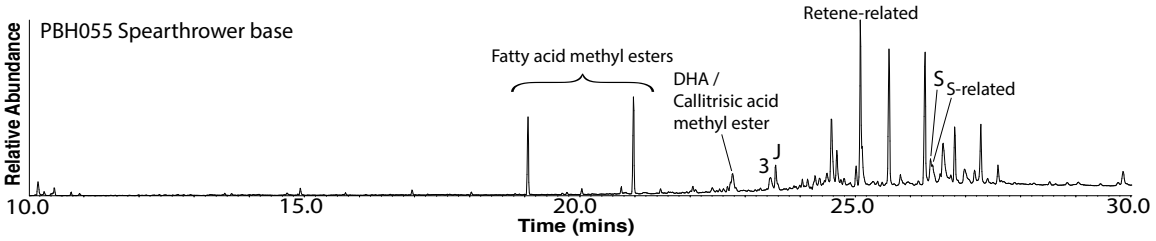


FIGURE 6.15: Partial chromatogram of sample PBH055

well as something containing fatty acids.

6.5 Conclusion

Xanthorrhoea resins have previously been recovered archaeologically and successfully identified. *Xanthorrhoea* resin is known to have commonly been used in a number of areas in Australia, particularly for hafting stone tools to handles. The ability to identifiy *Xanthorrhoea* resins to species is possible by chromatography, and important for ethnographic studies as well as archaeological finds, particularly because of the distinct geographical distributions of the individual species.

Xanthorrhoea resin is confirmed as a phenolic resin. Sakuranetin is present in all of the *Xanthorrhoea* samples and is therefore a strong indicator for the presence of phenolic resin in a sample, and at least a partial taxonomic marker for resin from the genus *Xanthorrhoea*. The composition of the resins from each of the species of *Xanthorrhoea* included in this study are distinct enough to confidently distinguish by GC-MS analysis. Some candidates for biomarkers for specific species are apparent, particularly if present alongside sakuranetin. Further work on resins from additional species is required to confirm biomarkers for the species included in this project.

Two separate aged ethnographic resin specimens from museum collections have been positively identified to resin of a particular species of *Xanthorrhoea*, indicating that the composition of pure *Xanthorrhoea* resin can remain stable enough to be recognised when aged up to around 100 years. Two other samples of resin from a museum artefact have also been cautiously identified to source species. Several other ethnographic resin samples have successfully been identified as *Xanthorrhoea* resin, forming two distinct groups possibly representing two other species.

This work suggests that *Xanthorrhoea* resin on museum artefacts has the potential to be identified to species level, however, as expected, identification to this level is more difficult

in an aged sample. Further work on the degradation pathways of *Xanthorrhoea* resins is required, along with a wider range of reference species. More replicate reference samples are also needed to better understand the variation in composition within and between the resins of different species of *Xanthorrhoea* in order for the proposed identification criteria to be made more robust.

There are at least two types of phenolic resin that have been used on ethnographic artefacts that are not from *Xanthorrhoea*, and are of unknown origin. This finding presents an interesting prospect of ethnobotanically important plants producing unknown phenolic resins in Australia.

Chapter 7

Discussion of the resin analysis results in context of the ethnographic museum artefacts

7.1 Introduction

It is generally well recognised that resin has been an important material in the manufacture of objects in Oceania, and this has been highlighted by the results of this study. The chemical analysis of amorphous residues thought to be resin on artefacts currently in museum collections, that originate from this region, will be discussed in context of the artefacts and relevant surrounding ethnography.

It is evident from these results that several different resins have been exploited in Oceania and that these resins can be distinguished and potentially identified to some extent, as discussed in Chapters 3 to 6. Identification of the resins on these artefacts is important

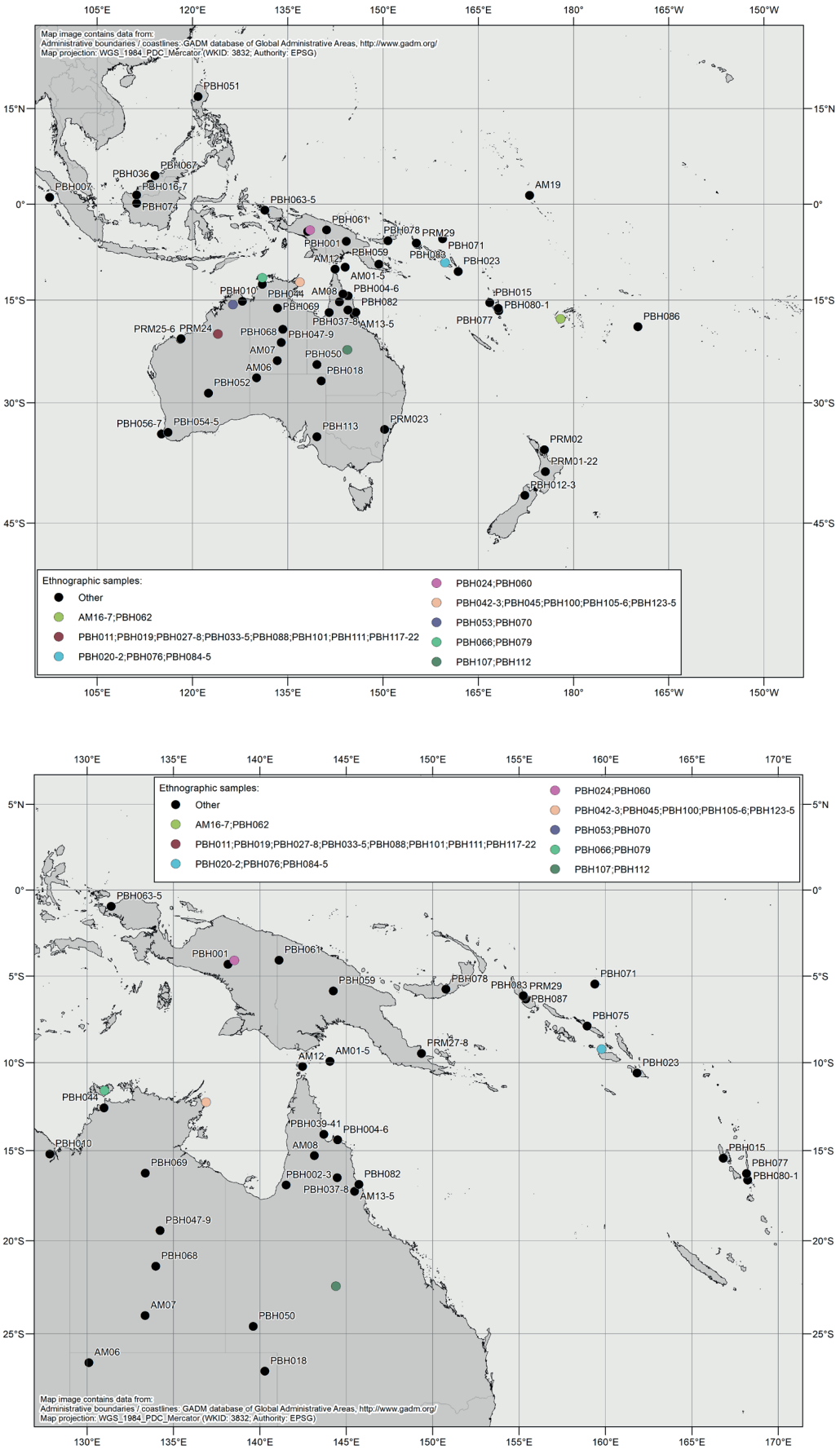


FIGURE 7.1: Map showing the origin of aftefacts analysed in this project Whole area (above); NE Australia, PNG and Solomon Islands (below)

for the ability to develop a framework for analysing similar materials from an archaeological context with a view to better understanding the relationship between plant resin and Indigenous culture in Oceania, in the more distant past. Aspects of this human-plant relationship includes their choice of resin source as well as how they adapted the resins for specific purposes.

In terms of resin function, the most notable differentiation within the collection analysed in this project was between resin used for hafting of composite tools and weapons, and resin used for other non-hafting purposes. In a few cases these different functions occurred on the same item. The other main factor that was expected to affect the source of resin chosen for exploitation is geographic. Natural distributions of the main sources of resin in Oceania are presented in Chapters 3 to 6.

The items from the museum collections will be discussed in light of the results of the analysis of the amorphous samples, firstly focussing on the items with hafting material. They will also be discussed in terms of geographical origin of the artefacts as recorded in the museum notes, and shown in Figure 7.1.

7.2 Hafting in Australia and other parts of Oceania

Eighty-four samples of residues from hafted items from the ethnographic museum collection for this project were analysed to investigate the presence of solvent-soluble resin in the hafting material, as well as resinous materials used elsewhere on the same items. The presence of plant resin was indicated in 53 of these cases, and demonstrated a range of different types of resin from a range of botanical sources.

7.2.1 Hafted weapons and tools in Australia

Archaeologically, resinous substances are most commonly found adhering to stone tools, which allows the direct association of the resins used with specific tool types. There are many ethnographic examples of hafted tools and weapons in the museum collections, particularly ones from Australia.

7.2.1.1 Spears and spearthrowers

Perhaps the most common tools or weapons from Australia, at least of those collected ethnographically, are spears and spearheads. Examples from the ethnographic collections in this project indicate that a range of materials were used for hafting spearheads to shafts.

Spearthrowers or "woomerahs", were used in conjunction with spears and as is noted in the museum records for one of the items, the two together superseded the use of the bow and arrow in Queensland. As artefacts they are particularly interesting for studying resin use as they often represent two or three different functions for resin and/or other cementing materials on the same item. Fortuitously, there are examples from several different regions of Australia.

Northern Territory

Ethnographic descriptions of spinifex resin being used for hafting in Northern Australia, as discussed in Chapter 4, are corroborated by two samples from spears from the Northern Territory. Conversely, three similar items collected from Arnhem Land did not have spinifex-type resin as the hafting material. These items were hafted with either beeswax, or unknown materials. A conifer-type diterpenoid resin was used on the base end of one of the spears, and a vegetable oil or wax has been used in most of the samples. In total,

6 different adhesive materials were used on the 5 spears from the Northern Territory (see Table 7.1). One of these items is a two-pronged fishing spear.

Table 7.1: Spears from the Northern Territory

Sample	Sample location	Artefact information	Results
PBH044	Hafting residue	Spearhead point from Darwin, NT	Diterpenoid spinifex-type resin
PBH079	Hafting residue	Spear from the Melville Islands, NT	Diterpenoid spinifex-type resin plus a vegetable oil
PBH125	Haft	2-pronged fishing spear from Arnhem Land, NT	A vegetable oil or wax plus kaurenoic acid-related diterpenoids
PBH123	Haft	Stone-pointed hunting and war spear from Arnhem Land, NT	A vegetable oil or wax
PBH124	Base end		Conifer diterpenoid resin, possibly from *Callitris* plus a vegetable oil
PBH108	Hafting residue	Flaked stone spearhead with 'bitumen' from Arnhem Land, NT	Beeswax

According to Veth et al. (2011, p. 56) multi-pronged spears are generally associated with fishing, and are found in Australia with two, three or four prongs, yet very few specimens are found in museum collections and the majority appear to be from the Cape York region. Because of this Veth et al. (2011, p. 56) suggests that multi-pronged spears may have come from New Guinea although there are no references of them there, however they are known in other parts of the Pacific. The two-pronged fishing spear from the Peabody Harvard collection analysed here (see Table 7.1) is from the Northern Territory and so does not support Veth's hypothesis. However, on each of the prongs, the barbs are cut into the solid wood, and according to Veth et al. (2011, p. 58) these kind of barbs are found in three main distributions: a south-eastern area, a western area and a northern area (Veth et al.; 2011, p. 58). It is possible that the fatty acid based hafting material containing traces of kaurenoic acid found on this example is specific to the northern area in which these type of barbs are known to have been used. There is no information in the literature on the hafting materials used, so rare items such as this offer an important insight. Further analysis of the

hafting residue may provide insight to the development of multi-pronged spear technology in this region.

It is also interesting to note the example of a hunting and war spear from Arnhem Land (Table 7.1), which has different amorphous materials used for separate purposes on the same item. The only examples of spearthrowers from the Northern Territory in this collection are also from Arnhem Land (Table 7.2). There is a similar instance of different materials being used for the hafting and non-hafting purposes on the same item.

TABLE 7.2: Spearthrowers from the Northern Territory

Sample	Sample location	Artefact information	Results
PBH042	Haft at tip	Cylindrical type spearthrower from Arnhem Land, NT	Putative ironwood resin
PBH043	Base		Not resin, possibly inorganic
PBH105	Peg haft (black resin)	Spearthrower from Arnhem Land, NT	Unknown resin with kaurenoic acid-related diterpenoids plus a vegetable oil
PBH106	Peg haft (red resin)		Unknown resin with kaurenoic acid-related diterpenoids

Two samples were taken from the haft of the second spearthrower due to a difference in colour, but the results showed the resin to have the same composition. This type of resin is similar to that found on one of the spears also from Arnhem Land (Table 7.1). It is likely that the difference in colour is an addition of red ochre, which may have the effect of making the resin more crumbly as well as adding colour, and in contrast the addition of a vegetable oil to the black resin may have made it more maleable. This is a different hafting material to that reported by Spencer and Gillen (1912, p384-385) in their description of two types of spear-throwers used by tribes elsewhere in the Northern Territory:

> In both these types the knob, which fits into the slight hole in the end of the

> spear, is made of wood, and is attached to the thrower by means of porcupine-grass resin in the Warramunga and interior tribes, and beeswax in the coastal tribes.

Contrary to this description, *Xanthorhorroea* (porcupine-grass) resin and beeswax were not found on the items in this collection, which either suggests that different hafting and adhesive materials were used for spearthrowers in Arnhem Land compared to other areas of the Northern Territory, which is suggested by the spears (Table 7.1), or a wider range of materials were generally used throught the Northern Territory. Beeswax was identified on one of the spearheads from Arnhem Land, which corroborates its use in the area as a hafting material.

Western Australia

Kimberley points are distinctive and common in Australia. They are spearheads that were made in the Kimberley region of northwest Western Australia for fighting, hunting and and importantly, exchange, originally from stone, then glass and ceramics after the late nineteenth century (Akerman et al.; 2002, p 13). There is some reference to the use of beeswax to haft the points to a shaft (Akerman et al.; 2002, p 17, p 23), but the use of resin was common and according to Akerman et al. (2002, p 21), the method of hafting with just resin was employed as it reduces damage to the points by releasing them on impact. Spinifex (*Triodia* sp.) or the native cypress (*Callitris columellaris*) resin are suggested by Akerman et al. (2002, p 23) as possible sources of the resin. This is partly supported by the findings of three examples of each stone and glass points (see Table 7.3).

Non-conifer diterpenoid resins, possibly a type of spinifex (group E, see Chapter 4), were detected on the stone Kimberley points, but not the glass points (see Table 7.3). Probable ironwood resin was identified on one of the glass Kimberley points, but there was no evidence

TABLE 7.3: Spears from Western Australia

Sample	Sample location	Artefact info.	Results
PBH120	Hafting residue	Spears with stone	Diterpenoid spinifex-type resin
PBH121	Hafting residue	Kimberley points	Diterpenoid spinifex-type resin
PBH122	Hafting residue	from Panton River, WA in 1922	Diterpenoid spinifex-type resin
PBH117	Hafting residue	Spears with green glass	Ironwood resin
PBH118	Hafting residue	Kimberley points	Not resin
PBH119	Hafting residue	from 120 miles inland from Derby, WA pre-1920	Not resin
PBH010	Hafting residue	Spear from Forrest River Mission, Kimberley, WA, collected in 1916	Unknown material

of resin in the hafting material on the other two samples. These samples represent four different types of material used for attaching spear points to shafts[1] in the Kimberley region, with a notable difference between the two point types.

There are many other examples of these type of points in the museum archives. Analysis of a much larger selection of hafted points would be interesting for comparing the hafting materials on a larger scale to see if there is a strong pattern in the use of hafting material compared to material of point. Particular questions of interest would be whether: the use of different hafting materials reflects changes in point manufacture from pre- to post-European contact; the resin choice reflects the intended purpose of such points, for example for use, trade or the tourist market; the differences in hafting material choice are part of a wider phenomenon of adaptation to the use of new materials such as glass and metal, or if it is restricted to the Kimberley area. An example of spinifex resin used on a metal point was discussed in Chapter 4.

Some spearthrowers from the Kimberley are recorded to have been made with spinifex (*Triodia*) or *Callitris* resin to reinforce the sinew lashings holding the peg in place (Akerman

[1]See photographs in the Catalogue. The spear lengths were shortened for travel by horseback when collected by Mr. Walter Badenach in 1922.

Table 7.4: Spearthrowers from Western Australia

Sample	Sample location	Artefact info.	Results
PBH052	Resin on base	Spearthrower from Laverton, Goldsfields-Esperance, WA	*Xanthorrhoea* resin
PBH053	Resin on tip	Spearthrower from Drysdale River, Kimberley, WA	Non-conifer diterpenoid resin, not group A-E
PBH054	Hafting material on tip	Spearthrower from Bridgetown, WA	No resin, only fatty acids present
PBH055	Resin on base		Mix of *Xanthorrhoea* and possible *Callitris* resin
PBH012	Hafting on tip	Spearthrower from Mt. Vernon, Murchison, WA	No resin, only fatty acids present
PBH013	Resin on base		Not resin, only fatty acids present

et al.; 2002, p 16). Although not from the Kimberley (north WA), *Callitris* resin may well be present in one of the samples from a spearthrower from southern Western Australia, but on the base end not the peg haft, and mixed with *Xanthorrhoea* resin (Table 7.4). The hafting material did not contain resin. *Xanthorrhoea* resin was also used on the base of another example of a spearthrower in south-western Western Australia. A material not containing resin was used on a third example from the west of Western Australia, although *Xanthorrhoea* resin is known to have been used in the Murchison district of central WA (Clarke; 2012, p 139).

According to Gould (1970), resins used in Laverton include those from *Triodia pungens* and *Xanthorrhoea thorntonii*, for both hafting the peg as well as to repair small cracks in the wood of spearthrowers. It is noted that *Xanthorrhoea thorntonii* resin is not commonly used in the desert areas that are dominated by spinifex (Gould; 1970, p 40). It is suprising then that none of the samples contained spinifex resin. The examples of *Xanthorrhoea* resin identified here may well be from *X. thorntonii* but would need comparing to an

authenticated sample to confirm. Identifying the non-resin materials on these items is outside the scope of this project.

Queensland

Xanthorrhoea resins have also been identified on spearthrowers from Queensland.

TABLE 7.5: Spearthrowers from Queensland

Sample	Sample location	Artefact info.	Results
PBH004	Haft on tip	Spearthrower from ?Cape Melville, collected by Dr. Joseph B. Birdsall and Norman B. Tindale	Phenolic resin from *Xanthorrhoea*
PBH005	Handle		Conifer-type diterpenoid resin
PBH006	Resin on base		Phenolic resin from *Xanthorrhoea*
PBH039	Haft on tip	Spearthrower from ?Port Stewart, collected by Dr. Joseph B. Birdsall and Norman B. Tindale	Ironwood resin
PBH040	Handle		Triterpenoid resin from *Canarium salomonense*
PBH041	Adhesive on the baler shell base		No resin, probably wax
AM03	Haft on tip	Spearthrower from Mer Island, Torres Strait	Phenolic resin from *Xanthorrhoea*
AM04	Resin on base		A mixture or a type of resin with unusually both triterpenoids and diterpenoids
AM05	Handle		Phenolic resin from *Xanthorrhoea*
PBH112	Haft on tip	Womarah from Queensland	Conifer-type diterpenic resin, with marker for high temperature heating

In 1951, the directors of the University of California, Los Angeles and the South Australian Museum, Adelaide, Dr. Joseph B. Birdsall and Norman. B. Tindale, collected several items from Aboriginal Australians as part of the Peabody Museum South Australia Expedition. This collection includes two Queensland spearthrowers, one from Cape Melville and one from Port Stewart. Both of these spearthrowers from Far North Queensland are examples of

a particular type of spearthrower with a baler or melo shell handle. *Melo* is the taxonomic name for the genus of the baler shell sea snail. Another similar spearthrower with a shell handle was collected from the Torres Strait, with a note from the collectors that it was a Cape York type of "Queensland melo-woomerah" that was not used in the eastern Torres Strait islands and probably obtained by exchange. This spear thrower is categorised in the museum record as being a hunting/fishing weapon.

Multiple applications of resin have been analysed from these three similar Queensland spearthrowers, from the hafting material on the tip, adhesive on the base, and a coating on the handle. Evidently the same resin was not used for all three functions on the spearthrowers. In each case, at least two different materials were used (see Table 7.5).

The use of *X. quadrangulata* may indicate trade of resin, or complete tools (although less likely considering the specific type of the spearthrower) from areas where *Xanthorrhoea* is more dominant. If made locally to Cape Melville, the resin most likely to have been used based on local species distribution would be from *X. johnsonii*.

The presence of *Canarium salomonense* resin, a species that is native to New Guinea and the Solomon Islands, on an Australian spearthrower may indicate the use of a trade link through the Torres Strait from New Guinea. The use of *Xanthorrhoea* resin on the spearthrower collected in the Torres Strait reflecting the Cape Melville spearthrower, reinforces the connection between Far North Queensland and the Torres Strait Islands. Both of these findings support the idea of regular exchange.

However, there are Australian species of *Canarium* that have not been analysed in this study, which should be compared in order to be discounted. A description by Roth as referenced by Haddon and Rivers (1912, p. 198), reports the use of 'cement' for the handle of a similar spearthrower from a similar area of Far North Queensland, specifiying it as

Canarium australicum cement, which appears to have been an addition by Haddon and Rivers:

> The handle is covered with [Canarium australicum][*sic*] cement, so as to prevent it from slipping through the hand. The cement at one or both extremeties of the blade may be occasionally decorated with the dried (yellow) strips from the outer covering of the 'Rock Lily' (*Dendrobium bigibbum.* Lindl.) orchid. The shell haft is formed of two oval-cut pieces of pera shell (*Melo diadema*, Lamk.) attached with beeswax, while a few *Abrus precatorius* beans may help to ornament the edges in-between; the angle at which the shell-haft is affixed varies a good deal, and appears to depend on individual caprice.

It is not clear where the identification of the cement as being resin from *Canarium australicum* came from. Contrary to such, the presence of ironwood resin on a melo shell spearthrower was found in this study and is discussed in Chapter 4. This example matches the description by Khan (2004, p. 79), of resin to hold the peg in place, and beeswax used at the hand-held end where the melo shells are attached. The identification of ironwood as the resin in this case leads to a hypothesis that the straight spearthrower in the Roth collection, from Gunnani people between Mitchell and Staaten Rivers in Far North Queensland, that is made of ironwood, may also have ironwood resin as the hafting cement. Chemical analysis would be required to test this hypothesis.

A different type of womerah or spearthrower also from Queensland, is described as having resin hafting on the tip. The sample (PBH112) was found to contain a diterpenoid resin of the conifer type. A chemical marker indicating intense heating (causing extreme degradation of the diterpenoid compounds, which produces such an end-product) was also detected in this sample (Chapter 3). High heat processing is used in making pitch from conifer resin,

but the only reference to conifer pitch in this region, known to the author, is from Papua New Guinea (see Chapter 3).

The only example of a spear from Queensland is also from the far northeast (Table 7.6). The resin on the haft appears to be a mixture of at least two different materials probably representing a repair, or at least a re-application of resin.

Table 7.6: Spear from Queensland

Sample	Sample location	Artefact info.	Results
PBH082	Haft	Hafted spear from Cairns, northeast Queensland	Mixture of a triterpenoid resin, probably from the Burseraceae family, with a conifer-type diterpenoid resin

These findings are different to what was expected from the information gathered by Clarke (2012, p. 139), in the use of the northern grasstree (*Xanthorrhoea johnsonii*) resin at Bloomfield River north of Cairns, for fixing barbs to spears, and that the same resin was used across northern Queensland for attaching the double shell handles to spear throwers.

South Australia

The only example of a spearthrower from South Australia was collected from River Murray (Table 7.7). The 'gum' on the end of the concave spearthrower has been identified as a conifer-type diterpenic resin. Similarly to sample PBH112 from the Queensland spearthrower, a marker for high temperature heating was detected (Chapter 3).

Table 7.7: Spearthrower from South Australia

Sample	Sample location	Artefact info.	Results
PBH113	'Gum' on end	Concave spearthrower from River Murray, South Australia	Conifer-type diterpenic resin, with marker for high temperature heating

This type of resin is again different to the accounts reported by Clarke (2012, p 137-9) for southern South Australia. Clarke's 2012, p 137-9 examples are of the 'aromatic' grasstree

gum, referring to *Xanthorrhoea* resin, being used as a cement for spears and spearthrowers, noting that it is mixed with sand to form a kind of glue. There is no mention of conifer resin being used in this way. Evidently, conifer resins were used in Australia more often than is generally reported.

7.2.1.2 Axes and Adzes

Axes and adzes are often hafted, as we know from the ethnographic and archaeological evidence (Chapter 4). The examples in this study show a range of resins being used for hafting these types of tools across Australia.

Northern Territory

Table 7.8: Axe from the Northern Territory

Sample	Sample location	Artefact info.	Results
PBH045	Haft	Ground hafted axe from Arnhem Land	No resin, possibly polysaccharide gum

An axe from Arnhem Land is the only example from the Northern Territory, and was found not to be hafted with resin but with a non-resinous adhesive material, possibly a polysaccharide gum (Table 7.8).

Western Australia

Akerman and Bindon (1984) report the use of *Triodia* resin in the Kimberley region of Western Australia for hafting adzes: "According to older Nyikina, Walmatjeri and Kitja informants (Kimberley tribal groups still familiar with these artefacts) the common type of edge-ground flakes were hafted and used as adzes." Spencer and Gillen (1912, p. 370) note that resinous material obtained from "porcupine grass", but for which they reference *Triodia* spp. (not *Xanthorrhoea* that porcupine grass usually refers to), was used by the

men of the Warramunga in central Australia for fixing the stone when making axes, which was then rubbed with red ochre. Although their assessment of the end-product is not too positive:

> The most unsatisfactory feature of the Central Australian axe is the method of hafting[...]As it is, their axe is at best a clumsy tool, because the resin is very brittle and cracks easily, so that anything like a hard blow results at once in the loosening of the stone.
>
> Spencer and Gillen; 1912, p. 373

The results of this study show that a small axe hafted onto a thin wooden handle from southwestern Western Australia has indications of *Xanthorrhoea* resin in the hafting material. From the Kimberley region, another phenolic resin (probably not *Xanthorrhoea*) was found on two examples of hafted axes. Another example suggests the use of wax as the hafting cement (Table 7.9). *Triodia* or spinifex-type resin was not found on any of the examples from the Kimberley. No examples from the central Australia part of WA were analysed.

Table 7.9: Axes from Western Australia

Sample	Sample location	Artefact info.	Results
PBH097	Haft	A small axe hafted onto a thin wooden handle from southwestern WA	*Xanthorrhoea* resin
PBH070	Haft	Hafted axe from Kimberley, WA	Phenolic resin (not *Xanthorrhoea*)
PBH101	Hafting residue	Axe handle from Kimberley, WA	Phenolic resin (not *Xanthorrhoea*)
PBH019	Haft	Stone axe from Kimberley, WA	No resin, possibly wax

Xanthorrhoea does not grow naturally in the Kimberley region and they would have to rely on trade or exchange to procure it. They appear instead to be using an unknown type

of phenolic resin, which is probably not from *Triodia* sp., based on other examples in this study thought to be from *Triodia* that are diterpenic in composition.

Queensland

One example of each an adze and an axe from Queensland were included in this collection (Table 7.10).

Table 7.10: Axe and Adze from Queensland

Sample	Sample location	Artefact info.	Results
PBH050	Haft	Wooden adze from Diamantina, western Queensland	Unknown resin or mixture of resins containing triterpenoids and amides
PBH098	Haft	A ceremonial stone axe rubbed over with ochre from North Australia	Mixture of vegetable oil with unknown pine-like diterpenoid resin and triterpenoid resin hypothesised to be from *Canarium australasicum*

The example of an adze from Diamantina, western Queensland has a hafting material with an unusual composition. There is a possibly that it could be the exudate from the tangled leschenaultia shrub (*Leschenaultia divaricata* Goodeniaceae). Clarke (2007, p. 121,159) mentions use of a 'pitchy substance' from the roots of the tangled leschenaultia, called 'mindrie', for making artefacts such as knives, axes and adzes. People in the Diamantina River area of Central Australia are known to have used mindrie pitch for attaching handles and grips to their knives, hatchets, spear throwers and adzes (Clarke; 2012, p. 147). A reference sample of *Leschenaultia divaricata* would need to be analysed to assess this hypothesis.

The hafting material on the axe from North Australia appears to be a mixture of vegetable oil and at least two different resins, because the sample shows some oxidation markers for conifer-type as well as kaurane-related diterpenoids plus a non-elemi type triterpenoid resin, possibly from the *Canarium* genus.

Sample PBH098 most closely resembles sample AM01 from a model shell hoe from the Torres Strait, suggesting the origin of this 'North Australian' item is most likely to be from Far Northeast Queensland, fitting in with a narrative of regular exchange between the two regions.

South Australia

Two examples of adzes from South Australia both interestingly contain triterpenoids in the hafting material, but of different types (see Table 7.11).

Table 7.11: Adzes from South Australia

Sample	Sample location	Artefact info.	Results
PBH018	Haft	A stone adze mounted on a wooden handle from Cooper Creek, SA	Dammarane-type triterpenoids
AM06	Haft	A wooden adze with a quartz flake attached with 'resin' from the Pitjantjatjara people of Amata, SA	Non-conifer diterpenoid resin and a trace material with lupane-type triterpenoids

Dammarane-type triterpenoids, as found on the adze from Cooper Creek, are most commonly found in resins from the Dipterocarpaceae family. Dipterocarps are not native to Australia and these findings may indicate trade with southeast Asia, or else a different type of triterpenoid resin from an unknown source that is native to Australia.

The adze collected from the Pitjantjatjara is hafted with a diterpenoid resin of the non-conifer type. There is also evidence of lupane-type triterpenoids in the hafting material, which may indicate a previous haft using a different resin, a deliberate mixture of resins, or a contamination from elsewhere.

These are both very interesting finds as ethnographic sources mention mainly *Xanthorrhoea* resin, and specifically *X. quadrangulata*, for hafting hatchets and adzes in South Australia (Clarke; 2012, p. 138-9).

7.2.1.3 Knives, sticks and clubs

Spinifex resin appears to be common on knife handles, which is consistent with ethnographic reports (Gould; 1970, p. 149). Examples from knives, sticks and clubs from across Australia are discussed below.

Northern Territory

Three hafted stone knives from the Northern Territory bear the same type of non-conifer diterpenoid resin of the presumed spinifex type (Table 7.12), possibly representing a specific species of *Triodia* (see Chapter 4). This may reflect the resinous material obtained from 'porcupine grass' referenced by Spencer and Gillen (1912, p. 370), as discussed above regarding axes.

Table 7.12: Knives from the Northern Territory

Sample	Sample location	Artefact info.	Results
PBH046	Haft	Stone knife with a sandstone blade and "gum haft" collected by Nancy Movius in 1934 from Newcastle Waters, central north of NT	Spinifex-type non-conifer diterpenoid resin
PBH047	Haft	Hafted stone knife with sheath collected from the Warramunga at Tennant Creek, NT by Dr. Hallam L. Movius, Jr. before 1936, when it was sold to the museum by Dr. Robert Pulleine	Spinifex-type non-conifer diterpenoid resin
PBH049	Haft	Stone knife with wooden handle collected from the Warramunga at Tennant Creek, NT by Dr. Hallam L. Movius, Jr. before 1936, when it was sold to the museum by Dr. Robert Pulleine	Spinifex-type non-conifer diterpenoid resin

The consistency in the material used on these knives from generally the same area is notable. It would be interesting to compare these knives to other hafted items from the Warramunga,

and to knives made by other tribes in the same region.

Western Australia

Non-conifer diterpenoid resins of the spinifex type possibly from *Triodia* sp. have also been identified in samples from two knives from the Kimberley region of Western Australia (Table 7.13).

TABLE 7.13: Knives and Sticks from Western Australia

Sample	Sample location	Artefact info.	Results
PBH027	Handle	Stone knife set in gum from the Kimberley	Spinifex-type non-conifer diterpenic resin
PBH026	Handle	Chipped stone knife from an unknown location in Australia	Spinifex-type non-conifer diterpenoid resin
PBH111	Blade mount	Ceremonial throwing stick with jasper carving knife or chisel from the Leopold Ranges, Kimberley	No resin, trace fatty acids
PBH056	Resin on stick tip	Stick from Karridale in southwest Western Australia	Phenolic resin from *Xanthorrhoea*
PBH057	Resin on stick base		Phenolic resin from *Xanthorrhoea*

The chipped stone knife is hypothesised to have originated in the Kimberley, based on the fact that all the other items with the same type of resin (group C) originate from the Kimberley. Also from the Kimberley, the ceremonial throwing stick with jasper blade is noted as having an ambiguous/unusual double use. However, no resin and only trace fatty acids were detected in the material that the jasper blade is mounted into.

The stick from southwest Western Australia has the same *Xanthorrhoea* resin covering both the tip and base ends, though the materials are visually different: reddish brown resinous material with some plant inclusions on the stick tip; and reddish brown, glassy, brittle resinous material on the stick base. The inclusions of plant fibres in the processing of the resin on the tip may have reduced the brittleness of the resin compared to that on the base.

The purpose of the resin on the ends of the stick or club is not clear and may not be for hafting.

Queensland

An example of a duelling knife with a blade of shark teeth from Far North Queensland is similar to the one described by Khan (2004) from the Australian Museum, which has a handle made of ironwood, though the source of the adhesive is not mentioned. There is no ironwood resin, or any resin at all, present in the sample of hafting material on the handle of the shark tooth knife, or in the adhesive for the tooth inserts of the blade (Table 7.14).

TABLE 7.14: Knife from Queensland

Sample	Sample location	Artefact info.	Results
PBH002	Haft on handle	Shark tooth duelling knife from the Yir Yorant people of Coleman River, Cape York Peninsula in Far North Qld	No resin present, fatty acid-based material
PBH003	Adhesive for the tooth inserts of the blade		No resin present, fatty acid-based material

A possible source of the material is *Grevillea striata* (beefwood) gum that is often used in the same regions as ironwood, though this cannot be characterised with the method used in this project as it is not a resin.

Unknown origin in Australia

Three items from Australia, with no known region of origin, represent the use of three different resins for knife hafts (Table 7.15).

Sample PBH028 was from flakey, blackish brown resinous material along the edge of a stone blade, which is likely to be residue from a resin handle of what appears to be a hand-held tool such as a scraper. There is no collection information with the item, however, sample PBH028 was identified as resin from a *Xanthorrhoea* sp., which is chemically more similar

TABLE 7.15: Knives from Unknown Origins in Australia

Sample	Sample location	Artefact info.	Results
PBH028	Resin residue along one edge	Small knife with a chipped stone blade from an unknown location in Australia	Phenolic resin from *Xanthorrhoea*
AM11	Haft	Quartz knife from Central Australia donated to the Australian Museum pre-1932 by Sir William Dixson	Non-conifer diterpenoid resin
PBH025	Haft	Handle fragments of unknown origin within Australia	Unknown conifer-type diterpenoid resin

to the *X. preissii* and *X. quadrangulata* type than the east-coast species, suggesting the knife is likely to originate from southwest WA or south SA.

Sample AM11 from the haft of a knife from central Australia is similar to the spinifex-type resins, but does not fit in any of the groups A-E (Chapter 4). Spinifex-type resins have been identified on items from both the Northern Territory and Western Australia.

Sample PBH025 contains an unknown diterpenoid resin with predominantly labdane-type compounds. More research is needed on this type of conifer resin in Australia. The more precise origin of this item remains unknown.

7.2.2 Hafting in other parts of Oceania

Examples of several different hafted artefacts from Oceania also show the use of a range of hafting materials, though with distinct differences to mainland Australia in the lack of spinifex and *Xanthorrhoea* resin and the addition of elemi-like triterpenoid resins (Table 7.16). These differences were to be expected from the natural distributions of the botanical sources of these resins, as well as previous ethnographic and archaeological findings.

Table 7.16: Hafting in Oceania

Sample	Sample location	Artefact info.	Results
PBH058	Haft	Stone headed club from Papua New Guinea	Conifer-type diterpenoid resin
AM01	Haft	Model shell hoe (ponigob) dance accessory from Mer (Murray) Island in the East Torres Strait. Collected in 1907 by C. Hedley and A.R. McCulloch	Vegetable oil with kaurane-type diterpenoid and triterpenoid resin hypothesised to be from *Canarium australasicum*
AM02	Haft		Unknown triterpenoid resin
PBH086	Haft	Hafted spear from Niue in Polynesia	Elemi-type triterpenoid resin from Burseraceae
PBH071	Haft	Shell adze with wooden handle from Liuangniua, Ontong Java, Solomon Islands	Unknown phenolic material
PBH072	Haft	War club ('subi'), in the shape of a clitoris, from Lafumaasi village, Lau Lagoon, North Malaita, Solomon Islands, carved by Bakalei Maesua of Lafumaasi, between 1886 and 1996 probably specifically as a tourist piece	No resin, only fatty acids present

There were indications of a conifer type resin in sample PBH058. This sample was taken from the haft of an artefact from Papua New Guinea and is therefore hypothesised to be the resin from New Guinea kauri (*Agathis spathulata*), which is a conifer native to the island. However, only trace amounts of the resin diterpenoids were detected, plus chemical comparison with an authenticated reference sample would be needed to test this hypothesis.

The hafting cement of two model versions of a shell hoe 'ponigob', of the type used for gardening and hollowing out canoes, were both found to contain a mix of a vegetable oil with unknown resins, but the resin content is slightly different. Sample AM01 displays a mix of two resins: a triterpenoid resin probably from the Burseraceae family (non-elemi type, see Chapter 5); and an unknown diterpenoid resin with kaurane acids. Whether the addition of a second resin was an intentional mix, a repair, or a contamination is unknown. Sample AM02 contains an unknown triterpenoid resin, probably from a different source to the Burseraceae family as α- and β-amyrin were not detected. Carved in the shape of a crocodile at one end, and decorated with red and black (possible paint and/or ochre), these items from Mer or Murray Island in the East Torres Strait may have been dance accessories, according to the museum notes.

A hafted spear from Niue in the Cook Islands is the only example from Polynesia, and the triterpenoid resin detected in sample PBH086 is very similar to the elemi-type resins from the Burseraceae family. This resin may represent an elemi-producing species of Burseraceae native to this part of Polynesia, or else trade from Melanesia or Australia.

The two hafting materials from the Solomon Islands were not identified. The haft of the shell adze appears to consist of an unknown phenolic material, dissimilar to *Xanthorrhoea* resin. The war club haft sample does not exhibit any resin, only methyl esters and dimethyl esters of fatty acids were detected. This item, however, may not be representative of Indigenous use if it was made especially to sell to tourists, as is noted in the museum records.

7.2.2.1 Fishhooks

According to Thomson (1936, p. 73) the resin of either *Canarium australasicum* or *Erythrophleum laboucheri* (syn. of *Erythrophleum chlorostachys*) is employed in the making of

fishhooks in Australia. Neither of these resins were present in any samples from fishhooks included in the project. These fishhooks from Papua New Guinea and New Zealand, in which no resin was detected at all, were evidently hafted with a different non-resin material (Table 7.17).

Table 7.17: Fishhooks in Oceania

Sample	Sample location	Artefact info.	Results
PBH008	Haft	Shark hook from Papua New Guinea	No resin
PBH009	Handle		No resin
PBH014	Haft	Fishhook from New Zealand	No resin

There was no indication of the presence of any resin in the haft or handle of these fishhooks. Only fatty acid esters were detected in samples PBH008 and PBH009, and unidentified non-terpenoid peaks in sample PBH014. The amorphous hafting and handle materials represented in these three samples therefore remain unknown. No reference to hafting material used for fishhooks in Papua New Guinea or New Zealand has been found by the author.

7.2.2.2 Bows and Arrows

Bows and arrows, though largely replaced by spears and spearthrowers in Australia, were still common in other parts of Oceania in the early 19th Century.

The museum collections include examples from New Guinea, the Solomon Islands and Vanuatu (Table 7.18). A wooden hunting bow is labelled as having been "Traded from N. Central to Southern Region" from the Rotoke speaking people from Bougainville Island, Papua New Guinea (North Solomon Islands). A sample was taken from the black, very hard resinous material at the end of the bow joining the string to the wood, but no resin was detected. This is a similar result to the corresponding arrow from the same location,

Table 7.18: Bows and Arrows in Oceania

Sample	Sample location	Artefact info.	Results
PBH087	Material at the end of the bow joining the string to the wood	Wooden hunting bow "Traded from N. Central to Southern Region" from the Rotoke speaking people from Bougainville Island, PNG (North Solomon Islands)	No resin, trace fatty acid esters
PBH083	Haft	Hunting arrow with bamboo shaft and barbed palm wood point	No resin, trace fatty acid esters
PBH084	Haft	Bamboo long arrow from Solomon Islands	No resin, trace fatty acid esters
PBH085	Residue on tip		No resin, trace fatty acid esters
PBH060	Adhesive material where the tip is inserted into the bamboo cane shaft	Single prong bamboo arrow with hard wood tip was collected from the Dani people in the Jaffi area of (Upper Sepik River) Indonesian New Guinea	Triterpenoid resin from *Canarium salomonense*
PBH061	Thin coating on shaft	Arrow from Wogumas of the Upper Sepik in Papua New Guinea	No resin, trace fatty acid esters
PBH063	Thin coating over haft binding	Bamboo arrow with blade point from Sainke Doek, West Papua	No resin, no significant peaks
PBH064	Material sealing prong insert	Two-pronged barbed arrow of bamboo from Sainke Doek, West Papua	No resin, no significant peaks
PBH065	Material sealing prong insert	Single barbed bamboo arrow from Sainke Doek, West Papua	No resin, no significant peaks
PBH059		Arrow with a bamboo point from the Chim and Wahgi Rivers in Kundiawa, Papua New Guinea	Fatty acids and alkanes, plus DDT insecticide
PBH080	Haft	A bamboo arrow from Nikaura, Epi island in Vanuatu	No resin, no significant peaks
PBH081	Residue on the tip of the arrow		Trace lupane-type triterpenoids

though the appearance of the material is quite different. However, a single prong bamboo arrow from the Dani people did contain a triterpenoid resin in the haft adhesive, which has been identified as *Canarium salomonense*. This makes geographical sense as the species is native to New Guinea.

Several other arrows from the Solomon Islands and New Guinea had amorphous residue either as a haft or seal at the join, or as a thin coating over the arrow. These residues did not contain any resin, although sample PBH059 did contain a synthetic DDT insecticide (as well as apossible vegetable oil), presumably applied to the item for museum storage.

A bamboo arrow from Nikaura, Epi island in Vanuatu, however, although no significant peaks were detected in the haft sample, traces of lupane-type triterpenoids were detected in the material on the tip. Though no information has been found directly referring to Vanuatu, the practice of dipping the tip of an arrow is not unheard of in Oceania. Heider (1970, p. 285) discuss the practices of Dugum Dani of Highland New Guinea:

> Fighting arrows are often daubed in grease or mud to irritate a wound. Narrow strips of orchid fibre are often wound around the tip near to the point; they often are left in the wound when the point is removed and cause irritation. Beyond these irritants, no specific poison is used on arrows.

Why a triterpenoid resin would be on the tip of a Vanuatu arrow is unclear, but is extremely interesting.

7.2.2.3 Hafted items from elsewhere

Not from Oceania but included for comparison, the resinous material on two knives from Borneo was analysed (Table 7.19).

Table 7.19: Hafting outside of Oceania

Sample	Sample location	Artefact info.	Results
PBH036	Haft	Small knife and "Parang ilang" collected by Smith in 1910 from the Kayan group in Malaysian Borneo	Dammarane-type triterpenoid resin
PBH067	Resin fragment	Sword "Parang" in scabbard and 2 fragments of crumbling resin collected by Smith in 1912 from Baram River in Sarawak, Malaysian Borneo	Dammarane-type triterpenoid resin

Both samples were found to contain dammarane-type triterpenoids indicative of dammar resins of the Dipterocarpaceae family as would be expected in such a location where dipterocarps are abundant and dammar resin is known to often be used.

The dammarane-type triterpenoid resins appear to be from two different sources. Further identification of these resins is outside the scope of this project.

7.3 Non-hafting uses in Australia and Oceania

Plant resins are used for a number of non-hafting purposes, providing functions that are not only practical, but medicinal, recreational, and spiritual. A total of 173 resin samples from the ethnographic museum items represent a number of these functions. Resins used as adhesives are discussed first, and have been found on a range of artefacts types.

7.3.1 Adhesives

7.3.1.1 Tools

Decoration on firestick sheaths

Three examples of sheaths for holding firesticks, decorated with Abrus seeds, all originate from Far North Queensland, and all contain triterpenoid resins in the adhesive material (Table 7.20). Intriguingly, they exhibit at least three different types of triterpenoid resin.

Table 7.20: Adhesive for decoration on firestick sheaths

Sample	Sample location	Artefact info.	Results
PBH037	Main part of the sheath	Collected from Konani:n tribe in Mitchell River, in Far North Qld by Tindale and Birdsell in 1951	Non-elemi type triterpenoid resin hypothesised to be from *Canarium australsicum* plus vegetable oil
PBH038	Ball of sheath covered in red abrus seeds		
AM09	Sheath handle	A cover for the tips of a pair of unused firesticks collected from the Weipa in Queensland, by Allport sometime before 1977	Non-Burseraceae triterpenoid resin with ursane- and lupane-type triterpenoids plus vegetable oil
AM10	Ball of sheath covered in red abrus seeds		
AM08	Plant fibre, resin and red seeds over whole sheath except for the middle	Collected by Dixson from Cape York Peninsula, Queensland, sometime before 1912	Triterpenoid resin with lupane-type triterpenoids plus vegetable oil

Both samples (PBH037 and PBH038) from the first example are consistent in composition and are identified as triterpenoid resins, probably from the Bursearaceae family and possibly

the *Canarium* genus. Based on their geographical origin and similarity with other items (Chapter 5), samples PBH037 and PBH038 are hypothesised to be *Canarium australasicum* resin, but comparison with a reference sample would be needed to test this hypothesis.

From the second sheath, both samples (AM09 and AM10) indicate a triterpenoid resin probably not from the Burseraceae family as they contain *alpha*- but not *beta*-amyrin (see Chapter 5). There are also traces of a possible lupane-type triterpenoid in both samples, which therefore represent the use of either a mixture of resins or an unknown triterpenoid resin (Table 7.20).

The sheath of the third example is atypical as it has no bulbous resin end, and sample AM08 exhibits a third triterpenoid resin, this time with predominantly lupane-type triterpenes (Table 7.20).

Potentially three slightly different types of resin have been used on this specific type of artefact as demonstrated here, but it is noteworthy that they are all triterpenic resins. Descriptions of some firesticks in sheaths from Far North Queensland by Roth as reported by Khan (2004, p. 32) include beeswax noted as being at the uncharred end of the sticks, and have the following description:

> The hollowed pipes were then bound together and closed at one end with beeswax. Occasionally, two pieces of bamboo could be used as a cap. The cap was decorated with poisonous red Jequirity seeds, *Abrus precatorius*, stuck into the beeswax at the end of the cap.

It is interesting that the ethnographic description mentions the use of beeswax to stick the Abrus seeds on, as these museum items clearly show the use of triterpenoid resins for the same purpose.

Decoration on clubs

There are four examples of resin adhesive used as decoration on clubs within the museum items included in this project (Table 7.21). The three items with shells attached to the clubs all have triterpenoid resin in the adhesives. One sample (PBH077), from the adhesive attaching eyes of shell to the head-shaped club from Vanuatu, is identified as breadfruit (*Artocarpus alitilis*) resin.

TABLE 7.21: Adhesive for decoration on clubs

Sample	Sample location	Artefact info.	Results
PBH077	Adhesive for eyes of shell	"Wooden club with carved Janus head, rare style, similar to one collected by captain Cook", collected in 1947 from southeastern Malakula (Ambrym) Island, Vanuatu	*Artocarpus altilis* (breadfruit) resin
PBH078	Cement for row of shells	Stone-headed club from Papua New Guinea	Trace triterpenoid resin with α-amyrin, and vegetable oil
PBH076	Cement for shell inlaid on one side of pointed end	War club "keatau" or "kwaetau" collected by Maranda from Lau Lagoon in North Malaita, Solomon Islands	Trace triterpenoid resin without α- or β-amyrins, but with ursane/oleanane-type compounds
PBH107	Band of resin	Throwing club from Queensland	Conifer-type diterpenoid resin with heating marker

Another sample (PBH078) from a stone-headed club from Papua New Guinea contains a vegetable oil and a triterpenoid resin with ursane and oleanane-related compounds, including α-amyrin, but is probably not from the Burseraceae family. A trace amount of a different unknown triterpenoid resin was detected in a sample (PBH076) of the shell adhesive on a war club from the Solomon Islands.

Two more examples of shells adhered to a club and a staff only produced fatty acid esters during analysis of the adhesive, PBH062 (war club from Fiji) and PBH075 (staff inlaid with shell from the Solomon Islands).

A throwing club from Queensland bears a conifer-type diterpenoid resin (Table 7.21). The resin is in a band around the club, which does not appear to be an adhesive for decorative shells, rather is likely itself the decoration. A chemical marker for high temperature heating was also detected, suggesting that the conifer-type resin was heated prior to application.

7.3.1.2 Ornaments

Resin on ornaments appears to usually either be used as an adhesive to joint two parts of other materials together, or to form a large part of the ornament itself. Most of the ornamental pieces represented in this collection are body accessories. Some of these accessories use resinous mounts to hold decorative shells.

Adhesive for body accessories with shells

Several different resins were found to have been used to fix shells on body accessories (Table 7.22).

These examples include another possible use of an Australian species of *Canarium*, this time on a body ornament from Northern Queensland, however, again a lack of β-amyrin may suggest a non-*Canarium* source of triterpenoid resin. Further examples of unknown triterpenoid resins are on shells embedded in resins thought to be from Java in Indonesia, and a star-like ornament from the Torres Strait (Table 7.22), reinforcing the need for further research into this type of resin in this region. A shell pendant from Papua New Guinea does not appear to contain resin, however, in a study by Baraldi et al. (2012) a terpene-base resin has been identified as a binder to fix shells to a mask from Papua New Guinea.

TABLE 7.22: Adhesive for body accessories with shells

Sample	Sample location	Artefact info.	Results
PBH096	Body ornament	Collected from Northern Queensland by Hallam and Movius in 1936	Non-elemi-type triterpenoid resin, hypothesised to be from *Canarium australasicum* plus vegetable oil
PBH029	Black cement holding the shells	Shells in resin. Possibly from Java in Indonesia, (found uncatalogued in a box in the museum with other objects from Java), not known when collected, but has been in the museum since before 2004	Mixture of triterpenoid resins from *Artocarpus altilis* and elemi-type resin from Burseraceae
PBH030	Yellow cement holding the shells		Unknown material with triterpenoid acetates
PBH031	Body of shell pendant	Collected from Papua New Guinea by Dr. W. V. Nance	No resin, fatty acid methyl esters
AM12	Cement with reeds joining two pieces of turtle shell together to make a star-like ornament	Worn as a body accessory, collected in 1907 by C. Hedley and A. R. McCulloch from the Torres Strait	Triterpenoid resin not from Burseraceae, plus a kaurane diterpenoid
PBH095	Resin mount for shell	Woman's pendant from Noil-Noil Tribe in the Kimberley, northwest Western Australia, collected by Emile Clement, in 1926	Spinifex type non-conifer diterpenoid resin from Group B

The use of mixtures of resin is again evident in sample AM12, through the presence of a kaurane-type diterpenoid as well as the unknown triterpenoid resin (without α- or β-amyrins, but with ursane/oleanane-type compounds) (Chapters 3 and 5). This resin mixture is very similar to that of AM01 also from the Torres Strait, and AM04 from Far North Queensland, on an item known to have been traded from the Torres Strait Islands.

The final example, a pendant from the Kimberley in Western Australia bears a diterpenoid resin of the non-conifer, possibly spinifex-type (Table 7.22). This is of particular interest as it shows that the use of this type of resin is not reserved for the hafting of tools and weapons but extends to ornamental uses as well.

Adhesive on other body accessories

Amorphous materials from some further accessories that are worn on different parts of the body have also been analysed. Several of these items use animal parts, often held together using the resinous adhesives.

Table 7.23: Adhesive on other body accessories

Sample	Sample location	Artefact info.	Results
PBH015	Cement holding teeth	Necklace of pig's teeth covered with basketry, collected by Jackson in 1880, from Vanuatu (New Hebrides)	Conifer-type diterpenoid resin mixed with lupane-type triterpenoid resin
AM07	Cement holding teeth	Forehead ornament of kangaroo teeth from central Australia, Northern Territory	Conifer-type diterpenoid resin with callitrisic acid methyl ester
PBH109	Adhesive at base	Murrindi, emu feather ornaments, worn behind on corrobberie, which is a ceremonial event with singing and dancing. Collected by Emile Clement in 1922 from the Kimberley, WA	Spinifex type non-conifer diterpenoid resin from group A, probably *Triodia* sp.
PBH110	Adhesive at base		Spinifex type non-conifer diterpenoid resin from Group C
PBH032	Material covering the back side	Ornament, tusk fragment from Papua New Guinea	Beeswax
PBH089	Black resin on end	Rare mourning nose stick, collected in 1910 from Mt. Keith in Western Australia	Unknown triterpenoid resin, contains lariciresinol

The pig-tooth necklace from Vanuatu is another example of an unknown resin lupane-type triterpenes from an unknown source. It is also a mixture of triterpenoid and diterpenoid resins as PBH015 also shows some oxidation markers for abietane type compounds and therefore probably contains some conifer resin as well as the unknown triterpenoid resin (Table 7.23).

A conifer-type resin is also present in the resinous body of a forehead ornament of kangaroo teeth from the Northern Territory (Table 7.23). This sample exhibits an unknown diterpenoid resin including a compound that is possibly the methyl ester of callitrisic acid. Callitrisic acid has previously been isolated from sandarac resins and is used as a biomarker for *Callitris* resin, but the overall profile does not match the samples of *Callitris* resins in the reference collection. This suggests the use of an unknown conifer-type resin, or a mixture of materials. This result is not consistent with a description of a forehead ornament by Pitman and Wallis (2012, p. 115) as "a small lump of spinifex resin in which kangaroo teeth or small bright seeds were fixed." Spinifex-type resin has, however, been identified on ornamental artefacts from the Kimberley.

The amorphous material at the base of some decorative emu feathers is identified as the same spinifex-type resin as the 'cuyallie' (PBH104) and 'burga' (PBH011) samples (Table 7.23). Strangely, another emu feather ornament specimen with the same description, has a resin that is very slightly different in composition, still probably spinifex but fitting better into the non-conifer diterpenoid group 'C' (see Chapter 4). It is hypothesised that the two resins are sourced from different species of *Triodia* sp.

Similar uses of resin are reported by Clarke (2012, p. 138) in Cooper Creek, in northeast South Australia, but using resin from *Xanthorrhoea* sp.: "grasstree resin was used to fix together bunches of emu feathers used in dances." Clarke (2012, p. 138) also mentions that yellow grasstree gum (presumably *Xanthorrhoea resinosa*) was used to fasten items including kangaroo teeth, hair and feathers of birds, among other things, in a similar way, in the Sydney area of New South Wales (Clarke; 2012, p. 139). The equivalent use of putative spinifex and *Xanthorrhoea* for the same non-hafting functions is intriguing, particularly when considering the different locations as they are generally consistent with the natural distributions of *Triodia* and *Xanthorrhoea* respectively.

In a variation to the themes of triterpenoid resins and spinifex, and despite the description of an ornament from Papua New Guinea as "...back side covered with resin", it is apparent from the chromatographic data that the material covering the back side is not resin, but is beeswax (Table 7.23).

The nosestick represents yet another unknown triterpenoid resin (Table 7.23). The black, shiny and brittle resin is found to have triterpenoids present, but is not the elemi-like triterpenoid resin of the Burseraceae. This is not consistent with the description by Pitman and Wallis (2012, p. 115) that mentions the use of spinifex resin on the versions of the nose bone or peg, worn through the pierced nasal septum to mark the end of childhood, that are more commonly found in museum collections. There may be significance to the type or resin used for a nose stick with special meaning, such as for use when in mourning. Notably, the sample (PBH089) contains lariciresinol, which is a naturally occuring phenolic compound, but also an antifungal agent.

Sample PBH074 was taken from the adhesive holding the eyes in place on a wooden ornament of a Hornbill bird from the Kantu Dyak in Malaysian Borneo, and although outside the region of focus, was analysed for comparison. The use of adhesive on the Hornbill ornament is more similar to the use of adhesives on the clubs, where the attachment of an 'eye' was also described (section 7.3.1.1). However, the adhesive used is not the same as on the clubs, neither is it the same as the hafting material used on other artefacts from Borneo. There is no evidence of resin in this sample of unknown material. However, again there is evidence of an antibacterial or fungistatic. These types of compounds were presumably added during museum curation to protect the artefacts.

7.3.2 Pigment

Twenty-two similar 'amber-coloured' resin specimens have been gathered by six different collectors. These are all pieces of plant resin from New Zealand, labelled as 'resin' or 'Kauri gum' used for making tattooing pigment, and all but PRM2-5 and PRM22 recorded as belonging to the cultural group 'Māori', although the rest presumably are as well. All 22 samples produced similar chromatograms to each other, and resembled those of the reference samples of *Agathis australis* resins, as would be expected from the description of 'Kauri gum' or resin from New Zealand (Table 7.24).

More detail on the use is provided for one of these samples. The handwritten label for PRM19 reads "Kauri - pine resin, the soot from burning which was used by Maoris as tatuing pigment". This suggests that these resins were used for producing 'lamp black' for Māori tattooing, which is obtained by the imperfect combustion of carbon rich materials such as resins, by burning them with an insufficient supply of air so carbon is deposited as soot (Natural Pigments; 2018). This soot is collected and mixed with oil or liquid from hīnau, māhoe, tī (cabbage tree), kāretu or poroporo plants, to form a solid mass, in a process called whakataerangi (Higgins; 2013). The pigment, made from the charcoal of resinous trees, is known as wai ngārahu, also māpara, kāpara or awe kāpara, kauri kāpia and ahi tā moko or ruangārehu (Higgins; 2013).

The other examples of pigments in this collection include a lump of what is described as a vegetable gum or resin from Papua New Guinea used for figure decoration (Table 7.24). This sample has been identified as an elemi-like triterpenic resin and is probably from *Canarium* sp. *Canarium indicum* is used in Papua New Guinea as a red paint when mixed with an alkali such as lime (Hill; 2001), and is likely to be the source of this resin sample as

TABLE 7.24: Pigment

Sample	Sample location	Artefact info.	Results
PRM01 PRM06-18 PRM20-21		Maori tattooing pigment	
PRM02-05		Pieces of plant resin from New Zealand, labelled as 'resin' or 'Kauri gum'	
PRM22	Sample of 'amber-coloured' resin specimens	used for making tattooing pigment	Conifer diterpenoid resin, from *Agathis australis*
PRM19		"Kauri - pine resin, the soot from burning which was used by MAORIS as tatuing pigment. N. ISLAND, NEW ZEALAND. C. Smith coll. Purch. 1923."	
AM18	Sample of the 'vegetable or gum resin' specimen	Collected from British New Guinea by Rev. Dr. G. Brown in 1895. "USE: — Ornamentation of faces in figure decoration".	Elemi-like triterpenic resin probably from *Canarium* sp.
PBH048	White pigment	A white pigment, over brownish white material on the sheath for stone knife from Tennant Creek, NT	No resin, only fatty acid methyl esters

the chromatogram for AM18 is consistent with the *C. indicum* reference samples, although this is not conclusive (see Chapter 5).

A white pigment, over brownish white material on the sheath for a stone knife from Tennant Creek, NT (see section 7.2.1.3 for the corresponding knife sample) was found not to contain any resin, bearing only fatty acid methyl esters (Table 7.24).

7.3.3 Glazing and waterproofing

Glazing

A sample of 'Bani gum' from the Ifugao people of Luzon, Philippines is similar in composition to *Agathis alba* and *A. dammara*, which are both native to the Philippines (Table 7.25). Lampert (2003) references accounts of *Pinus* being used by Ifuago potters, and also use of *Agathis philippinensis* in Luzon. *A. philippinensis* is therefore also a potential source of this resin but analysis of a reference sample would be needed for comparison.

Table 7.25: Glazing

Sample	Sample location	Artefact info.	Results
PBH051	Sample of floral specimen	'Bani gum', described as used for glazing pottery, collected from the Ifugao people of Luzon Island in the Philippines by Tuganai Pait and H. Otley Beyer in 1906-7.	Conifer diterpenoid resin, possibly from *Agathis alba*
AM16	Glazing at base	Glazed clay pottery container, of three spherical units joined together with handles at the top, collected by Miss E. A. Farran from Fiji in the South Pacific sometime before 1920	Conifer diterpenoid resin from *Agathis macrophylla*
AM17	Glazing at base	Glazed clay pottery container, 'Saqa drua,' of two elliptical units joined together with a handle, collected by Mr Henry Morton sometime before 1984	Conifer diterpenoid resin from *Agathis macrophylla*
PBH016 PBH017	Outer glaze Inner glaze	Wooden bowl from Borneo	No resin, only fatty acid methyl esters

There are two examples of glazing on pottery vessels from Fiji (Table 7.25). The item collected by Miss E. A. Farran was sold to the Australian Museum as part of a collection of 27 Fijian artefacts. This collection is referred to on the RDA (2017) website, stating that a:

> [...]significant piece is a clay water container (saqa moli). Due to the limited access to good clay, only a small number of villages produced pots such as this one, which is comprised of a cluster of connected spheres, joined by the stems.

It seems to reasonable to assume that this description refers to the same item as the description and collection details correspond. The name 'saqa moli' is notable, as it is similar to that given for the other piece of Fijian pottery sampled, recorded as having the local name 'Saqa drua'.

Samples from the glaze of both Fiji pots produced chromatograms that are consistent with that of *Agathis macrophylla* (syn. *Agathis vitiensis*). *A. macrophylla* is a conifer (pine-related) resin that is native to Fiji, and known as Fiji kauri. This identification is as would be expected from the ethnographic descriptions of a 'kauri resin' or 'species of pine' used for glazing pottery, in the location of Fiji. MacLachlan's (1940, p. 244-248) collation of ethnographic accounts on pot-making in Fiji contains some references to the glazing of the pottery by Gordon-Cumming, C.F. (1881, p. 125); Wilkes (1845, p. 148); Smythe (1864, p. 38-9); Williams (1858, p. 70-1); 1888, p. 99; and Roth (1935, p. 232). They invariably note that the glazing of pots is done whilst still hot from baking, and that the pots are made exclusively by women.

There are, however, variations in the accounts of the glaze. Descriptions by the ethnographers include references to kauri gum, to resin from a species of pine resembling the kauri pine of New Zealand, or just a species of pine. Two accounts mention the use of Mangrove bark, for the dark red dye or 'tire' rubbed on the pot to give it colour, only for cooking pots in one account, and water-pots are glazed with 'nadukua' resin. The local name for the glazing or varnish in another location was noted as 'makandi' described as a mixture of the mangrove bark 'decoction' with the pine resin (MacLachlan; 1940).

Potmaking in Fiji is described as a 'tribal speciality' with certain districts noted for particular kinds of pottery, and the societal rank of a woman expected to be reflected in the quality of her pot-making (MacLachlan; 1940, p. 254). Comparisons of the Fijian pottery are made to Tongan pottery, and ancient examples from the New Hebrides (Vanuatu), suggesting the level of similarity indicates a common source, later acquiring individual characteristics in the different locations (MacLachlan; 1940, p. 266). All pottery in the north of Vanua Levu (Fiji smaller island) was found to be unglazed (MacLachlan; 1940, p. 246). Analysis of the glaze of these pots, in addition to typology, could provide more of an insight to the history of Melanesian pottery.

Not from Oceania, but included for comparison, are two samples from the inner and outer glaze of a wooden bowl from Borneo (Table 7.25). These samples were also analysed and found not to be resin. The use of conifer resin for pottery glazing may be unique to the Philippines. There is definitely scope for much more research in this area.

Waterproofing

Four examples of buckets or baskets with waterproofing material on have been sampled. Two of these have multiple sample sites, which show that different resins have been used on the same items, either for different purposes or have been added at different times.

Samples from the seam (AM13), a repair patch (AM14), and the inner coating (AM15), of a water carrier from Atherton, Qld show the latter two materials to be very similar to each other, probably an unknown conifer resin (Table 7.26). Interestingly, the sample from the seal on the seam of the same bucket appears to be a triterpenoid resin with some dammarane-type compounds, as well as ursane/oleanane-type compounds, suggesting a dammar-type resin similar to that of the Dipterocarpaceae in Southeast Asia. There are some trace triterpenoids in the inner coating sample, which could be contamination from

Table 7.26: Waterproofing

Sample	Sample location	Artefact info.	Results
AM13	Seam	Water carrier collected by Roth in 1905 from Atherton in Queensland	Triterpenoid resin probably dammar, plus fatty acid methyl esters
AM14	Repair patch		Conifer-type diterpenoid resin, plus fatty acid methyl esters
AM15	Inner coating		Conifer-type diterpenoid resin, trace triterpenoids and vegetable oil
PBH033	Seam	Paperbark bucket collected in 1907 from Port George IV, Kimberley, WA	Unknown phenolic resin containing sakurantetin
PBH034	Rim		Unknown phenolic resin containing sakurantetin
PBH035	Inner coating		Unknown triterpenoid resin and fatty acid esters
PBH066	Rim	Painted bark basket collected by Supreme Court Justice William O. Douglas in 1954 from the Tiwi people in Snake Bay (the present Milikapit) on Melville Island off the coast, NT	Vegetable oil and sesquiterpenes indicating essential oils from an Angiosperm
PBH073	Inner coating	Basket from an unknown location in Oceania	No resin, trace fatty acid esters

the resin on the seam. Or, this pattern may represent an original application of triterpenoid resin to the seam and inner, with a later application of a diterpenoid resin on the repair and inner.

Samples from a paper bark bucket from Kimberley, WA, taken from the seam (PBH033) and from the rim (PBH034), are consistent with each other, but not similar to the reference phenolic resins as they contain sakuranetin, proposed by the author as a partial marker for *Xanthorrhoea* resin (Chapter 6), but give a very different type of chromatographic response to the *Xanthorrhoea* spp. A sample from the inner lining of the same bucket (PBH035) does

not match the others and appears to contain triterpenoids (Table 7.26). This suggests that different resins may have been deliberately chosen for their uses, perhaps for example, a strong but more flexible adhesive for the bucket construction and a more fluid resin suitable for waterproofing for the lining.

A painted bark basket collected from the Tiwi people in Snake Bay (the present Milikapit) on Melville Island off the coast, in the Northern Territory, has a resinous material sealing the stitching around the rim. The sample from this material (PBH066) contains a vegetable oil and sesquiterpenes, but no di- or triterpenoids (Table 7.26). This indicates the material is relatively fresh, and is probably an unknown material mixed with essential oils from the leaves of an Angiosperm.

The last example of waterproofing is from a basket from an unknown location in Oceania. Sample PBH073 showed no resin and only trace levels of fatty acid esters in the waterproofing material (Table 7.26). Pitman and Wallis (2012, p. 113) discuss an example of a bark water carrying vessel made by the Worora in the Kimberley (northwest Australia) caulked with 'spinifex wax' (Oc1953,03.6), and note that the material of the waterproof lining of most other museum examples of vessels is rarely defined. There are evidently many suitable waterproofing materials, other than *Triodia* spp.

7.3.4 Medicine and sorcery

Medicinal use of plants has a long tradition in Oceania, certainly in Australia, Papua New Guinea, and the Solomon Islands. Resin has a number of effective medicinal uses, owing to the anti-bacterial, anti-fungal, and anti-microbial properties of terpenoids, and both resin and leaves of spinifex are known to have been used in the treatment of a range of medical conditions and ailments by Indigenous Australians (Pitman and Wallis; 2012,

p. 126). Knowledge of the positive effects of resin, amongst other plant-based materials, would have been developed over generations within a community, often with one person or family as the dedicated healer(s) (Holdsworth; 1980). According to Holdsworth (1980, p. 33-34), in the Northern Solomon province of PNG specifically, but probably true for other regions in Oceania:

> Often the medicine man would be a sorcerer and the use of magical phrases, psychology, impressive ritual and fear would go hand in hand with the use of medicinal plants and poisons.

This section includes all items within the museum collection that relate to medicine, narcotics and sorcery (Table 7.27).

Table 7.27: Narcotic

Sample	Sample location	Artefact info.	Results
PBH001	Sample of specimen	Amber-coloured resin from within "Small basketry 'medicine' box with folding lid, used also to hold lime" collected by Charis Denison Crockett from the Bearese people of Kamwa, West Papua (Dutch New Guinea at the time) in 1938	Hypothesised to be a latex from the Umbelliferae family
PRM29	Resin inside palm packet	"Gum from the canarium almond tree" in a native packet of palm leaf, with the note "Mixed with tobacco to make a cool smoke" and thought to be used as a narcotic. Collected by Blackwood in 1930 from Kurtachi in Bougainville Island	Elemi-like triterpenoid resin from *C. salomonense*

The function of the piece of 'resin' from Kamwa, West Papua, kept in a medicine box is unknown (Table 7.27). This sample (PBH001) was found to contain 7-hydroxycoumarin, also known as umbelliferone, which occurs in many plants of the Umbelliferae or Apiaceae

family. No reference samples of Umbelliferae exudates, mainly latex, have yet been analysed for comparison.

An interesting sample from the Northern Solomons province of PNG is the canarium almond tree gum in a palm packet thought to be used as a narcotic (Table 7.27). A sample of the canarium almond resin from inside the palm packet was previously identified as *Canarium salomonense* (Bradshaw; 2013). This identification makes sense geographically as *C. salomonense* is native to the Solomon islands and PNG, and is one of three species known as canarium almond. This identification has been confirmed on re-analysis.

One of the samples in the reference collection from the Kew Economic Botany Collection (EBC), K083 labelled as *Canarium commune*, is also wrapped in a leaf. *Canarium commune* is a synonym of *C. indicum*, however, analysis of this sample showed it to contain diterpenoids rather than the triterpenoids expected for a *Canarium* resin. Whether the practise of wrapping resin in leaf is related to the intended use of the resin, or if it is merely a convenient way to carry it, these resins are clearly valuable enough to wrap up for storage.

Medicine shells, headbands and bone

Medical items in the form of filled shells, headbands and a gummed bone are represented in this collection and all have associated resinous amorphous materials.

Two 'medicine shells' labelled as 'spinifex in cowrie shells' were collected from the Ngarluma (Gnalluma) people at Sherlock River, WA (Table 7.28). This label identifying the resin inside the shells as spinifex was originally assumed to be correct based on the ethnographic information (Clement and Schmeltz; 1903), and hypothesised to be the resin of *Triodia pungens* (Bradshaw; 2013). If correct, this would suggest that all the group B spinifex resins were sourced from *T. pungens*, however, an authenticated sample is needed to test this hypothesis.

Table 7.28: Medicinal

Sample	Sample location	Artefact info.	Results
PRM25	Resin inside shell	"Cowrie filled with spinifex gum, used by the TAKETA (doctor) for rubbing over the affected part", these 'medicine shells' were collected by Emile Clement sometime before 1924, from Ngarluma (Gnalluma) people at Sherlock River, WA.	Non-conifer diterpenoid resin, spinifex group B possibly *Triodia* sp.
PRM26	Resin inside shell		Non-conifer diterpenoid resin, spinifex group B possibly *Triodia* sp.
PBH090	Resin inside shell	Medicine shells. "Prepared cowrie shell, aperture filled with gum; Used by doctor to rub sore spot," collected by Emile Clement in 1922 from the Kimberley, WA.	Non-conifer diterpenoid resin, spinifex group C possibly *Triodia* sp.
PBH091	Resin inside shell		Non-conifer diterpenoid resin, spinifex group C possibly *Triodia* sp..
PBH092	Resin inside shell		Non-conifer diterpenoid resin, spinifex group C possibly *Triodia* sp.
PBH093	Red coating	Women's medicinal headbands collected from the Wardaman people of the Northern Territory, collected sometime between 1896 and 1931	No resin, fatty acid methyl esters and probably ochre
PBH094	Red coating		No resin, fatty acid methyl esters and probably ochre
PBH088	Gummed end of medical bone	Medical bone "mehredi corrada", collected by Emile Clement in 1922 from the Kimberley in Western Australia, with the note "The gummed end is rubbed on sore spot for hours."	Non-conifer diterpenoid resin, spinifex-type but not group A-E

A very similar set of items, filled cowrie shells from the Peabody collection, labelled as 'medicine shells' also contain non-conifer diterpenoid resin (Table 7.28), hypothesised to be spinifex resin from *Triodia* sp. (Chapter 4). The resin from the 'aperture' was sampled from each shell and produced chromatograms consistent with each other. This spinifex-type resin is slightly different to both group B, with the other medicine shells, and group A, with items from the same area. They do however, match with the data from the second emu feather ornament (PBH110), also from the Kimberley, and have been placed in the spinifex-type resin group 'C' (Chapter 4).

Two women's medicinal headbands collected from the Wardaman people of the Northern Territory were coated in a red amorphous material (Table 7.28). Headbands are mentioned by Spencer and Gillen (1912) as being commonly worn, made of opossum-fur string, moistened with pipe-clay and decorated with red and yellow ochre. The brick red soft, friable material from the headbands was found not to be resin, and probably is clay and ochre as described by Spencer and Gillen (1912). Fatty acids were detected, which may have come from the string.

Another medical item, a 'medical bone' or 'mehredi corrada' from the Kimberley in Western Australia has a lump of 'gum' on the end (Table 7.28). This 'gum' was found to contain diterpenoids of the spinifex type, but does not fit into the spinifex groups A-E, thought to probably be from *Triodia* sp. (Chapter 4). According to Pitman and Wallis (2012, p. 122), another medicine stick collected by Clement 'mahredie corrada' (REM 1207-23) is in the Royal Ethnological Museum (Leiden), and is described as a "lump of spini- fex-gum fixed to the end of an ornamented, pointed stick from 9 inches to 18 inches long or to some bone of kan- garoo or bustard." The specific reference to spinifex in this case is different, but corroborates the findings of the PBH sample. The item in the Royal Ethnological Museum

(Leiden) also comes with the additional information, as cited in Pitman and Wallis (2012, p. 122):

> On returning to his patient, he blows hard upon the sore part, in order to insert a good spirit, and rubs his mahredie corrada over the spot. ... Frequently the mahredie corrada is carried by him with the gum- end for an hour or more under his arm-pit and then suddenly placed under the arm-pit of the patient, or between his legs.

This description of use is slightly different, but complemetary to the description of the PBH sample being rubbed on the sore spot for hours. Pitman and Wallis (2012, p. 122) note some similar medicine sticks collected by Clement, which can be found in the British Museum (BM Oc1896,1046, Oc1896,1044, Oc1896,1045) and the Pitt Rivers Museum (PRM 1898.75.102, 1898.75.105, 1924.63.10).

Pointing stick

Another gummed bone, but with a very different purpose as a pointing stick, rather than a 'medical bone', is also represented. Pitman and Wallis (2012, p. 122) draw a comparison between a medicine stick and a pointing stick used for sorcery, in that the value of a medicine stick is a physical use of the resin for healing, whereas the pointing stick is used to invoke a non-physical power intended to cause harm.

Table 7.29: Sorcery

Sample	Sample location	Artefact info.	Results
PBH099	Gummed end	Bone pointer "Used in magical rites" collected from an unknown location in Australia by Russell H. Harris in or before 1967	Phenolic resin from *Xanthorrhoea* sp.

The bone pointer[2] from an unknown location in Australia has lump of 'gum' on the end, similar to the 'medical bone' but the 'gum' on this pointing stick is not spinifex (Table 7.29). The resin has been identified as *Xanthorrhoea* sp. As per the other artefact types in this chapter, spinifex and *Xanthorrhoea* appear to be used for many of the same purposes in different parts of Australia with the corresponding local plant distributions, the presence of *Xanthorrhoea* on this bone pointer may indicate its origin as within the natural distibution of *Xanthorrhoea*, in a more temperate, coastal region.

[2]An ethnographic excerpt from Spencer and Gillen (1912) describing pointing sticks and bones: "These, in some form or another, are used by all Australian tribes. Amongst the Arunta any one may make and use them, though it is rather a risky game, and is carried on more or less in secrecy. There are various forms of them, the two commonest being called by the Arunta Irna, or pointing stick, and Injilla, or pointing bone... The former is nothing more than a small piece of wood, varying in length from three inches up to eighteen, and resembling a skewer in general shape. At one end it tapers to a point, and at the other it is tipped with a little knob of resin to which a strand of human hair string is attached. Usually it is ornamented with knotches, or circles, or a spiral groove made with a fire stick, and in addition it is often decorated with white or red bird's-down arranged in various ways. To endow it with evil magic it must be "sung." When this is done the man who intends to use it, goes, sometimes alone, sometimes accompanied by a friend, into the bush, to some spot far away from the camp where he will be free from observation, and placing the stick in the ground, crouches over it muttering some such curse as the following:

Ita pukalana purtulinja apinia-a — "May your heart be rent asunder."
Purtulinja apinia-a intapa inkirilia quin appani inta-pakala-a —"May your backbone be split open and your ribs torn asunder."
Okinchincha quin appani ilchi ilcha-a — "May your head and throat be split open."

"In this way the stick, and the same is true of the pointing bone, is charged with evil magic and is then left in the ground for a few days. The actual pointing may take place out in the bush... the man who does this thrusting his beard into his mouth, as the native often does when he is performing any special ceremony in connection with which he feels fierce and savage. All the while he jerks the pointing stick in the direction of his enemy, muttering incantations to the evil magic to go forth, straight, and kill him. Sometimes the pointing is done close to the camp, in which case, after it is dark and while the men are sitting round the camp fires, the man carrying the Irna creeps up stealthily, taking care that no one sees him, until, by aid of the firelight, he can see his enemy's face. Then he stoops down and jerks the stick either over his shoulder or between his legs. The evil magic goes from the point, of the Irna straight to the man, who very soon afterwards sickens and dies, unless his life be saved, as fortunately it often is, by the aid of a medicine man who can discover and remove the stick. In some cases, when the man is ill, the string attached to the resin is slowly burnt in the fire, an act which is supposed to render the death of the man just as certain as the destruction of the string. There is really very little difference between the greater number of the magic implements [...] used by all the tribes of the Central area, but every now and again we met with a form which was peculiar to some special locality. Possibly the head man of the group of natives inhabiting that part, being of an ingenious turn of mind, set himself to work to invent some specially effective piece of apparatus wherewith to injure his enemies; for it must be confessed that, though he has many good points, the Australian savage is particularly fond of injuring an enemy when the latter is unable to help himself. A man who can invent any implement which is, rightly or wrongly, supposed to be especially effective and deadly, is regarded as a really great man and a benefactor to his people, in much the same way in which, among civilised nations, a Krupp or an Armstrong, a Maxim, a Brennan or a Whitehead, is regarded as one who has aided the particular nation with which he may be associated" (Spencer and Gillen; 1912, p. 346-348).

7.3.5 Miscellaneous items

Table 7.30: Miscellaneous Items

Sample	Sample location	Artefact info.	Results
AM19	Sample of specimen	Raw resin sample from Kiribati, Gilbert Islands, donated by Mrs. C. F. Eliot in or before 1982	Conifer diterpenoid resin from *Agathis labillardierei*
PBH024	Sample of specimen	"Amber-like stone" from the Kutelu Area, Grand Valley of the Baliem River, in Indonesian New Guinea (West Papua) collected from the Dani people by Karl G. Heider in 1961-1964	Conifer diterpenoid resin from *Agathis labillardierei*
PBH068	Lump of resin used as a weight on top of a wooden boomerang	Boomerangs collected in 1951 by Norman B. Tindale and Dr. Joseph B. Birdsell during the Peabody/South Australian Museums joint expedition, from central Australia in Barrows Creek, NT., and Daly Waters, NT, respectively	No resin, probably polysaccharide gum
PBH069	Lump of resin used as a weight on top of a wooden boomerang		No resin, probably polysaccharide gum
PBH114	Brown amorphous material on the end		No resin, type of wax or oil
PBH115	Brown amorphous material around the hole	Totemic pipes from Northeast Arnhem Land, NT, collected in 1929 by Lloyd Warnern	No resin, type of wax or oil
PBH116	Inner coating		No resin

Raw resin

A raw resin sample (AM19) from Kiribati, Gilbert Islands in Micronesia has been identified as resin from *Agathis labillardierei* (Table 7.30). The use of this resin, however, is unknown. Another resin specimen (PBH024) also identified as *Agathis labillardierei* resin is again of unknown use, labelled only as "Amber-like stone", this time from West Papua (Table 7.30). *Agathis labillardierei* is also known as New Guinea Kauri as it is endemic to New Guinea. Kiribati is a small pacific island northeast of New Guinea. If this species is not naturally

occuring on the island, the sample from Kiribati may indicate contact and even trade of the resin between the two locations.

Boomerangs

There are two examples of lumps of resin used as a weight on top of a wooden boomerang (Table 7.30). The boomerangs were collected from central Australia, in Barrows Creek, NT, and Daly Waters, NT, respectively. No significant peaks were detected in either sample, indicating the lumps are not resin, but probably a polysaccharide gum.

Clay pipes

Three samples from a totemic pipe from Arnhem Land in the Northern Territory show that a wax or oil based material was used around the hole and on the end of the pipe, but not on the inside. No resin was detected in the samples.

Combs

Four examples of wooden combs, three from Santa Cruz Islands in the Solomon Islands (PBH020, PBH021, PBH022) noted as being worn by both sexes, and one from San Cristobal Islands, Solomon Islands (PBH023) bear a blackish brown, friable material around the handle holding the prongs in place. The samples of this material were found not to contain any resin, only fatty acid esters. This result is reflected in the report of an assemblage of similar wooden combs excavated from a swamp site at Kauri Point, in the western part of the Bay of Plenty area of the North Island, New Zealand (Shawcross; 1964, p. 382). A different, non-resinous material is evidently used for this purpose.

Illumination

Four of the samples in the reference collection from the Kew Economic Botany Collection

(EBC) are torches, or fuel for torches. Sample K080, labelled as *Aucoumea klaineana*, sample K101, labelled as *Canarium schweinfurthii* and sample K102, labelled as *Canarium* sp. are all resin wrapped in plant material to form torches, as can be seen in the photos in Appendix A. Sample K065 is also noted as being resin from Papua New Guinea that is used as a fuel. Both K102 and K065 have been identified as *Canarium salomonense* based on their molecular composition. These are all similar types of resin that may be specifically chosen for their suitability as illuminants.

7.4 Conclusion

The results of this project show there is a much wider range of different types of plant exudate material having been used than is indicated by the written accounts. It is apparent that ethnographic accounts are not a true representation of resin use in Australia and wider Oceania. However, some of the accounts have been corroborated, for example, the use of spinifex, particularly in the Northern Territory and Western Australia, and *Xanthorrhoea* resin in Australia, as well as *Canarium* resin in Papua New Guinea. However, the assumption of the use of these materials in these locations cannot be relied upon, as demonstrated in this thesis, and chemical analysis is recommended wherever possible.

There is a notable lack of spinifex resin on Australian axes and adzes compared to the impression given by written ethnographic accounts. More examples of these tools need to be sampled, but it appears that a wider variety of resins are being used for the hafting of them. Axes are the oldest known hafted tools in Australia (Hiscock et al.; 2016), for which spinifex is often the presumed to be the hafting material (Haslam et al.; 2009). It would be interesting to find if resins other than spinifex were used to haft these tools throughout the past, or if the range of hafting materials is a recent development.

There appear to be many different materials being used for all different uses. The most notable pattern of use is based on geography. It appears as if spinifex and *Xanthorrhoea* are used for essentially the same purposes in different areas, depending on the local plant distributions for the region. However, conifer resins are used in Australia more often than was expected from the literature review, as well a range of non-resins, including wax, and possible 'mindrie' pitch as was suggested in the literature. There is also evidence of a wide range of unknown resins such as phenolic resins, and triterpenoid resins for which much more research is needed, particularly in wider Oceania.

It appears as though resin is often mixed with materials high in fatty acid content, presumably to make them softer and more malleable. This appears to be specific to hafting uses, as resinous materials on many of the same artefacts but with different functions are not mixed in the same way.

There is evidence of trade from Far North Queensland to the Torres Strait Islands, and probably via the Torres Strait into Papua New Guinea. *Xanthorrhoea* resin may also have been traded into the Kimberley region in Western Australia where it does not grow naturally.

There is some indication of conservation practices where DDT insecticide and antifungals have been detected on the organic artefacts, demonstrating that there are several levels of information provided by chemical analysis. The application of resin analysis to materials on museum artefacts allows the study of all stages of life of an artefact, as well as benefiting a much wider field of research.

Chapter 8

Resin use in Oceania: discussion of patterns of use and the implications for future archaeological research

8.1 Patterns in resin function

8.1.1 Museum specimens of resin with known intended function

8.1.1.1 Spinifex and ironwood resin

In the Peabody Museum at Harvard collection, two specimens from the Kimberley, WA were labelled as spinifex gum: one unrefined "cuyallie", the other purified "burga", which were both chemically characterised and found to be consistent with other indicating they

are most likely to be from the same source (Chapter 4) (Table 8.1). These specimens are ready-to-use processed spinifex resin.

Spinifex resin was often kept as cakes or on sticks for storage and trading purposes, for example, the Warlpiri people in Central Australia rubbed red ochre into the flattened cakes to signify they were gifts and probably make them better suited for travel (Clarke; 2012, p. 146). According to Pitman (2010) it was common for a surplus of spinifex resin to be produced specifically for these purposes and there are many examples of spinifex resin cakes within museum collections. Analysis of more of these examples would contribute significantly to understanding the chemical composition of spinifex resin, allowing it to be properly identified on artefacts and shed light on the chemical relationship of the resin from different species.

Table 8.1: Resin specimens with recorded uses: Spinifex and Ironwood

Sample	Sample location	Artefact info.	Results
PBH104	Resin specimen	"Spinifex gum, unrefined, cuyallie" obtained by burning green spinifex plant collected by Emile Clement in 1922 from the Kimberley, Western Australia	Non-conifer diterpenoid resin, hypothesised to be from *Triodia* spp.
PBH011	Resin specimen	"Spinifex gum, purified by continued re-melting and squeezing, burga" used for attaching implements to haft and for many other uses. Collected by Emile Clement in 1922, from the Kimberley,Western Australia	Non-conifer diterpenoid resin, hypothesised to be from *Triodia* spp.
PRM24	Resin specimen	"Round lump of gum" used as an adhesive, collected by Emile Clement in 1898, from Touranna Plains, Western Australia	Non-conifer diterpenoid resin, hypothesised to be from *Triodia* spp.
PBH103	Resin specimen	"Lump of gum 'cagera'" collected by Mrs. Walter Badenach in 1924 from Drysdale River in the Kimberley, Western Australia	Non-conifer diterpenoid resin
PBH100	Resin specimen	"Lump of iron wood rosin on end of stick" collected by W. Lloyd Warner in 1929 from the Murngin people of Arnhem Land, northeast Northern Territory	Non-conifer diterpenoid resin, hypothesised to be from *Erythrophleum chlorostachys*

The 'burga' specimen is described as intended for "many other uses" as well as hafting, and there is a written reference to the similar sounding 'bulga' as resin used for decorative beads as well as fastening spear-heads to shafts for fighting purposes, i.e. hafting (Clement and Schmeltz; 1903). The 'cuyallie' and 'burga' spinifex gum specimens are very likely to be the corresponding exhibits to the description by Clement and Schmeltz (1903), and the results of analysis agree with the accounts in that they appear to be from the same source. These spinifex resins are further, but possibly contradictorily, defined by the collector, Clement and Schmeltz (1903):

- Cuyallie gum, described as, "gum; obtained from burned grass (Spinifex = *Triodia irritans*)"
- Burga, the same as Cuyallie but cleaned
- Bulga, described as "gum obtained by burning green Spinifex"

The description of the sources of these resins does not quite correlate with the museum notes with the'cuyallie' and 'burga' specimens, as the 'cuyallie' was described as being obtained by burning green spinifex. *Triodia pungens*, which is commonly known as 'green spinifex' grows in Western Australia, locally to the Kimberley, where the specimen was collected. *T. irritans* however, occurs in central and southern Australia. With mention of both *Triodia irritans*, and 'green spinifex' which usually refers to *T. pungens*, it is unclear which species the two specimens are likely to be from. As the specimens are from the Kimberley, WA, the species used is more likely to be *T. pungens*, however if identified as *T. irritans*, this may indicate that this material was traded.

Additionally, the reference sample, K070, as described in Chapter 4, labelled as *T. irritans* is definitely not chemically the same as the cuyallie and burga samples. This specimen is

thought to have been collected by J. H. Maiden and to correspond with an ethnographic description of being collected near Derby in Western Australia (Chapter 4). It is possible that the plant in this case was mis-identified, as for example, the description states the resin came from the roots of the plant. The roots of the ironwood tree (*Erythrophleum chlorostachys* (F. Muell.) Baill.) were a common source of hafting adhesive, particularly across the north of Australia, and according to Roth its use extended throughout Cape York Peninsula and the Gulf regions (Powell et al.; 2013, p. 216). However, it is seemingly unlikely that "Mr. Froggatt" would mistake an ironwood tree for a tussock grass, and taking the resin from the roots may not be unusual: "At Daly Waters in the Top End, 'wax' was gathered from ant nests at the bases of soft spinifex tussocks, as well as from the stems of the plant itself" (Clarke; 2012, p. 146), and resin "collected from the termite nests established at the base of spinifex tufts" (Powell et al.; 2013, p. 216). However, the natural distribution of *T. irritans* does not cover the area around Derby in North-west Australia where Mr. Froggatt collected his sample, and so it is more likely to be from a different species of *Triodia*, such as *T. pungens, T. bitextura* or *T. stenostachya* (see Fig. 4.1).

In conclusion, the cuyallie and burga specimens are from the same species, which is different to the species K070 is from. One of these species may or may not be *Triodia irritans*, but definitely not both, and one of these species may or may not be *T. pungens*, but not both. Further analysis of a range of samples alongside authenticated *Triodia* spp. samples would be necessary to clear up this confusion.

A specimen from the Pitt Rivers Museum collection has also been identified as probably spinifex from *Triodia sp.* based on similarities with the 'cuyallie' and 'burga' samples (Table 8.1). A sample from a specimen labelled 'gum cagera' (Table 8.1) was also chemically similar to the two spinifex samples but with significant differences, and placed into the non-conifer diterpenoid resin group 'E' (see Chapter 4).

Erythrophleum chlorostachys (F.Muell.) Baill. in the family Leguminosae, commonly known as ironwood, produces a resin that is used for hafting in Australia. A specimen labelled as "rosin" of ironwood (Table 8.1) showed a similar chemical composition to the putative spinifex samples, but with many different and unknown diterpenoid compounds (see Chapter 4). This sample (PBH100) is presumed to be ironwood resin from *Erythrophleum chlorostachys*, based on ethnographic and geographical information, and has been used to identify similar resins that have also then been tentatively identified as *E. chlorostachys* (Chapter 4). The resin was on the end of a stick, presumably for storage or transport as has been described with reference to spinifex resin, and is therefore thought to also have been used for adhesive and hafting purposes.

8.1.1.2 *Canarium* resin

Four lumps of adhesive labelled as beeswax or resin, and another four lumps labelled as beeswax, all from southeastern Papua New Guinea, appear to contain elemi-like triterpenoid resin, and no strong indicator of beeswax (Table 8.2). These samples suggest that this triterpenoid resin probably from *Canarium* sp. was used as an adhesive in PNG.

Table 8.2: Resin specimens with recorded uses: *Canarium*

Sample	Sample location	Artefact info.	Results
PRM27	Resin specimen	Four lumps of beeswax collected by Chignell sometime before 1908 from the Ubir people of Collingwood Bay on the coast of the Oro province in southeastern Papua New Guinea	Elemi-like triterpenoid resin from the Burseraceae family, possibly from *Canarium* sp.
PRM28	Resin specimen	Four lumps of beeswax or resin used as adhesive collected by Chignell sometime before 1908 from the Ubir people of Collingwood Bay on the coast of the Oro province in southeastern Papua New Guinea	Elemi-like triterpenoid resin from the Burseraceae family, possibly from *Canarium* sp.

As discussed in Chapter 7, all of the resin samples with reference to torches or fuel for illumination are from species of *Canarium* (K065, K101, K102), with the exception of one sample from *Aucoumea klaineana* (K080) also in the Burseraceae family. There were no additional ethnographic examples of torches from the museum collections included in this project, but it is apparant that illumination was a key use for the non-elemi type Burseraceae resin (with more peaks than two large amyrin peaks) (see Chapter 5).

The finding of *Canarium*-like resins found on artefacts from Australia is interesting as there is not much reference to the use of *Canarium* in the ethnographic literature on resin use in Australia. The presence of *Canarium* resin on artefacts such as these from Far North Queensland could indicate either that the resin and/or complete artefacts have been traded in from Papua New Guinea or the Solomons, or the resin could have been obtained from the locally growing species. *Canarium australianum*, *C. australasicum*, *C. vitiense*, *C. muellerii*, and *C. acutifolium* are the only currently known native species of Burseraceae to Australia, occurring across the tropical north and east of Australia. The only references found in the literature to *Canarium* species from Australia refer to *C. australasicum* resin being used for hafting, for example by Nugent (2015, p. 75) (see also PBH096 in Chapter 5).

8.1.1.3 *Xanthorrhoea* resin

Two examples of *Xanthorrhoea* resin recorded as being used as adhesive and fixing spear-heads to shafts, respectively, are included in the museum collections (Table 8.3).

Sample PRM23 was identified in the pilot study for this project as the resin from *X. resinosa* (Bradshaw; 2013) despite being noted as red in colour at the time of sampling. The specimen was collected from the Blue Mountains, New South Wales, which is within the

TABLE 8.3: Resin specimens with recorded uses: *Xanthorrhoea*

Sample	Sample location	Artefact info.	Results
PRM23	Resin specimen	Large lump of reddish-brown, brittle resin and attached plant matter labelled as "*Xanthorrhoea* ('blackboy') gum from the base of a burnt grass-tree stem", used as an adhesive. Collected in 1914 by Henry Balfour, the first curator of the Pitt Rivers Museum, from near Mount Victoria in the Blue Mountains, New South Wales	Phenolic resin from *Xanthorrhoea resinosa*
PBH102	Resin specimen	"*Xanthorrhea* [sic] resin, shaped into spheres", collected from southwest Western Australia in 1924. Labelled as "Black gum, used for fixing spearheads"	Phenolic resin from *Xanthorrhoea preissii*

natural distribution of both *X. resinosa*, which produces yellow resin, and *X. arborea*, which produces red resin. However, the chromatographic profile of the sample was consistent with the resin of *X. resinosa*, and less so with that of *X. arborea*, as has been confirmed on re-analysis (Chapter 6). Both the burnt state of the plant, as it has been previously documented that *Xanthorrhoea* resin darkens on heating (Valis; 1991, p. 64), as well as oxidation of the resin during the hundred years of storage, could reasonably explain the reddish-brown appearance of the specimen. The identification of the sample PRM23 as *Xanthorrhoea resinosa* has therefore been retained.

This specimen was described by the collector as an adhesive, with no specific mention of hafting. However, from Clarke's (2012, p. 138), research, we know that *Xanthorrhoea resinosa* was used for hafting in New South Wales by such ethnographic reference to "black boy gum" and the specified 'yellow' variety of the dwarf grasstree (*Xanthorrhoea resinosa* subsp. *resinosa*) being used for fastening stone heads on tomahawks, attaching hooks to fishing lines and hafting spears in Eastern NSW. Clarke (2012, p. 138), also reports the use of grass-tree resin (*Xanthorrhoea* sp.) for reinforcing the joints of fishing spears, hafting

hatchets, attaching shells or stones to spear thrower shafts, mending damaged canoes and baskets in the Sydney area of NSW.

Another specimen was described as *Xanthorrhoea* resin used for fixing spearheads (Table 8.3). A similarity in the chromatographic data, although not an exact match with the reference sample, tentatively identifies the resin as *Xanthorrhoea preissii*. This identification makes sense with the ethnographic literature, as the main *Xanthorrhoea* resin known to have been used for hafting in that area is *X. preissii*. According to Clarke (2012, p. 137) and references therein, *X. pressii* resin, called balga, was used by the natives in making their hatchets, hammers etc. and in fixing the glass to their spears, and "Blackboy" gum was noted as being used for almost everything being made, probably including hafting hatchets in southwest Western Australia.

As discussed in Chapter 6, it is often referenced that *Xanthorrhoea* resin is less favourable than *Triodia* resin, for hafting particularly. It is apparent, however, that *Xanthorrhoea* resin has been used in areas where *Triodia* naturally occur, specifically in South Australia and NE Queensland. It is also apparent that *Xanthorrhoea* resin is used for other purposes than hafting. The reason behind the choice of *Xanthorrhoea* resin in these areas is not clear but may reflect intended function of the resin, or the particular species of *Triodia* available as it has also been suggested that only spinifex resin from certain species are suitable for purposes such as hafting (see Chapter 4).

8.1.1.4 Unknown resin

A specimen of resin used for hafting, from Nias Island in the Dutch East Indies, Philippines is an example of an unknown resin (Table 8.4). The solvent-extracted material is not recognisable as a resin known to have been used in Oceania, and did not match any of

the ethnobotanical reference samples. A review of resins of the Philippines is outside the scope of this project, and this sample was included for comparative and contextual purposes. The results demonstrate the need for further large-scale characterisation work on the ethnobotanically significant resins of the world.

TABLE 8.4: Resin specimens with recorded uses: *Unknown resin*

Sample	Sample location	Artefact info.	Results
PBH007	Resin specimen	Stick of resin, used to fix blades in hafts, etc." collected by Dr. Barbara Lawrence in 1937 from Central Soliga, Nias Island Dutch East Indies, Philippines	Unknown resin

8.1.2 Resin types and function

The majority of the amorphous materials on the museum artefacts were found to contain some resin. In the samples that did contain resin, the majority of the resins could be identified in terms of general chemistry and placed into one of the four main categories: conifer diterpenoid, non-conifer diterpenoid, triterpenoid or phenolic resin. Each of the four main types of resin have been used for both hafting and non-hafting purposes, as can be seen in Figure 8.1.

There is a slight preferance towards hafting material in the non-conifer diterpenoid (spinifex-type) resins, and a slight preferance towards the non-hafting uses in the conifer-diterpenoid and triterpenoid resins, but overall the findings suggest that certain resins are not function-specific, at least in terms of hafting.

There is, however, more of a difference as to whether the artefacts were collected from Australia or other parts of Oceania, as can be seen in Figure 8.2.

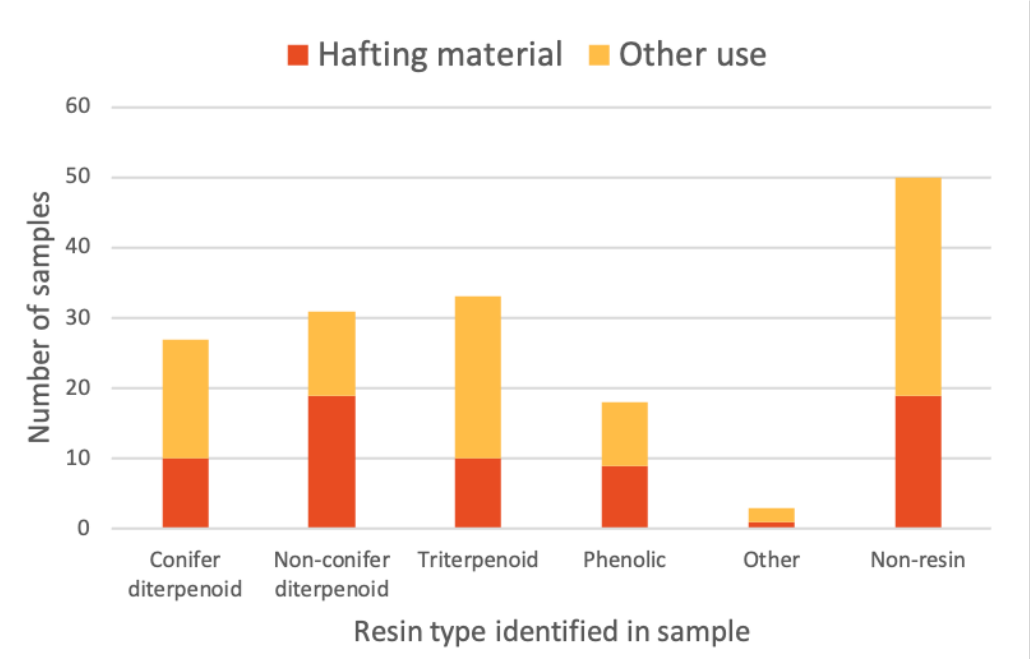


FIGURE 8.1: Bar chart showing the four main categories of resin plus non-resins identified in the hafting and non-hafting materials on ethnographic museum artefacts (NB Samples PRM03-PRM22 in the conifer diterpenoid resin/non-hafting group are effectively replicates and have been counted once as a group to avoid a misleading skew)

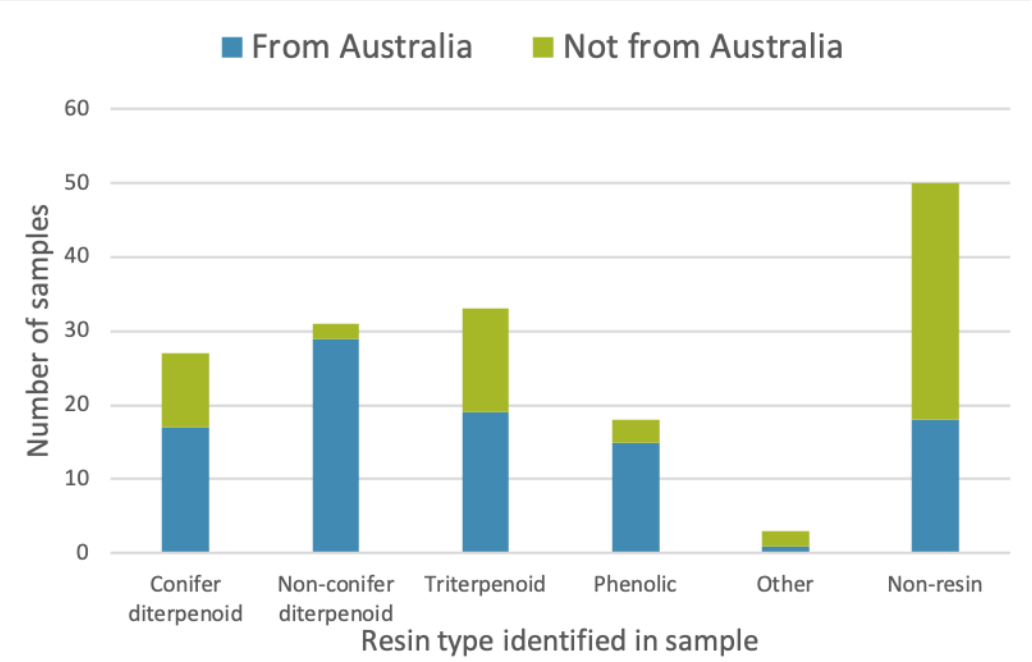


FIGURE 8.2: Bar chart showing the four main categories of resin plus non-resins identified materials on ethnographic museum artefacts from Australia, and other parts of Oceania (NB Samples PRM03-PRM22 in the conifer diterpenoid resin/not from Austalia group are effectively replicates and have been counted once as a group to avoid a misleading skew)

The choice of which source of resin to exploit appears to be geographically-based, rather than function-based. As would be expected, the majority of non-conifer diterpenoid (spinifex-type) resins and phenolic resins are used in Australia and the majority of materials used outside of Australia were conifer diterpenoids, triterpenoids and non-resins. However, there were more conifer diterpenoid and triterpenoid resins used in Australia than was suggested in the ethnographic literature and the specimens of known sources of adhesives described in Section 8.1.1.

8.1.3 Meaning beyond function

In the Solomon Islands, *Canarium salomonense* is seen as a sacred species, as discussed in Chapter 5. There is more than a physical and functional meaning for certain trees and plants to First Nations communities in the Solomon Islands, and this needs to be considered when interpreting the role of plant resins, and other organic materials within their culture. A meaning beyond function must also be considered for materials used by Aboriginal Australians and Torres Strait Islanders, in terms of the Dreaming and the significance of ancestral connections in the landscape. Dreamings: the stories connected to the ancestors, the spirit world and the physical world are known to be passed on through ceremonial body painting, storytelling, song and dance (Artlandish Aboriginal Art Gallery; 2019). When studying artefacts it is important to consider the spiritual relationships between past Indigenous communities and the natural materials they used.

Resins are a material with a functional purpose, but either in themselves or connected with composite items, they have a role in the passing down of stories, connections with ancestors and the life cycle, and with spiritual health. This spiritual significance is more obvious for certain artefacts in this collection, mainly through their descriptions in the museum notes.

8.1.3.1 Religious and ceremonial uses

A number of artefacts are connected with religious and ceremonial uses (see Chapter 7). A ceremonial stone axe from North Australia (PBH098) is hafted using a resin mixture and ochre for decoration. There is also a ceremonial throwing stick from the Kimberley (PBH111), again hafted using cement to hold a jasper blade in place, though not with resin. These items suggest that functional tools and weapons can be made specifically for ceremonial use: a purpose other than that which appears obvious. This is particularly important knowledge for when considering the interpretation of archaeological finds.

From Mer Island in the East Torres Strait Islands, two model shell hoes (AM01, AM02) called *ponigob* have carved handles in the shape of crocodile heads, and are painted red and black. Rather than tools for hoeing gardens and hollowing out canoes, these model hoes are thought to have been dance accessories (Stan; 2005).

Other dance accessories from the Kimberley in the Northern Territory are in the form of emu feather ornaments (PBH109, PBH110) called *Murrindi*. These emu feathers, held together with putative spinifex resin, are described as being worn specifically on *corrobberie*, a ceremonial event involving singing and dancing. The feathers are worn "behind" presumably as a tail. Emus had particular significance in Australia and many uses, both practical and spiritual (McCarthy; 1965).

A mourning nose stick from Western Australia (PBH089), noted as being rare, has an unknown resin on one end. It is not known whether the item itself has spiritual significance or is simply jewelry for a special occasion. It is also not clear if the resin is for decoration or whether it had another purpose. Similarly, tattooing is strongly connected with community and identity in New Zealand, but whether the source of the pigment, kauri resin in this

case (PRM01-22), is important for anything other than practical application is not apparent from the museum notes.

8.1.3.2 Medicine and sorcery

Other artefacts in the collection are connected with magical (and perhaps in some cases chemical) healing and cursing. Resin as well as non-resinous amorphous materials are connected with several healing implements: medicine shells; medicinal headbands; and a medical bone (PRM25, PRM26, PBH090-2, PBH093, PBH094, PBH088), as well as a cursing stick (Chapter 7). The use of resin on some of these items may be practically significant due to healing properties of some resins, particularly those containing terpenoids. However, in the case of the pointing stick (PBH099) for cursing without any physical contact with the subject of the curse, the significance of the resin is presumably due to a magical or spiritual force.

There are two examples of resin stored for later use (PBH001, PRM29), for medicinal or narcotic effects (Chapter 7). This again highlights the significance of the resin itself, particularly the one identified as *Canarium salomonense*, which as mentioned earlier, is considered sacred in some places. In Australia and the Torres Strait Islands, bush medicine is linked with the Dreaming and the spirit world, with valuable information of the local flora being passed down through generations as part of the stories. There is again a ceremonial aspect of paying homage to the spirit of the medicinal plant, as is also sometimes depicted in Aboriginal art (Wroth; 2019).

8.2 Geography of resin exploitation

8.2.1 Geographical patterns of specific resin use

There are clear geographical patterns to the use of the resins studied in this project, as shown by the following maps that show the geographical origins of museum artefacts containing each type of resin, for both hafting and non-hafting uses.

Conifer-type diterpenoid resin

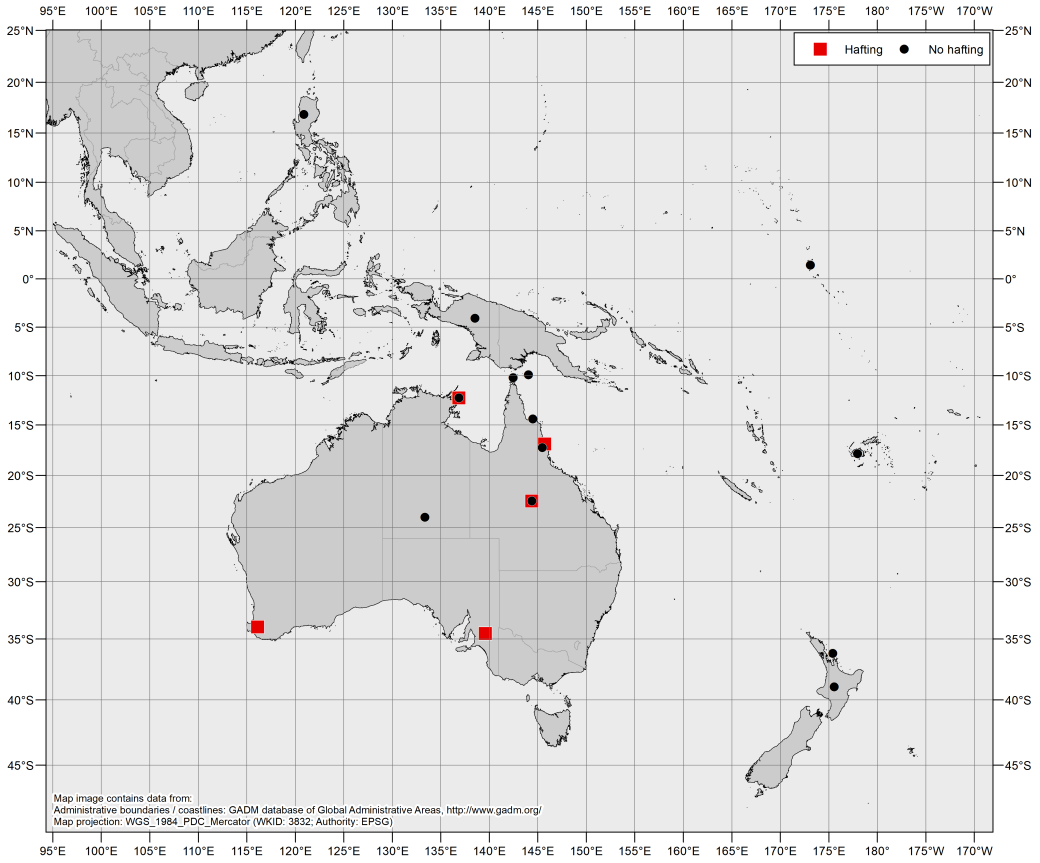


FIGURE 8.3: Map showing origin of aftefacts on which conifer-type diterpenoid resins were identified

Conifer-type diterpenoid resins were identified on artefacts from throughout Oceania, including some of the more remote islands (Figure 8.3). Its use as a hafting material, however,

appears to have been restricted to Australia. This type of resin is probably the most consistently used resin across all the geographical regions within Oceania.

In the cases where identification to species was possible, resin from the locally growing species are generally used, for example, New Zealand kauri (*Agathis australis*), Fiji or Pacific kauri (*Agathis macrophylla*) and Western New Guinea kauri (*Agathis labillardierei*). It may also be likely then that the resin on sample PBH058 from Papua New Guinea, is from New Guinea kauri: *Agathis spathulata*. This hypothesis should be tested by comparison with an authenticated sample.

It is also possible that the conifer-type diterpenoid resins occuring on items from Queensland are from the Queensland kauri, *Agathis robusta*, or other locally growing species *A. atropurpurea* or *A. microstachya*, even though a confident identification was not possible by comparison with the reference samples in this project.

Non-conifer diterpenoid resin

Diterpenoid resins not of the conifer type, such as the spinifex and ironwood examples, were identified on artefacts almost exclusively from the Australian mainland (Figure 8.4). The use of these resins appears to have been restricted mainly to the arid and semi-arid regions in the north and west of Australia where *Triodia* spp. and *Erythrophleum chlorostachys* grow naturally.

These types of resin appear to have been mainy used for hafting, and used for other purposes only in north Western Australia.

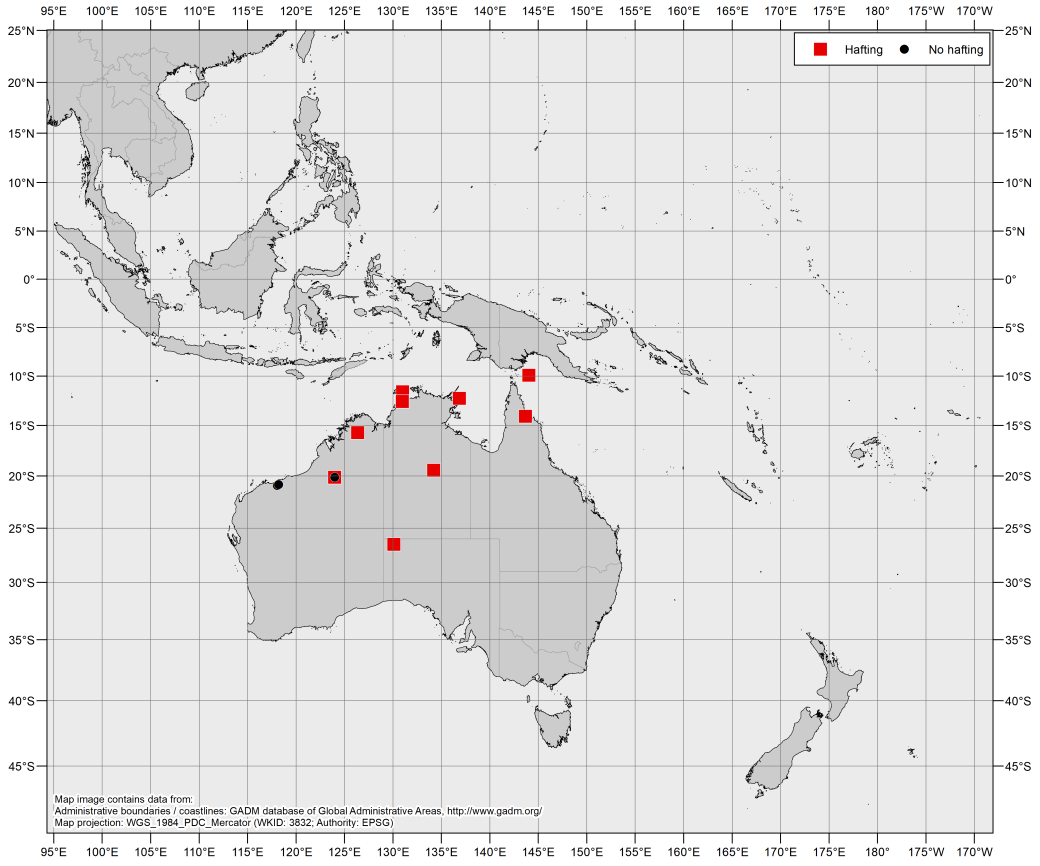


FIGURE 8.4: Map showing origin of aftefacts on which non-conifer diterpenoid resins were identified

Triterpenoid resin

Triterpenoid resins were identified on artefacts from Borneo as expected, as their use is well known throughout Southeast Asia and Indonesia. The use of this type of resin in New Guinea is also well documented, and is corroborrated by the identification of triterpenoid resins from both the west and east of the island.

The results of this project show that triterpenoid resins were used across Melanesia and Australia, but probably not as far as Polynesia (Figure 8.5). In Australia, their use is mainly restricted to the north and central areas. Triterpenoid resins appear to have been used for both hafting and non-hafting uses.

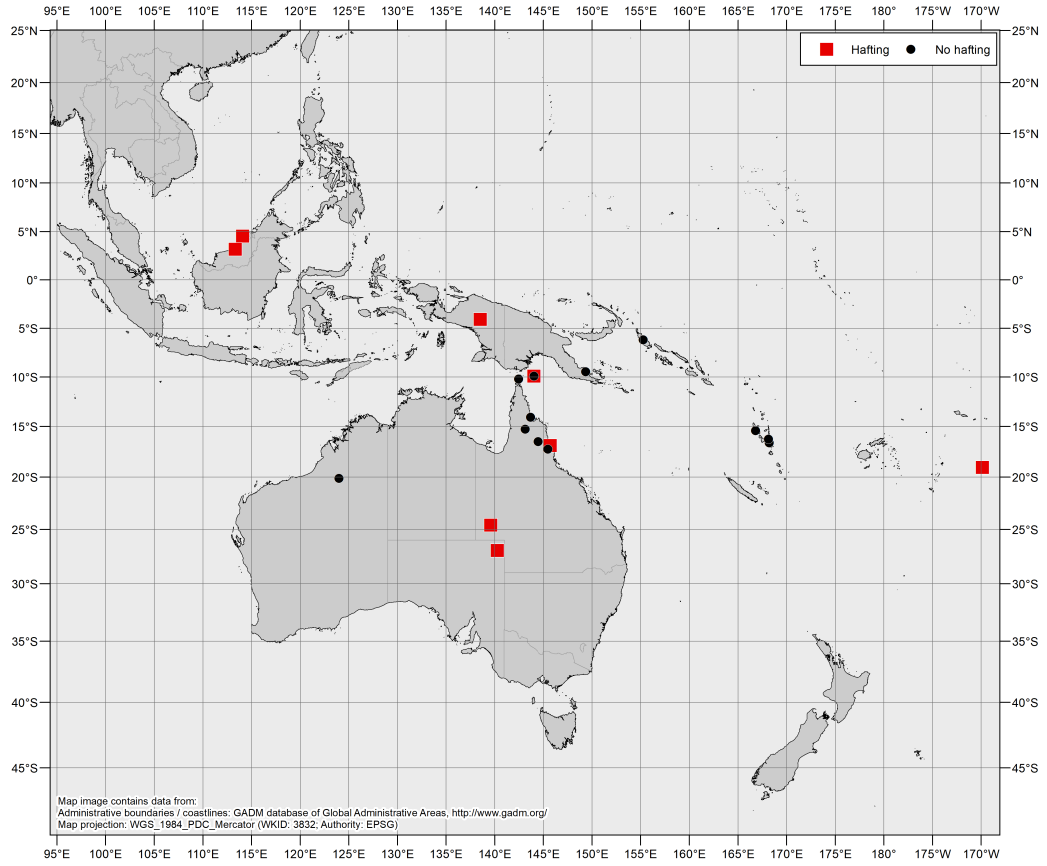


FIGURE 8.5: Map showing origin of aftefacts on which triterpenoid resins were identified

Phenolic resin

Similarly to the non-conifer diterpenoid resins, phenolic resins such as *Xanthorrhoea* spp. were identified on artefacts almost exclusively from Australia (Figure 8.6). Though as expected, their use appears to be more restricted to the coastline and wetter regions.

The evidence suggests that these resins, or artefacts made using phenolic resin, were probably traded through the Torres Strait to New Guinea. Perhaps surprisingly, phenolic resins also appear to have been used for both hafting and non-hafting purposes.

Materials with no resin present

There is evidently a much wider range of resins being used in Oceania than has been previously been appreciated, for which much more research needs to be done to be able to

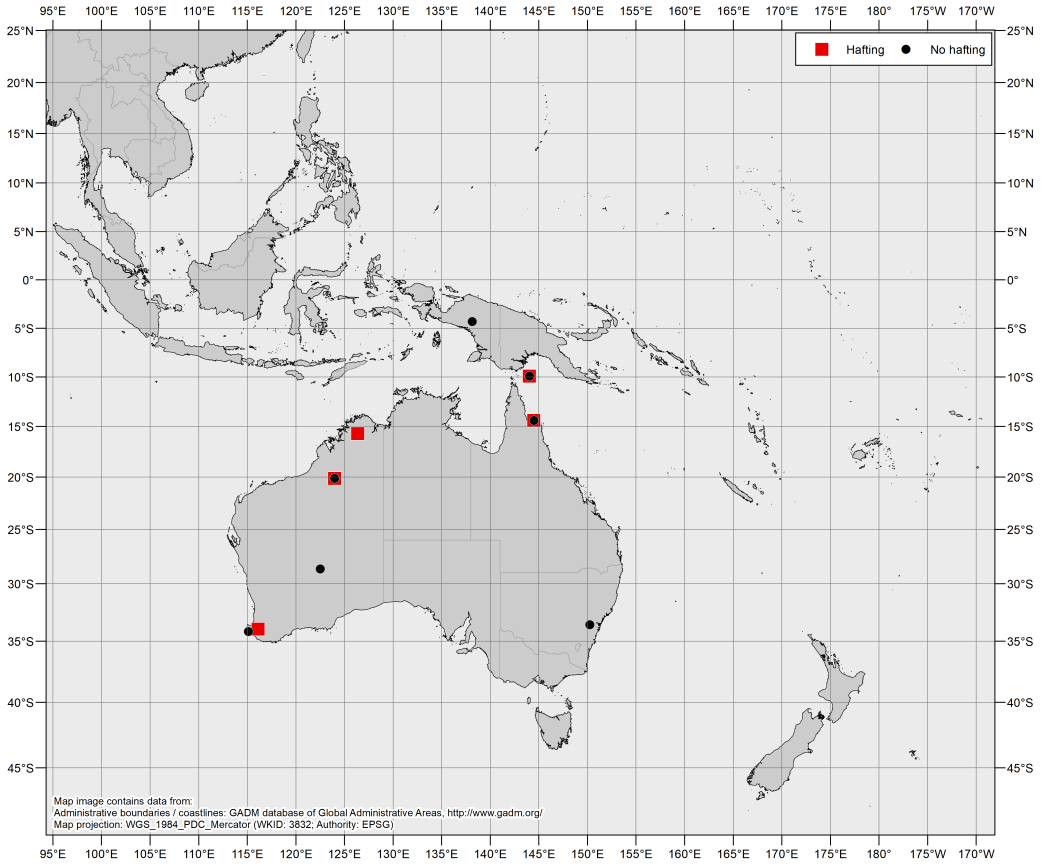


FIGURE 8.6: Map showing origin of aftefacts on which phenolic resins were identified

identify them. However, this does not just apply to resins as there is clearly also a large variety of non-resins being used for similar purposes.

It is evident that amorphous materials not containing resin have been used for both hafting and non-hafting purposes across Oceania (Figure 8.7).

Non-resinous natural amorphous materials such as those present on these artefacts have been studied to some extent elsewhere, particularly gums and waxes (Nussinovitch; 2010; Mills and White; 1994). In order to identify the different types of amorphous material present on the museum artefacts, other preparation methods prior to GC-MS analysis, as well as other analytical methods would need to be applied in conjunction with GC-MS, such as FTIR (see Chapter 2).

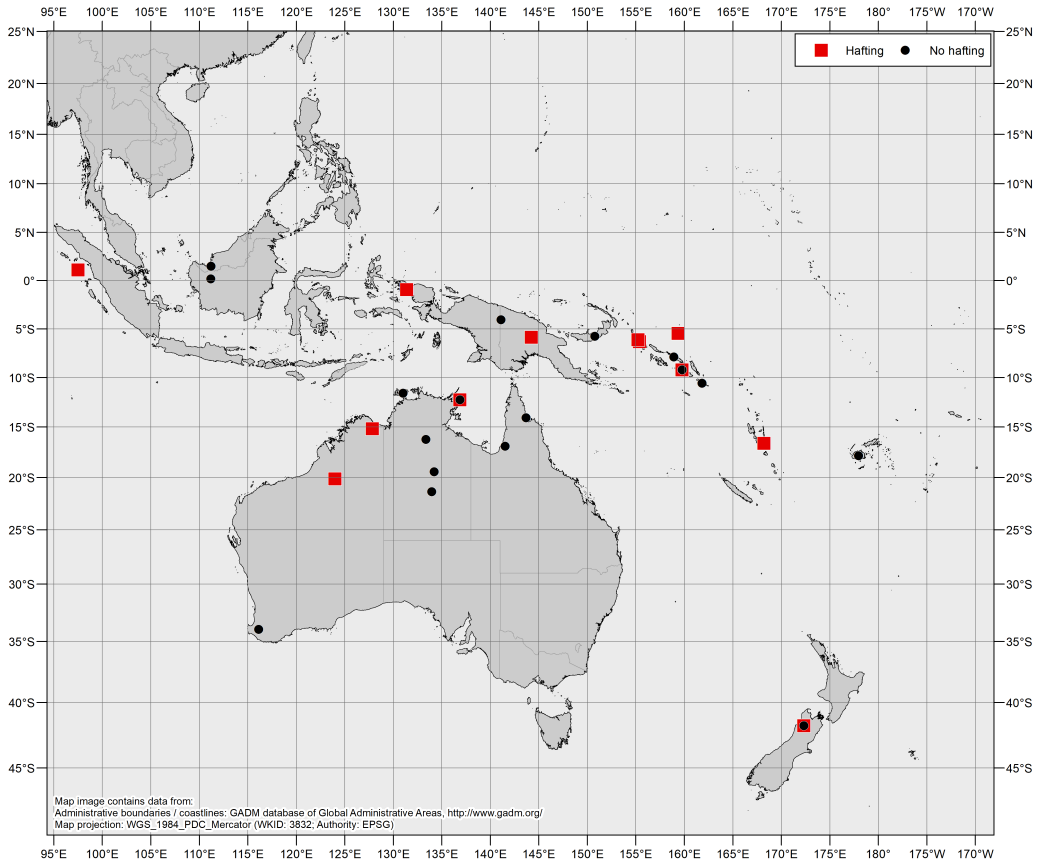


FIGURE 8.7: Map showing origin of artefacts on which no resins were detected

8.2.2 Regional patterns in resin use

Australia: Queensland

The largest range of resins being used in Australia, as suggested by this study, is in Queensland, particularly in the far north. The resins include conifer-type diterpenoid and and at least three different types of triterpenoid resin, but also *Xanthorrhoea* and ironwood resins, plus non-resins including wax. The triterpenoid resins include *Canarium salomonense* resin, which is also found on items from Papua New Guinea, and resins with lupane-type triterpenoids, similar to other samples from the Torres Strait, and dammarane-type triterpenoids usually seen in the dipterocarps from Southeast Asia. These resins may all be indicative of trade or exchange from outside mainland Australia, or else represent unknown native Australian resinous species. No spinifex-type resins were identified in this region.

Australia: New South Wales

There is only one sample from New South Wales, which is identified as the resin from the locally abundant species *Xanthorrhoea resinosa*.

Australia: South Australia

Diterpenoid resins of both the conifer-type and spinifex-type were identified on items from South Australia, as well as a possible dipterocarp triterpenoid resin. Again, this type of triterpenoid resin may indicate a trade link with Southeast Asia where dipterocarps are abundant.

Australia: Western Australia

Non-conifer diterpenoid resins of the spinifex type and *Xanthorrhoea* and other phenolic resins are dominant on the artefacts from Western Australia. There is also one example of the use of ironwood resin, and a possible use of the conifer-type diterpenoid resin from *Callitris*. An unknown resin and a few non-resins add to the variety of materials used in this region, but the majority of resin used appears to be from spinifex or *Xanthorrhoea*. No triterpenoid resins were identified on artefacts from this region.

Australia: Northern Territory

Resin use in the Northern Territory seems to be split between both types of diterpenoid resin, conifer-type and non-conifer-type including ironwood. There is one example of the use of beeswax and one of an unknown material. No *Xanthorrhoea* or triterpenoid resins appear to be used in this region. It is notable that resin use in Arnhem Land appears to be significantly different to other areas of the Northern Territory.

Torres Strait Islands

All samples from the Torres Strait Islands appear to be triterpenoid resins, including one containing lupane-type triterpenoids. One sample also has evidence of a phenolic resin, possibly from *Xanthorrhoea*, which may indicate trade with mainland Australia.

New Guinea and Solomon Islands

Most samples from Papua New Guinea and the Solomon Islands were non-resins, including one example of the use of beeswax. One sample contained a diterpenoid resin of the conifer type and another was identified as a triterpenoid resin from *Canarium salomonense*, a native species to New Guinea. The artefact originated geographically in the Solomon Islands.

West Papua and Kiribati

Again, most samples of artefacts from West Papua did not contain resins, or were of unidentified resinous materials. There are, however, samples from two artefacts, both collected from the Dani people of West Papua, that were identified as resin. One triterpenoid resin from the native *Canarium salomonense*, and one conifer-type diterpenoid resin from *Agathis labillardierei*, which is another native species known as West New Guinea kauri. *A. labillardierei* resin was also detected in a sample from Kiribati, an island far into the Pacific to the east of New Guinea. It is not clear whether this species grows locally on Kiribati or whether it would have likely been traded from New Guinea.

Vanuatu and Fiji

From this collection of artefacts, there are examples of resin use in Vanuatu from both an unknown triterpenoid resin and a conifer-type diterpenoid resin identified as *Agathis alba* resin. A similar conifer resin, but from *Agathis macrophylla*, known as Fiji kauri, was identified on two artefacts from Fiji, along with another sample of a non-resinous material.

New Zealand

The samples from the North Island of New Zealand were all identified as the locally abundant *Agathis australis* resin. Samples of resins with functions other than tattooing pigment would need to be analysed to confirm if this is representative of resin use in the region. Two non-resins were present on artefacts from New Zealand, at least one of which is from the South Island.

Interestingly, a sample from the Island of Niue much further out into the Pacific to the east, contained an elemi-type triterpenoid resin thought to be from the Burseraceae family. Unfortunately, information on the local flora of this island is very limited.

Unknown origin

Some samples of unknown origin have been analysed and identified to some extent. Likely regions of origin based on the type of resin present have been hypothesised. Samples found to contain *Xanthorrhoea* and non-conifer diterpenoid resin of the spinifex type are hypothesised to have originated in Australia. Samples found to contain triterpenoid resin of the elemi-type, probably from the Burseraceae family, are hypothesised to have originated either in Far North Queensland, Torres Strait, or outside Australia in or close to New Guinea or the Solomon Islands (see Chapters 3-6).

8.2.3 Indications of trade

There are indications of trade in a few cases, either where stated in the artefact information, or where the identified resin does not fit with the natural geographical distributions of the source plant.

There are a number of suggestions, from the results of resin analysis, of trade or exchange between Australia and Papua New Guinea, through the Torres Strait Islands, as was discussed in section 8.2.2. There are also hints towards potential long distance movements, for example, from Southeast Asia to both the far north, and South Australia, by the presence of possible dammar resins in Australia. These hypotheses would benefit from further research into known trade links in Oceania, and a more focussed analysis of artefacts from the areas in question.

Bellwood (1978, p. 92) highlights that Melanesian trade, at least in the west, is a distinctive phenomenon, differing from that in Polynesia, apart from New Zealand where there are more similarities to the Melanesian trade system. Polynesian societies are often specialised in production and rely on frequent trade, which is in many ways an individual activity, whereas the Melanesian system uses long distance trade with long-term collection and redistribution within tribes and is centred on a chiefly personage (Bellwood; 1978, p. 102). The results of this study show the potential for resin analysis to provide more insight to trade patterns of both types of trade by connecting the final destination of an artefact with the geographical origin of the resin material.

It must also be noted that it is likely that some artefacts have been made especially for tourists or the European market and may therefore not be completely representative of ones that would actually have been used. For example, longevity and robustness of materials would not be as important for a tourist item, and decoration may be prioritised. This is probably true for a war club ("subi") in the collection, from the Solomon Islands, that is labelled as being probably a tourist piece along with the name of the carver. This phenomenon, however, is interesting in itself and contributes towards research into the effects of European contact in these regions.

8.3 Indications of technological processes

In some cases the type of resin used may have been chosen deliberately because of its suitability for the intended purpose, in others, a locally sourced resin may have been altered to make it more suitable for its purpose. There are indications of some such technological processes in the resins on some of the ethnographic museum items, either from the ethnographic desriptions or from the resin itself. These processes include refining, mixing, and high temperature heating, which are each addressed in this section.

The choice of material and how it has been processed is even more intriguing when different materials have been used on the same item. In some cases this appears to represent a repair. The items displaying all these processes are discussed below.

8.3.1 Refining

According to the ethnographic descriptions, two specimens of spinifex from the PBH collection represent two different stages of spinifex processing 'cuyallie' and 'burga'. Evidently from the chemical results, they are from the same source, hypothesised to be a species of *Triodia*. No particular chemical differences were identified between the solvent extractable lipid portion of the two specimens (Chapter 4). The refining process of burga involving continued re-melting and squeezing as per the description with the specimen PBH011 is not likely to have caused any chemical changes, but probably has the effect of breaking down the plant fibrous material to make the resin smoother. This process therefore cannot be identified chemically, but may be visible by light microscopy. It is likely that this process of refining is only necessary for *Triodia* resin, which is collected in powder form and naturally prone to plant fibre inclusions.

8.3.2 Mixing

There are a few cases where the same resin has been used for different purposes on the same piece of weaponry. For example, on a spearthrower, the tip where the peg is hafted to the body includes the same resin (AM03), identified as *Xanthorrhoea* (Chapter 6), as the handle, where resin is added to the surface of the body presumably to improve the grip (AM05). There are no notable chemical differences between the two samples, however, the resin appears to have been processed differently as the hafting resin is lighter in colour and has fine plant fibre inclusions, yet the handle resin is black and shiny.

A stick/club also has the same *Xanthorrhoea* resin on both ends, but the resin on the tip (PBH056) has some plant inclusions making it more friable, whereas the resin on the base (PBH057) is much more glassy and brittle.

A spearthrower from Far North Queensland is another example where adhesive used on the tip and base appear very different, one (PBH004) is reddish brown and flakey, the other (PBH006) a dark blackish brown and shiny, but the analysis shows they have the same resin component, again from *Xanthorrhoea*.

These three items from opposite ends of Australia, and the Torres Strait Islands, suggest that it was a common practice to process resin used for hafting in a different way from resin used for non-hafting purposes, at least for *Xanthorrhoea* resin. Additionally, ethnographic accounts from central and Western Australia (Clarke; 2012, p. 139) suggest that *Xanthorrhoea* resin is easily gathered but considered less satisfactory, more brittle and inferior to spinifex resin and desert mulga gum (*Acacia minyura*), and must always be gradually heated to make it plastic as it froths up and crumbles if it is heated too quickly. This information makes the choice behind the use of *Xanthorrhoea* resin particularly intriguing, especially in areas where other options are available.

Processing of the resin before use by mixing it with other materials such as plant fibres, but also red ochre, charcoal, crushed shell, sand, and spit, which can all dramatically change the behaviour of the resin, is most likely done to make the resin more suitable for certain uses. Evidently there is a difference between hafting and non-hafting uses, but also between the hafting of different tools or weapons. Clarke's (2012) collation of ethnographic accounts of resin use provides an insight into the different methods of preparation of hafting cement for different intended uses. These accounts mention the use of charcoal for mixing with hafting cement for spear points to make it more brittle than the cement for hammers, so that the barbs or teeth come off in the wound more easily, but quartz-edged knives required a tougher resin (Clarke; 2012, p. 137).

Other organic materials were also detected in several of the samples, some without any resin and some in addition to resin, indicating mixtures. Many of these samples have alkanes present, with mostly C29 and C30 dominating. Without further analysis that is beyond the scope of this project, it is presumed that these compounds indiate a type of vegetable oil. This would suggest that many of the resins have been deliberately mixed with such vegetable oils probably to soften the resin and keep it malleable. Resarch into the different organic materials chosen for mixing with different resins would be valuable further work on the hafting and non-hafting technologies in Indigenous Oceania.

8.3.3 High temperature heating

High temperature heating causes irreversible chemical changes in resins, which will theoretically leave a signature in the form of particular chemical products that can be used as biomarkers for such a process. There has been very little experimentation and research on effects such as this, and also degradation in general, for the resins from Oceania.

However, research on conifer resins from elsewhere in the world notes retene as a marker for high temperature heating in pine resin (Chapter 3). It has therefore been hypothesised that the same marker will be seen in the conifer resins of Oceania due to the same precursory compounds being present.

Two samples of resin on spearthrowers, one from Queensland (PBH112) and one from South Australia (PBH112), were identified as conifer-type diterpenoid resins. Retene was detected in both of these samples, and not in any of the other conifer resin samples. It is therefore confidently suggested that these resins are likely to have been heated to a high temperature as part of the processing method before application to the spearthrowers.

In Western Europe and North America, conifer resin is known to have been used to make pitch through processes including high-temperature heating (Chapter 3). The only reference to "pitch" in Oceania, found by the author, is in reference to Papua New Guinea, but the definition of pitch in this instance is unclear. Further research is required to deduce whether a pitch making technology including high-temperature heating existed in Papua New Guinea, and if regular exchange with Australia across the Torres Strait is reflected by the spread of such technological practices.

8.3.4 Repairs

Repairs are often visible because of the obvious application of a resin to a localised area where resin would not normally be used, or the addition of new resin on top of old resin, most easily seen if they are two different types of resin. This may be the reason for a mixture of resin types in some of the samples analysed in this project.

Probably the most obvious repair is seen in a bark bucket, where a break in the bucket has been sealed up with resin (AM14). In this case, the resin used for the repair is from a

different source to the resin application on the rim but is similar to the resin covering the inner of the bucket. Repair may also be the reason for the presence of different resins on different parts of other items such as spearthrowers.

Hafting is an investment of time and materials, rewarded with a longevity of life of the artefacts, impelling reuse and repair when necessary. Like the bark buckets, this repairing may be the reason for presence of multiple types of resin in one sample, rather than a deliberate mixture (for example PBH082).

Because of this re-use and repair system, resins can potentially give indications of artefact biographies, for example, how long the artefact was likely to have been in use based on separate events of resin application.

8.4 Future archaeological analysis

The aims of this project included using the information gained from the study of resinous materials on ethnographic artefacts towards building a framework for the study of archaeological resins. The focus here has been specifically on the resin component of these artefacts. Ideally, resin analysis on ethnographic artefacts needs to be observed in the context of the full artefact including other materials, particularly other organic materials, present. Further analysis of the other materials on the artefacts studied in this project, in conjunction with the results of this project, would be beneficial for a more comprehensive understanding of the use of resin as a material on these types of artefacts in Oceania.

It is proposed that the methods used in this project would be suitable for applying to archaeological amorphous residues that are suspected to contain resin, in order to identify the resin and its most likely source. Analyses of archaeological hafting, adhesive, and coating materials through methods such as those used in this project are very important for finding the true identity of the resinous components of these materials as the aesthetics can be very misleading. However, this is only part of the picture and the organic chemical analysis by GC-MS needs to be carried out in conjunction with a series of other techniques starting with microscopic analysis to gain a comprehensive characterisation of the materials used.

8.4.1 Suggested methodological protocol for archaeological resin analysis

Firstly, microscopic observation of suspected resinous amorphous materials is essential for observing any heterogeneity of the material and obvious inclusions such as plant matter, charcoal, shell, sand and bone. This is important for understanding the process of how the material was made and what is included in the mixture, as well as if there is any layering

present indicating separate application events. It is also important for deciding on how many samples are needed for analysis and which areas to sample from. Colour, texture, brittleness, friability and such characteristics should also be noted, and where the presence of spinifex resin is suspected, the test proposed by Pitman (2010) as described in Chapter 4 may be of use.

Secondly, a non-desctructive spectrometric technique such as Fourier transform infrared spectroscopy (FTIR) could be employed for identifying the different types of organic compounds present based on their functional groups, such as oils, waxes and polysaccharide gums (Glavcheva et al.; 2014). This is particularly useful as many of the amorphous residues associated with artefacts analysed in this project appear to be mixtures.

FTIR is an excellent preliminary technique for identifying the presence of resin before committing to a destructive method of molecular analysis. This technique is also useful for identifying the degree of polymerisation of the resin, which may affect the choice of analytical method for further analysis, for example pyrolysis-GC-MS (py-GC-MS)or py-MS may be preferable for a highly polymerised resin (see Chapter 3).

The presence of inorganic components can also be identified by FTIR, for example ochre. This could be followed by XRF for further identification of inorganic inclusions if applicable, and ICP-AES if detailed information is sought (Attard Montalto; 2010).

Analysis by GC-MS is appropriate for the identification of specific organic components. If an analysis of all materials in the mixture is required, derivitisation using BSTFA followed by GC-MS may be suitable, although this will likely restrict the level of visible detail of the resin component, and still will not include polysaccharide gums if the sample was extracted into solvent. A method that first seperates each fraction to be analysed individually would

allow a more detailed and easily interpretable analysis, which may be preferable, though more costly and time-consuming (see Chapter 1).

If the presence of resin has been confirmed or is highly suspected, solvent extraction, derivitisation via methylation and analysis by GC-MS, as used in this study, is recommended. Detailed analysis of the resin component can arguably offer more information about local resource exploitation and trade than a more general analysis of a mixture as a whole, particularly in degraded samples. Comparisons with the mass spectral data presented in this thesis, alongside those in commercially available mass spectral libraries and the wider literature will be of value in characterising the resin component of the sample.

If the resin is suspected to be, or confirmaed by inital analysis, from conifers, the application of a pyrolisis techniques may be preferable to analyse the polymeric fraction, depending on the level of information sought. If the resin is suspected to be a triterpenoid resin, a GC-MS run with a longer retention time would be advised as Burseraceae resins contain a large amount of heavy, late-eluting compounds.

8.4.2 Framework for identifying archaeological resins

Based on the findings in this project, resinous materials excavated in Oceania are likely to contain resin that fits into one of the four categories: Diterpenoid resin from conifers; or diterpenoid, triterpenoid or phenolic resin from Angiosperms, as described in Chapters 3 to 6. If recovered outside Australia, such materials are most likely to be either diterpenoid resin from the conifers, or triterpenoid resins. Non-conifer diterpenoid and phenolic resins are more likely to have originated in Australia and if excavated elsewhere may indicate trade.

Unless resinous finds are still attached to points, blades and similar, it cannot be assumed that all archaeological resins are hafting materials, as it is evident that all types of resin have been used for a number of different purposes. Equally, it cannot be assumed that hafting materials in Australia are made using spinifex resin as it is evident that a wide range of different resins are used for hafting in Australia.

It seems that the way the resin is processed may be more important than the type of resin used for different applications, and geography is the main reason behind resin source choice. This means that the identification of resin on artefacts, particularly to species level where possible, could be particularly useful for provenencing artefacts, as well as indicating trade and exchange.

Indication of deliberate processes applied to the resin may be informative of the intended purpose of the resin, which would be particularly useful if resinous materials are found not adhered to an artefact. Chemical analysis of resinous archaeological finds is recommended.

Chapter 9

Conclusions

9.1 Research aims

The first aim of this project was to contribute towards the systematic application of resin analysis for archaeological research in Oceania. The premise of this aim builds on the proven success of the approach in Europe and Africa, and involves researching the much wider choice of resinous materials available in the largely tropical region of Oceania. The second aim was to collect and interrogate data from a selection of artefacts from Australia and other parts of Oceania that have previously been collected by ethnographers, and are currently housed in museums, that display a material that is likely to be resinous based on previous categorisation during museum accessioning. The research focuses on the historic and prehistoric Indigenous use of plant resins by First Nations communities in Oceania, specifically the exploitation of the plant material, technology involved in adapting the naturally occurring resin for use, and function of the resinous materials.

The objectives of the project were successfully met:

1. Gas chromatography-mass spectrometry (GC-MS) was used to characterise a range of resins from Oceania that have had limited previous investigation. A reference collection of mass spectral data from significant ethnobotanical Oceanian resins was built and used to identify unknown resin samples.

2. Resinous materials from a selection of ethnographic artefacts housed in museums, across a range of artefact types, and a range of geographic origins were analysed.

3. Ethnographic data related to the selected artefacts was researched and used alongside the new chemical data to address the research questions.

9.2 Summary

A total of 173 samples of amorphous material, suspected to contain plant resin, from ethnographic museum artefacts were analysed. Thirty-four of these materials were found to contain no resin, however, resin was successfully identified in the other 139 samples of material. Resin serves several functions that are demonstrated on a range of artefacts, the most notable (53 samples), being hafting, but with a significant representation (86 samples) of non-hafting uses.

From the 139 samples, four main types of resin were recognised, accounting for the majority of resins that were characterised molecularly in this project. Only six samples did not fit into any of the four categories based on general chemical composition. These categories are: conifer-type diterpenoid; non-conifer-type diterpenoid; triterpenoid; and phenolic resins, which appear to cover the majority of the range of resins of ethnobotanical importance in Oceania. These are all easily distinguishable by GC-MS. The aged resins on ethnographic museum artefacts can easily be identified and categorised into each of the four groups.

Botanical source of the ethnographic resins has been identified in many cases to some extent, including to species level in some, although species level identification still poses a problem for certain resin types.

This project achieved overall success in the chemical characterisation of Oceanian resins, both fresh and aged. Resins from some Oceanian species have been characterised for the first time. Differences between different resins, in many cases different species, have been identified, as has the use of mixtures of multiple resins and other materials. Some resins have been successfully identified to species. Suggested biomarkers may be suitable for identifying certain resins in a sample without direct comparison to a reference sample.

It was found that there has been a considerable range of plant resin used throughout Oceania, much larger than was expected from ethnographic reports and museum records. The use of spinifex type resin (hypothesised to be from *Triodia*) and *Xanthorrhoea* resin in Australia dominated the ethnographic accounts, yet appears not to be as common on the artefacts, most notably in the type of resin used for hafting cement. This is reflected particularly in the lack of spinifex resin on axes and adzes, and very few examples for hafting spearthrowers, when spinifex resin is almost invariably mentioned as the hafting material of choice. There is generally a large range of different types of resin used for hafting tools and weapons, much more than is reported ethnographically. This finding reflects the wide range of plant exudates used for hafting materials in Queensland reported by Powell et al. (2013), which appears to extend throughout Australia, and also may be true for other parts of Oceania. There appears to be a much wider range of triterpenoid resins being used in Oceania than is communicated in the ethnographic literature, and particularly unexpectedly so in Australia. The use of *Canarium* resins in Papua New Guinea is generally consistent with ethnographic accounts. In Australia, spinifex and *Xanthorrhoea* resins play roughly the same roles as each other, but within their respective natural distribution areas, and

therefore the choice between the use of these two resins appears to be based on local access to the plants. Overall, the choice of resin for exploitation appears to be related mainly to geographic distributions and proximity to the resin sources, rather than specific resins being chosen for certain uses. There is a slight pattern of resin choice related to function for hafting, however, the way the resin is processed appears to be more important in relation to intended function. There are some indications of trade of resin, but possibly more so the trade of whole artefacts made using local resin, which is largely in line with what has been previously recorded.

The importance of resin analysis for conservation work is highlighted by the detection of DDT insecticide in sample PBH059, and an antibacterial/antifugistatic detected in sample PBH074. GC-MS analysis is suitable for identifying contaminants such as plasticisers, anti fungal/microbe sprays, and other chemicals that are potentially harmful to the valuable artefacts.

Specific conclusions to each of the types of resins are discussed in the following sections.

9.2.1 Diterpenoid resins from the conifers (Gymnosperms)

Resins from Oceanian species of conifers were found to be distinguishable at species-level in most cases when the resin was relatively fresh, though inter- versus intra-species variation needs more research. Aged conifer resins were found to be identifiable by the same oxidation markers as conifer resins in other parts of the world. This is significant as no archaeological resinous finds from Oceania have been identified as conifer resin to date, as far as the author is aware, but this finding suggests it should be possible.

Conifer-like diterpenoid resins were identified in 35 of the 173 resinous samples, and suspected in another ten. It is therefore concluded that conifer resins have a significant ethnobotanical role in certain parts of Oceania such as Fiji and New Zealand. This is also true for Australia more than was expected from the minimal references in the ethnographic literature. Conifer resins appear to be the most consistently used type of resin across the whole of Oceania, usually with the locally growing species being exploited.

As conifer resins were recognised on a number of ethnographic museum artefacts, it is hypothesised that conifer resins are also likely to have been used in Oceania in the more distant past and are likely to be found archaeologically. It is also hypothesised that Oceanian conifer resins are detectable in archaeological materials. However, there is a possibility that commercial sources of pine resin have been used in making the ethnographic artefacts, and therefore what has been detected in this project may not be representative of what would be seen archaeologically. Similarly, markers of high temperature heating as seen in pine-pitch have also been detected in some of the Oceania samples, which is significant as pine-pitch type technology has not been previously recorded for Oceania. More research is required to deduce whether a process similar to pitch-making has been traditionally used in this region.

Resin from species of *Callitris, Actinostrobus* and *Prumnopitys* have been characterised for the first time. Callitrisic acid has also been detected in some ethnographic artefacts, tentatively identifying the presence of *Callitris* resin based on the biomarker principle. However, more research into these resins is required for a more confident identification.

9.2.2 Diterpenoid resins from the Angiosperms

The diterpenoid resins from the Angiosperms have been categorised here as spinifex- and ironwood-type resins. Spinifex resin is traditionally known to come from *Triodia* plants. No authenticated samples of *Triodia* were available to analyse, however ethnographic samples of putative spinifex and putative *Triodia* sp. resin have been molecularly characterised for the first time. There is an ambiguity around the identity of these resins as there is a discrepancy between the chemical composition of the samples and how they are often labelled or described in the literature.

The ethnographic sample labelled as "*Triodia irritans*" appears to be mainly a phenolic resin, with a diterpenoid component or possibly mixed with a diterpenoid resin, as well as a triterpenoid resin, or else a triterpenoid contamination. To consider the phenolic component as the *T. irritans* resin would make sense as *Triodia* it is a monocot plant, which excretes resin on the surface of the leaves, like *Xanthorrhoea*, which also produces a phenolic resin. However, the ethnographic "cuyallie" and "burga" samples, referred to as spinifex and therefore thought to be sourced from *Triodia*, are of the non-conifer type diterpenic resin. It has therefore been assumed (with caution) that the diterpenoid component of the sample would be *Triodia irritans*, unless the source of the sample has been misidentified totally. No other ethnographic samples showed similarities with the sample labelled as *Triodia irritans*.

Several other examples of the non-conifer type diterpenic resin, similar to the "cuyallie" and "burga" samples, were identified in the ethnographic artefact collection with variations but sharing many similarities. These diterpenoid based resins contain very different compounds to the conifers, and consist mostly of unknown or un-recognised diterpenoids. These samples have generally been referred to in this project as spinifex-type resins.

The non-conifer diterpenic resin characterised in the ethnographic materials formed six distinct groups, arbitrarily labelled A-F, which may represent six distinct species, possibly all in the genus *Triodia*. Similar unknown diterpenic compounds appear in a sample recorded as resin from ironwood, presumed to be the northern ironwood *Erythrophleum chlorostachys*. The ironwood resin has been characterised, and the same resin has been identified on three ethnographic samples.

The chemical characterisation of putative spinifex and ironwood samples is important as the recorded presence of these types of resins are often assumptions based on appearance such as dull colour and plant fibre inclusions. Based on the findings in this project it is hypothesised that the use of spinifex resin in Australia as described in the ethnographic literature may be overestimated, overlooking many other types of resin that may have been used instead.

9.2.3 Triterpenoid resins from the Angiosperms

Triterpenoid resins appear to have been used far more commonly in Oceania than was indicated by the ethnographic literature. The ethnobotanically important nut-bearing tree *Canarium* was hypothesised to be the most important source of triterpenoid resins, particularly in Papua New Guinea. This appears to be true to some extent as *Canarium* resin was identified on at least three ethnographic artefacts, and possibly on another four, plus a similar type of 'elemi' resin, probably also from the Burseraceae family, on a further three artefacts. However, a number of unknown triterpenoid resins were also recognised, either on their own or as part of a mixture with other types of resins. A much larger reference library would be required to identify the unknown triterpenoid resins.

Canarium trees as a resource have been recognised archaeologically by nut remains. It is therefore hypothesised that the resin is likely to also have been used in the more distant past, and that resin referred to as dammar in Oceania may at least in part be sourced from *Canarium*. Analysis of resins found archaeologically could potentially shed light on archaeological questions such as local and managed resources, trade systems and Lapita studies. It appears that triterpenod resin use in Melanesia was most likely similar to that in near-by Indonesia, Vietnam and the Philippines.

It has been found that *Canarium salomonense* resin is distinguishable from the resin from other *Canarium* species in the region. However, several other *Canarium* resins are not distinguishable from some other resins in the Burseraceae family, at least not using GC-MS analysis alone. These resins are hypothesised to be characteristic of the elemi-type, and are identifiable as originating from the Burseraceae family.

Dammar-type resins were not identified on artefacts from Oceania, only from Borneo, as expected. Several unknown triterpenoid resins have been highlighted, including some with a lupane-type skeleton. Triterpenoid resin use is less common in Australia compared to other types of resin, but is definitely present. Much more research is required for understanding the types of triterpenoid resins native to Oceania, how to identify them, and the scale of their use in Oceania.

9.2.4 Phenolic resins from the Angiosperms

A lot more is collectively known about *Xanthorrhoea* resins than the other types of resin in Oceania. Knowledge of the different species including correlation of certain vernacular names with scientific ones, and therefore which species were being exploited by some particular Aboriginal Australian communities, is relatively well documented. There has been

notable previous chemical research on these resins, which laid the groundwork for identifying *Xanthorrhoea* resins to source species (Duewell; 1997). Identification to species level was found to be possible for most species of *Xanthorrhoea* resin included in this project. Further research is required to test the claims made in this thesis but the results so far are highly promising.

Xanthorrhoea resin was identified in 12 samples, six of which were identified to species. Seven unknown phenolic resins were also highlighted, which deserve further investigation. *Xanthorrhoea resinosa* and *X. preissii* resin have both been identified in ethnographic samples. Some interesting mixes of resins have also been found, which have not been described in the ethnographic literature, such as *Xanthorrhoea* and possible *Callitris* resin. Another unknown resin containing sakuranetin, which has been proposed as a partial marker for *Xanthorrhoea*, but which does not match the overall chemical profile of *Xanthorrhoea* resin, has been highlighted.

9.3 Outcomes and Limitations

9.3.1 Contributions to the wider field

New molecular characterisations of a series of plant resins that have ethnobotanical importance in Oceania have been presented with chromatographic and mass spectral data. The analysis of both known reference materials and ethnographic artefacts with unknown amorphous residues has provided mass spectral information for several unknown resin components including terpenoids, as well as many known compounds that have been identified using a mass spectral library and data from the literature. This large dataset has been presented in sections by resin type in Appendices D to G as a contribution towards the fields

of analytical science and resin analysis. A physical collection of the authenticated resin samples collected from Australia will also be donated to the Economic Botany Collection (EBC) at Royal Botanic Gardens, Kew.

New information about the use of resins over the past 200 years has been discussed, based around the chemistry and identifications of resins on a large number of ethnographic artefacts, from various regions within Oceania and with various functions. This study of ethnographic examples of the use of resin from several identified and unidentified species or genera, the functions that resins serve and technological and social aspects of their use contributes to Oceanian ethnobotanical studies. Additional information on specific artefacts about the resinous material used also contributes to the museum records and collective knowledge.

Contributions to the field of archaeology include a framework for chemically identifying and understanding possible contexts of archaeological resinous finds from Oceania, and in assessing the suitability of GC-MS analysis for archaeological resinous finds from Oceania. This study highlights resin use for less-well documented functions such as medicine and narcotics, as well as the more commonly referenced adhesives and hafting cements. Degradation markers reflecting the use of high temperature heating have been identified in some artefact resin samples, demonstrating a certain amount of technological knowledge of altering the behaviour of resins to suit their purpose, and the first indication of possible pitch-type production in Oceania. Indications of trade based on resin source distributions may be a useful contribution to support and inform existing knowledge of trade in Oceania. Two examples of dammarane-type triterpenic resins in Australia may indicate long-distance trade from Southeast Asia or Indonesia, or else unknown local resins. Evidence of many different resins, possibly previously unrecognised as having ethnobotanical significance, supports an important call for giving archaeological resins more attention.

The addition of chemical information for ethnobotanical materials as well as reference samples from Oceania is important, as very little systematic molecular research has been conducted on resinous samples from Oceania. This project provides an excellent starting point for further investigation into resins and other natural materials in Oceania.

9.3.2 Main outcomes

- The first systematic molecular characterisation of resins from a substantial range of sources with ethnobotanical significance in Oceania, using a single method.
- The first molecular characterisation of resins from a range of types of artefacts from across different parts of Oceania.
- The largest contribution of mass spectral data for methylated components of resins from Oceania and beyond.
- The first molecular characterisation of authenticated resin samples from the conifer genera *Actinostrobus* and *Prumnopitys*, and some secies of *Callitris*.
- Valuable characterisation of samples of putative spinifex and ironwood resin prepared for use.
- Successful identification of certain resins to species in aged samples, including some species of *Agathis*, *Canarium* and *Xanthorrhoea*.
- Contribution of materials knowledge about many individual museum and herbarium items, including discrepencies in botanical identity of a few samples highlighted and suggestions for reassignment provided.
- Publication of results from some particularly interesting items from the pilot study: Bradshaw (2013).

- The first case of *Artocarpus altilis* (breadfruit) resin tentatively identified through chemical analysis on two artefacts, in one case mixed with elemi-type resin.
- Evidence of resins from a wide range of sources being exploited in Oceania, contradicting the impression given by the majority of ethnographic and recent literature on resin use.
- Evidence of mixing different types of resin on the same artefact in multiple cases.
- Evidence of high-temperature heating of conifer resins in multiple cases.
- Evidence that sources of resin are generally geographically defined and correlated with contemporary natural species distributions.
- An argument for the processes applied to resin being more important than source in regard to function.
- A clear indication of the need for further analysis of plant resins alongside other natural materials of ethnobotanical importance from Oceania.
- A methodology and interpretive framework for investigating archaeological artefacts with amorphous residues from Oceania, based on the findings of this study.

9.3.3 Limitations

Certain limitations of this project were foreseen and introduced in Chapter 1. How these and other limitations affect the interpretation of the results and lead to suggested further work is discussed here.

This project focussed solely on the resin within the samples, however it is evident that other materials play a large role in the use of resin in Oceania. The rest of the materials on

the artefacts require further analysis to understand the full context of resin use in Oceania. A larger sample size, and more in-depth studies of smaller research areas are also necessary to gain a more representative picture of resin use.

There are limitations as in any project, due to the size of the museum collection that was sampled, and the size of the reference collection. A satisfactory statistical analysis of chemical differences between different types of resins was not possible due to too few samples, and not enough replicates. Having only a few, and often no replicates of reference samples was anticipated as a limitation (Chapter 1). The main problem to arise from this limitation was a lack of data to investigate the natural variation of resins, for example intra-species variation, which is known to occur with seasonal and topographic differences. It was therefore difficult to deduce whether differences between samples are indications of different species, or natural variation as was most likely demonstrated by the large number of tattooing pigment samples from New Zealand, all identified as *Agathis australis* resin.

The samples included in this project have been characterised chemically, with the results presented largely as raw data. The flora of Oceania is distinct and almost completely different to other parts of the world, with less data available. Full identification proved not to be possible for a large proportion of the compounds separated out in the resin samples. Previous work and published data were used to recognise certain types of compounds; however restricted knowledge about composition and chemical pathways of the specific resins in this project means the identifications of compounds where direct comparisons were not possible should be considered as preliminary.

Methods complementary to GC-MS, for example, FTIR, would be beneficial in characterising unknown resins, however the use of additional methods was not in the scope of this project. This is largely because a second reference library for FTIR analysis would be

required. Work using combined FTIR and GC-MS for analysing some resinous materials has been attempted elsewhere, by Matheson and McCollum (2014).

The limited knowledge of degradation effects on these specific types of resins, for example, the effects of oxidation may also have hindered the identification of resin components. Existing information on the degradation of conifer resins from elsewhere in the world was valuable for extrapolating to the related resin-producing species in Oceania. However, how ageing and degradation affects the other less well studied resins, and how it is recognised in the chromatography, is yet to be researched.

Based on previous research on conifer resins, markers for high temperature heating were recognised in the Oceanian conifer samples. Experimentation would be required to find and recognise high temperature heating markers in the other resin types, but this was beyond the scope of the project. Other chemical changes resulting from anthropogenic processes, such as the uptake of calcium or other compounds from mixtures, have not been specifically considered in this project. More detailed chemical attention would be required to recognise these changes in the data, and ultimately connect them to the effects of technological processes.

As previously stated in Chapter 1, assumptions are inherent when using ethnographic material as analogous to archaeological finds, demanding caution. The main assumptions are that Indigenous communities would have been making similar choices in the distant past as in the more recent past, and that the resinous flora was the same and had similar distributions throughout the past. The first assumption is particularly problematic for example, in cases where commercial or non-traditional sources of resin may have been used for tourist items. Acknowledgement of the second assumption is also important for conclusions about

local resin exploitation, reasons for choice of resins, and apparent indications of trade, where they are based on geographic distributions of resin source species.

9.4 Further work

The next step for investigating the research problem addressed by this project would be geographically smaller, in-depth regional studies incorporating botanical, ethnographical, archaeological and chemical approaches. Areas in which hafting resin has been identified archaeologically would be obvious starting points, such as the Solomon Islands, Santa Cruz, Western Bismarck and New Hebrides (Crosby; 1973) as well as multiple areas within Australia. There is additional further work to be addressed within individual research fields suggested in the following sections.

9.4.1 Ethnobotanical research

The original research plan for this project developed around the extensive collection of resin-related items in the Pitt Rivers Museum (Chapter 1), which still provides a basis for a valuable project for further work in this area. It is proposed that the study of this collection be revisited particularly as such a project would benefit from the findings in this thesis, allowing quicker and easier identification of the resins within the collection. It is apparent from previous reviews of museum collections that there is a lack of information surrounding resinous materials, which has the potential to shed light on other information such as provenance, trade connections and technology about artefacts that may otherwise be unknown. The results of this project can be built on to address this need more widely.

Increasing the reference collection of resins is necessary for further work on resins in Oceania. This may be possible through a botanical study of smaller specific regions in Oceania, and

subsequent sample collection. This may be a way to increase knowledge of triterpenoid resins, and other unknown resin sources available in Oceania. Research on endangered species of conifers and other plants is particularly important for conservation by encouraging cultivation. Increasing the reference materials to include other plant exudates such as kinos, for example *Corymbia*, would also be beneficial.

Research on further ethnographic samples of spinifex, including the putative spinifex samples mentioned in Chapter 4 as well as those in other museums, plus freshly collected samples based on local Aboriginal knowledge, and botanically authenticated samples of *Triodia* spp. resins would help to decipher the confusion surrounding the chemistry and identity of spinifex resin. The results of this project has opened up a clear avenue for further research, and is a step in the right direction, albeit providing more questions than answers. Similar work for ironwood resin and authenticated samples of *Erythrophleum chlorostachys* would also be beneficial.

With regards to further chemical research (section 9.4.3): specifically the development of the mass spectral library of resin components; statistical analysis of the composition of resins; and the identity of specific compounds and potential biomarkers, a much larger reference collection with multiple samples of each species is required. Further work therefore requires the collection of multiple specimens of the same species.

Further qualitative research such as a social science survey would be beneficial to learn more from living First Nations peoples, asking specific questions about sources of resin and current, and historical use of resin within their specific cultures, if known. A guided sample collection expedition would be the ideal opportunity for collecting the most relevant ethnobotanical resin samples.

This type of research should also be applied to other areas of under-researched resinous plants, particularly in other tropical regions in the Americas, Africa and Asia.

9.4.2 Archaeological research

More analysis of archaeological samples is required. It would be beneficial for existing samples, including several suggested in this thesis, to be re-examined using molecular analysis. Resinous finds are thankfully being recognised more often by archaeologists, but the significance of chemical analysis needs to be disseminated to encourage sampling of such finds for analysis in a more standardised way. This may be achieved by reaching out to commercial archaeological units, particularly in Australia, and strengthening relationships between archaeological units and university research laboratories.

The application of the methodology used here is effective in characterising the resin components of samples but should be conducted as part of a larger analytical process, as suggested in Chapter 8. At the very least, this thesis should provide a better understanding of the range of resins used in different regions of Oceania, and can be used as a reference for future archaeological research in the area.

9.4.3 Chemical research

There is a need for more chemical research particularly on diterpenoid and triterpenoid resins to resolve taxonomic confusion, as the data in the literature are sporadic and more consistent analyses are required.

Commonly used Australian hafting materials, spinifex and ironwood, are in particular need of this research as problems with matching vernacular names and ethnographic descriptions of the source of the resin with chemical characterisation remain unresolved. Botanically

authenticated samples, alongside a larger scale study of 'spinifex' and 'ironwood' samples would help to resolve the confusion. Variability in these types of resins may be explained as mixtures of materials, or else represent the use of more resinous species than previously appreciated. Several unknown triterpenoid resins have also been highlighted in this study, demonstrating the need for continued research on triterpenoid resins.

Further work on these types of resins may be very significant as it would potentially identify new terpenoids, which may be of use in other research fields, such as pharmaceuticals.

The following paragraphs are suggestions for future chemical analysis of resins for archaeological research.

Statistical analysis

The use of statistical analysis on the chemical data acquired from resin analysis is becoming more common. There is potential for the progress made in fields such as metabolomics to be transferred to archaeological research. The application of chemometrics to plant resin analysis was assessed and attempted within this project for some sets of data and principal components analysis (PCA) was chosen as the most appropriate statistical test for distinguishing between different resins. The method looks to be promising, however, the data was not suitable in this case as the reference collection requires an increased sample size with multiple samples of the same species to produce effective results.

Further work in this area would be beneficial for researching the chemical differences between different resin types, with the potential to place unknown samples easily within a category of resin. It may also be possible to identify abnormalities which may be attributed to anthropogenic technical processes. Another area of important research that would be assisted by statistical analysis is intra-species variation. Again, a large number of resin

samples from the same species would be necessary to study this, probably more suited to narrower-focussed studies of individual resin species or types.

Instrumental analysis

In order to achieve easily comparable data that have been produced at different times, on different instruments etc., using an easily available pre-made set of alkane internal standards could be used to allow for comparisons using a retention index. Kovat's retention index was developed specifically for this purpose, in the analysis of essential oils, and retention indices are used systematically throughout the world. This would likely make future comparisons much easier and simpler. It is recommended that any future development of the resin compound mass spectral library should adopt this system.

The database of resin compounds needs to be improved, increased, and made accessible for analysts to use and contribute to, in order to build the database. The ChemStation library created and developed throughout this project needs further work including deconvolution and clarification of individual compounds before it is a suitable tool for further use as a mass spectral library, and transferring to a more up-to-date software platform. Potential new compounds need to be confirmed, then isolated and researched. This research could be beneficial to medical as well as archaeological, ethnographic and art-conservation research. As terpenoids have been found to have anti-bacterial, anti-fungal and even anti-cancer effects, the discovery of any new terpenoids could have great significance for medical research.

Experimental work

Experimental archaeology on the effects of different tempering materials on different resins, in terms of both physical properties and chemical signatures would be of interest for the

study of the processes applied to the resins, particularly regarding hafting versus non-hafting functions. Similarly, systematic heating experiments on conifer resins to test for heating markers as has been hypothesised in this study, would be of value, as would investingative heating experiments on non-conifer resins. Experimentation in pitch-making using the Oceanian resins, particularly *Araucaria* resin, would also hold value for observing the effects on the resin chemistry and if such effects could be recognised through biomarkers.

Further work on the degradation of the specific resins found to occur on the museum samples, and comparisons of different aged samples of resin from the same species would be advantageous for future analysis of museum resins from Oceania. Collaborations with other researchers would be advantageous for further work into the degradation of Oceanian resins, including using advanced analytical methods and accelerated aging experiments, as have been successful on resins from elsewhere.

Further investigation into the effective use of sterile swabs with wooden stems (to avoid plastic contamination) for the sampling of resin on museum samples *in situ* would be beneficial, as was requested by the Pitt Rivers Museum. The framework provided by this study should allow for a higher chance of success in one-shot analysis and smaller sample sizes.

Field-wide collaboration in the collation of chemical data on resins from Oceania using multiple methods would be ideal to achieve a more comprehensive analysis of existing and future archaeological and ethnographic amorphous materials.

Appendix A

The reference samples by taxonomy with photographs

Major group	Family	Genus	Species	Source	Catalogue / ID number	Sample number
Gymnosperms (Non-flowering plants) - Conifers	Araucariaceae Henkel & W.Hochst.	*Agathis* Salisb.	*alba* (Lam.) Foxw.	TRI, Sarawak, Borneo	-	SWF07
				RBG Kew EBC	31022	K001
				RBG Kew EBC	31023	K002
			atropurpurea Hyland	RBG Sydney	13914	S11
			australis (D.Don) Lindl.	RBG Kew EBC	27174	K003
				RBG Kew EBC	27185	K004
			dammara (Lamb.) Rich,	RBG Kew EBC	27225	K005
				RBG Kew EBC	27227	K006
			labillardieri Warb.	RBG Kew EBC	78700	K007
				RBG Kew EBC	78752	K008
			lanceolata Warb.	RBG Kew EBC	27242	K009
				RBG Sydney	-	S16
			macrophylla (Lindl.) Mast.	OU Plant Sciences Dept.	-	OUPS1
				RBG Kew EBC	27241	K010
				RBG Kew EBC	78675	K011
				RBG Kew EBC	27245	K012
				RBG Kew EBC	27244	K014
				RBG Kew EBC	27249	K015
				RBG Sydney	-	S10
				RBG Sydney	-	S17
			microstaschya J.F.Bailey & C.T.White	ABG, Mt. Annan	20010050	MA2
			moorei (Lindl.) Mast	RBG Sydney	-	S13
			ovata (C.Moore ex Vieill.) Warb.	RBG Kew EBC	27246	K13
				RBG Sydney	-	S18
			robusta (C.Moore ex F.Muell.) F.M.Bailey	RBG Sydney	-	S12
			sp.	RBG Kew EBC	31008	K058
			sp.	TRI, Sarawak, Borneo	-	SWF06
		Araucaria Juss.	*bidwillii* Hook.	RBG Sydney	-	S04
				RBG Kew EBC	79868	K059
				RBG Kew EBC	31007	K060
			columnaris (G.Forst.) Hook.	RBG Kew EBC	27293	K061
				RBG Kew EBC	78753	K062
			cunninghamii Mudie	RBG Kew EBC	78661	K016
				RBG Kew EBC	78754	K017
				RBG Sydney	-	S01
			heterophylla (Salisb.) Franco	RBG Sydney	15960	S09
		Wollemia W.G.Jones, K.D.Hill & J.M.Allen	*nobilis* W.G.Jones, K.D.Hill & J.M.Allen	BMBG, Mt. Tomah	-	MT01
				ABG, Mt. Annan	-	MA01
	Cupressaceae	*Actinostrobus* Miq.	*arenarius* C.A.Gardner	ABG, Mt. Annan	854330	MA04
			pyramidalis Miq	ABG, Mt. Annan	865921	MA05
				ABG, Mt. Annan	865921	MA06
		Callitris Vent	*columellaris* F.M.Bailey	RBG Kew EBC	31055	K041
				RBG Sydney	-	S08
			endlicheri F.M.Bailey	RBG Kew EBC	28666	K042
				RBG Kew EBC	28668	K043
				ABG, Mt. Annan	892013	MA07
				ABG, Mt. Annan	842770	MA08
			preissii Miq	RBG Kew EBC	28675	K044
				RBG Kew EBC	28678	K045
				ABG, Mt. Annan	870737	MA09
				ABG, Mt. Annan	853316	MA10
				ABG, Mt. Annan	865813	MA11
			sp.	RBG Kew EBC	40572	K063
	Podocarpaceae	*Prumnopitys* Phil	*ladei* (F.M.Bailey) de Laub	RBG Sydney	-	S19

Photographs of Gymnosperm Reference Samples


SWF07


K001


K002


S11

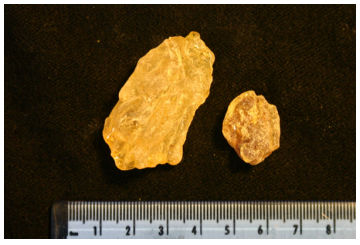

K003


K004


K005

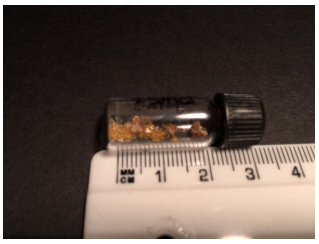

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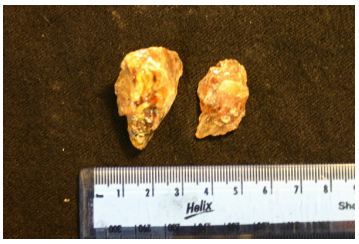

K008


K009


S16


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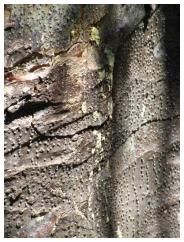

K010


K011


K012


K014


K015

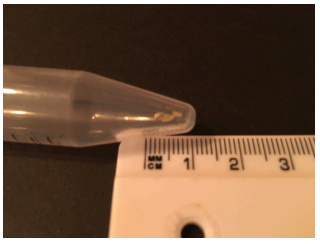

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S17

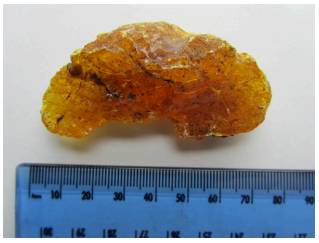

MA2


S13


K13


S18

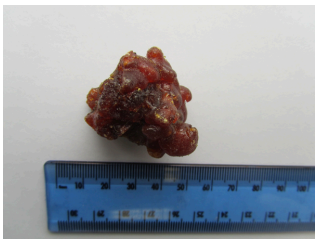

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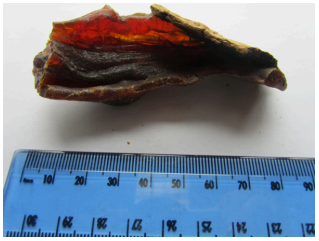

K058


SWF06


S04


K059


K060


K061


K062



K016



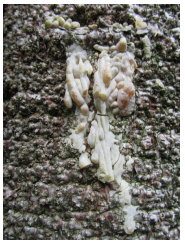
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S01


S09



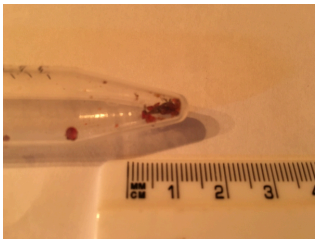
MT01



MA01



MA04



MA05



MA06



K041



S08



K042



K043



MA07



MA08



K044



K045



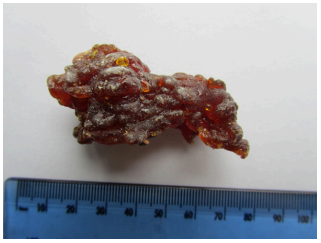
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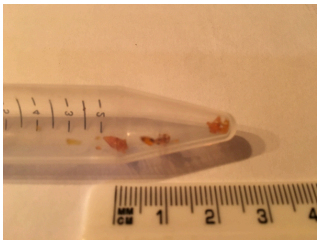
MA10



MA11



K063



S19

Major group	Family	Genus	Species	Source	Catalogue / ID number	Sample number
Angiosperms (Flowering plants)	Anacardiaceae	*Anacardium* L	*occidentale* L.	RBG Kew EBC	61856	K100
		Semecarpus L.f.	*atra* (G. Forst.) Vieill.	AM EBC, ABG Mt. Annan	7714	EB04
	Apiaceae	*Aciphylla* J.R.Forst. & G.Forst.	sp.	RBG Kew EBC	54032	K074
			sp.	RBG Kew EBC	54031	K075
	Araliaceae	*Polyscias* J.R.Forst & G.Forst.	*elegans* (C,Moore & F.Muell.) Harms	RBG Sydney	-	S15
	Arecaceae	*Daemonorops* Blume	*draco* (Willd.) Blume syn. propinqua	RBG Kew EBC	73015	K069
	Burseraceae	*Aucoumea* Pierre	*klaineana* Pierre	RBG Kew EBC	76035	K080
		Bursera Jacq. ex L	*simaruba* (L.) Sarg	AM EBC, ABG Mt. Annan	7443	EB08
		Canarium L.	*bengalense* Roxb.	RBG Kew EBC	63214	K081
			indicum L.	RBG Kew EBC	63226	K018
				RBG Kew EBC	63485	K083
				RBG Kew EBC	64319	K084
			luzonicum (Blume) A. Gray	RBG Kew EBC	63270	K019
				RBG Kew EBC	63494	K020
			oleosum (Lam.) Engl.	RBG Kew EBC	63230	K086
			paniculatum (Lam.) Benth. ex Engl.	RBG Kew EBC	64285	K082
			salomonense B. L. Burtt	RBG Kew EBC	63237	K021
			schweinfurtii Engl.	RBG Kew EBC	76033	K087
				RBG Kew EBC	78666	K088
				RBG Kew EBC	76038	K101
			similajau * unrecognized name	TRI, Sarawak, Borneo	-	SWF10
			strictum Roxb.	RBG Kew EBC	63276	K092
				RBG Kew EBC	63250	K093
				RBG Kew EBC	63248	K094
			sumatranum Boerl. & Koord.	RBG Kew EBC	63252	K095
			zeylanicum (Retz.) Blume	RBG Kew EBC	63254	K096
			sp.	RBG Kew EBC	63274	K089
			sp.	RBG Kew EBC	63264	K090
			sp.	RBG Kew EBC	63256	K091
			sp.	RBG Kew EBC	63280	K102
		Dacryodes Vahl	*edulis* (G.Don) H.J.Lam	RBG Kew EBC	64309	K085
		Protium Burm.f.	*guianense* March.	AM EBC, ABG Mt. Annan	7434	EB06
	Clusiaceae / Calophyllaceae	*Calophyllum* L.	*hosei* Ridl.	TRI, Sarawak, Borneo	-	SWF11
			inophyllum L.	RBG Kew EBC	66533	K097
			tacamahaca Willd.	RBG Kew EBC	66744	K098
			tomentosum Wight	RBG Kew EBC	66539	K099
	Cunoniaceae	*Ceratopetalum* Sm.	*gummiferum* Sm.	RBG Kew EBC	56968	K071
	Dipterocarpaceae	*Anisoptera* Korth.	*grossivenia* V.Sloot	TRI, Sarawak, Borneo	-	SWF08
			marginata Korth.	TRI, Sarawak, Borneo	-	SWF09
			thurifera (Blanco) Blume	RBG Kew EBC	78756	K054
		Dipterocarpus C.F.Gaertn.	*globosus* Vesque	TRI, Sarawak, Borneo	-	SWF02
			sarawakensis Slooten	TRI, Sarawak, Borneo	-	SWF01
		Shorea Roxb. Ex C.F.Gaertn.	*lunduensis* P. S. Ashton	TRI, Sarawak, Borneo	-	SWF04
			scabrida Symington*	TRI, Sarawak, Borneo	-	SWF05
			sp.	TRI, Sarawak, Borneo	-	SWF03
		Vatica L.	*mangachapoi* Blanco	TRI, Sarawak, Borneo	-	SWF12
			pafuna * unrecognized name	RBG Kew EBC	79870	K055
			rassak Blume*	RBG Kew EBC	78755	K057
			sp.	AM EB, ABG Mt. Annan	7116	EB02
	Moraceae	*Artocarpus* J.R.Forst & G.Forst	*altilis* (Parkinson ex F.A.Zorn) Fosberg	RBG Kew EBC	42761	K053

Photographs of Angiosperm Reference Samples

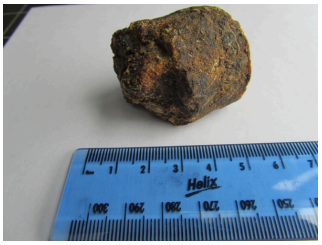


K100


EB04

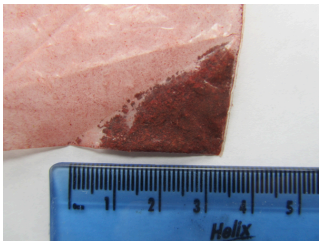


K074



K075

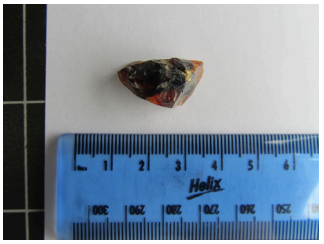

S15



K069


K080


EB08



K081



K018

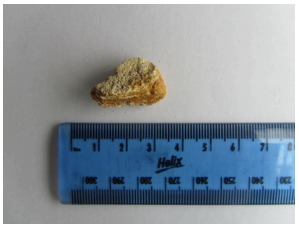


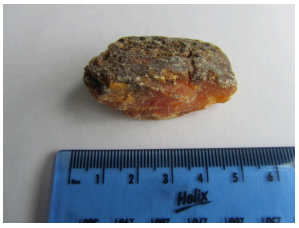
K083


K084


K019

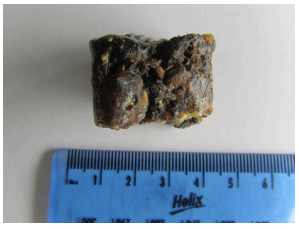

K020


K086

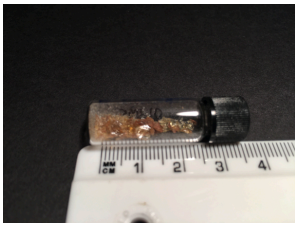

K082


K021


K087

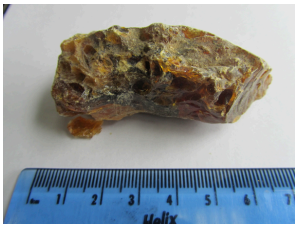

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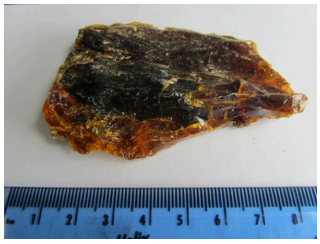

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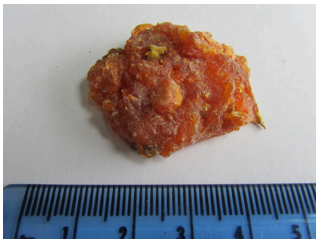

SWF10

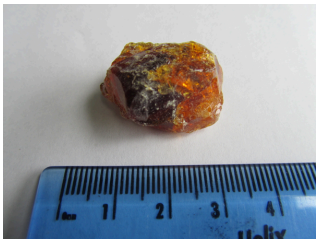

K092

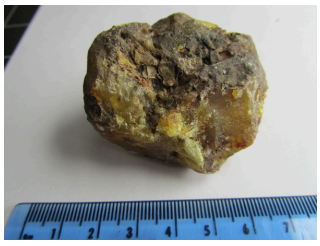

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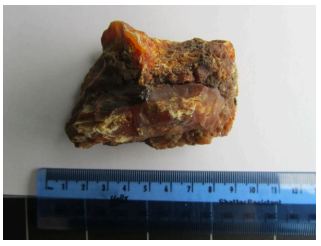

K094


K095

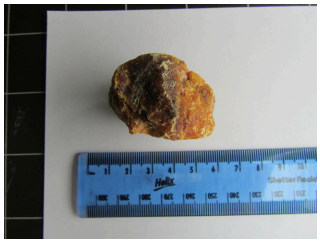

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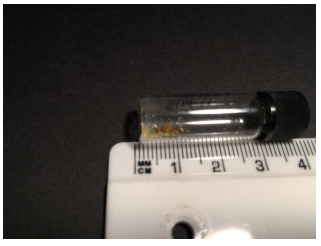

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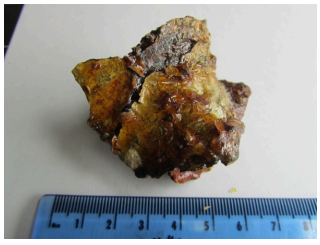

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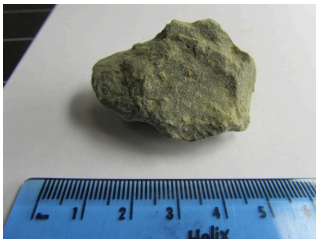

K102


K085


EB06


SWF11


K097


K098

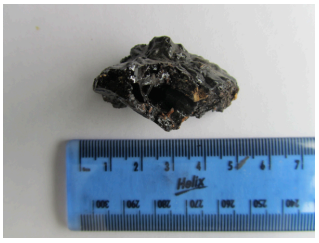

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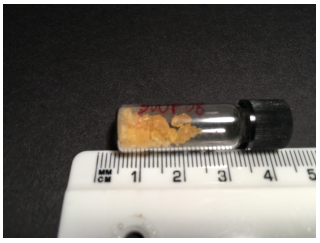
NB There are no photographs for samples SWF02 and SWF01

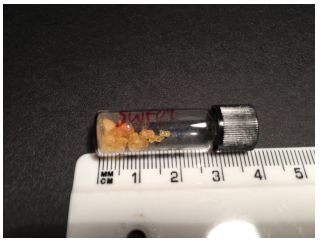
Major group	Family	Genus	Species	Source	Catalogue / ID number	Sample number
Angiosperms (Flowering plants)	Myrtaceae	*Angophora* Cav.	*costata* (Gaertn.) Hochr.	RBG Kew EBC	78668	K072
			floribunda (Sm.) Sweet	RBG Kew EBC	78665	K073
				RBG Sydney	-	S05
		Arillastrum Pancher ex Brongn. & Gris	*gummiferum* (Brongn. & Gris) Pancher ex Baill.	AM EB, ABG Mt. Annan	-	EB01
	Poaceae	*Triodia* R.Br.	*irritans* R.Br.	RBG Kew EBC	33340	K070
	Protaceae	*Grevillea* R.Br. ex Knight	*robusta* A.Cunn. ex R.Br.	RBG Kew EBC	44994	K076
				RBG Kew EBC	46683	K077
			striata R.Br.	RBG Kew EBC	44996	K040
	Rubiaceae	*Gardenia* J.Ellis	*aubryi* Vieill.	AM EB, ABG Mt. Annan	5963	EB15
	Rutaceae	*Flindersia* R.Br.	*maculosa* (Lindl.) Benth.	RBG Kew EBC	63858	K046
	Scrophulariaceae	*Myoporum* Banks & Sol. ex	*platycarpum* R.Br.*	RBG Kew EBC	46261	K047
				RBG Kew EBC	46262	K048
	Xamiaceae	*Macrozamia* Miq.	*spiralis* (Salisb.) Miq	RBG Kew EBC	29160	K064
	Xanthorrhoeaceae	*Xanthorrhoea* Sol. ex Sm.	*arborea* R.Br.	RBG Kew EBC	36438	K022
				RBG Kew EBC	36439	K023
			australis R.Br.	RBG Kew EBC	36423	K024
				RBG Kew EBC	40556	K025
			johnsonii A.T.Lee	RBG Sydney	-	S06
			media R.Br.	RBG Sydney	-	S03
			preissii Endl.	RBG Kew EBC	35426	K027
				RBG Kew EBC	36427	K028
			quadrangulata F.Muell.	RBG Kew EBC	36433	K033
				RBG Kew EBC	79872	K034
			resinosa Pers.	RBG Kew EBC	36453	K026
				RBG Kew EBC	35422	K029
				RBG Kew EBC	36440	K030
			semiplana tateana (F.Muell.) D.J.Bedford	RBG Kew EBC	36429	K031
				RBG Kew EBC	36430	K032
			sp.	RBG Kew EBC	36428	K066
			sp.	RBG Kew EBC	36454	K067
			sp.	RBG Kew EBC	36421	K068
			sp.	Ku-Ring-Gai Chase National Park, NSW	-	NSW1
			sp.	WA Bush	-	WA1
Insecta	Apidae	*Apis* Linnaeus	*mellifera* Linnaeus	Neal's Yard Remedies	-	BWX1

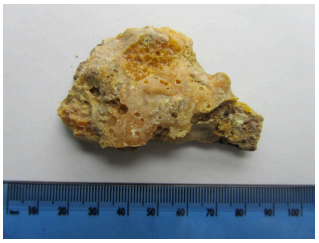
* Unresolved name (GBIF 2018)

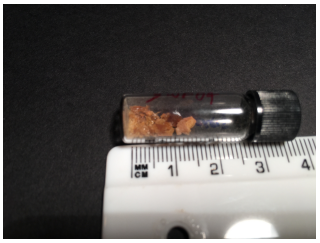
Photographs of Angiosperm and Beeswax Reference Samples


K071


SWF08

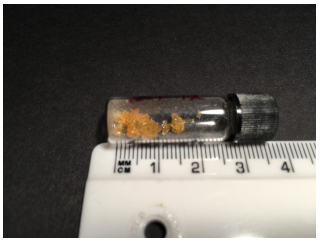

SWF09

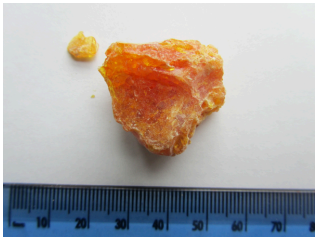

K054

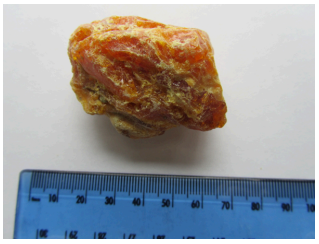

SWF04


SWF05


SWF03

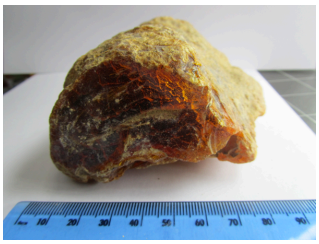

SWF12


K055


K057


EB02


K053



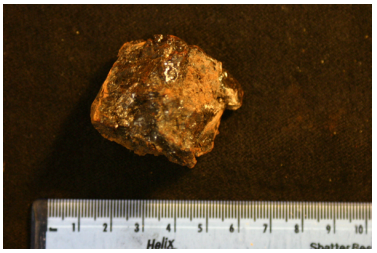
K064



K022



K023



K024



K025



S06



S03



K027



K028



K033



K034



K026



K029



K030



K031



K032



K066



K067



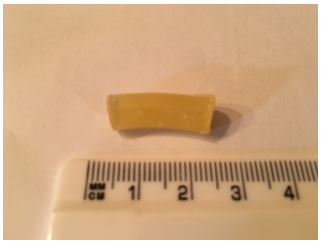
K068



NSW1



WA1



BWX1

Appendix B

The ethnographic samples by museum collection

Australian Museum

Sample Number	Accession Number	Item Description	Origin	Resin Description
AM01	E17281	Shell Hoe (Model)	Mer Island, Torres Strait	Dark, reddish brown.
AM02	E17283	Shell Hoe (Model)	Mer Island, Torres Strait	Dark, reddish brown.
AM03	E17241	Spearthrower Tip	Mer Island, Torres Strait	Dark, orangey brown. Long thin plant fibre inclusions.
AM04	E17241	Spearthrower Base	Mer Island, Torres Strait	Dark, orangey brown. Sand inclusions.
AM05	E17241	Spearthrower Handle	Mer Island, Torres Strait	Black, shiny.
AM06	E75660	Adze	North-West, SA	Dark brown. Straw-like plant fibre inclusions.
AM07	E67922	Forehead Ornament	Central Australia, NT	Very fine fibre inclusions, possibly hair.
AM08	E20705	Firestick Sheath	Far North, Qld	Dark brown.
AM09	E74915, c	Firestick Sheath Handle	Weipa, Qld	
AM10	E74915	Firestick Sheath Ball	Weipa, Qld	
AM11	E35571	Quartz Knife	Central Australia	Plant fibre inclusions.
AM12	AUR455	Ornament	Torres Strait	
AM13	E13335	Water Carrier (Bark Bucket) Seam	Far North, Qld	
AM14	E13335	Water Carrier (Bark Bucket) Repair	Far North, Qld	
AM15	E13335	Water Carrier (Bark Bucket) Inner Sealing	Far North, Qld	
AM16	E26007	Pottery Vessel Coating	Fiji	Yellow (taken from base).
AM17	E79383	Pottery Container Coating	Fiji	Yellow (taken from base).
AM18	E5349	Vegetable Gum Resin	PNG	
AM19	E78034	Resin	Gilber Islands, Kiribati, Micronesia	
K065	76107	Lump of tree resin used as fuel	Papua New Guinea	Orange, brittle.
K070	33340	Spinifex resin (*Triodia irritans* R.Br)	NW Australia	Dark brown. Plant inclusions.
K080	76035	Torch wrapped in bark (*Aucoumea klaineana*)	Unknown origin	
K083	63485	Resin wrapped in leaf (*Canarium commune*)	Unknown origin	Orange, black round edges.
K101	76038	Torch (*Canarium schweinfurthii*)	Unknown origin	
K102	63280	Torch (*Canarium* sp.)	Unknown origin	

Peabody Museum of Archaeology and Ethnology at Harvard University

Sample Number	Accession Number	Item Description	Origin	Resin Description
PBH001	39-17-70/1393	'Medicine' box	Kamwa, West Papua	Amber colour. Brittle.
PBH002	36-27-70/345	Shark Tooth Dueling Knife Handle	Far North, Qld	Dark, blackish brown. Soft.
PBH003	36-27-70/345	Shark Tooth Dueling Knife Teeth Inserts/Blade	Far North, Qld	Dark, blackish brown. Fairly soft.
PBH004	51-32-70/3290	Spear Thrower Tip	Far North, Qld	Reddish brown, flakey.
PBH005	51-32-70/3290	Spear Thrower Handle	Far North, Qld	Reddish brown, brittle.
PBH006	51-32-70/3290	Spear Thrower Base	Far North, Qld	Dark, blackish brown. Shiny, brittle.
PBH007	37-98-70/746	Stick of resin for hafting.	Qld	Dark, blackish brown. Friable.
PBH008	18-20-70/D-1224 (135383)	Shark Hook Haft.	Admiralty Islands, PNG	Dark, blackish brown. Flakey.
PBH009	18-20-70/D-1224 (135383)	Shark Hook Handle.	Admiralty Islands, PNG	Dark, blackish brown.
PBH010	32-68-70/D3947.1 SCR	Spear	Kimberley, WA	Dark black, orange surface. Brittle.
PBH011	23-46-70/D-1735	Processed Spinifex.	Kimberley, WA	Black. Crumbly.
PBH012	32-68-70/D-3962	Spearthrower Tip	Murchison, WA	Brownish orange. Brittle.
PBH013	32-68-70/D-3962	Spearthrower Base	Murchison, WA	Orangey brown. Brittle.
PBH014	67-10-70/249	Fishhook.	New Zealand	Amber colour. Brittle.
PBH015	46-78-70/2400	Pigtooth Necklace	New Hebrides, Vanuatu	Brownish black, friable.
PBH016	04-19-70/63232	Wooden Bowl Outer	Sarawak, Borneo, Malaysia	Orange. Sticky.
PBH017	04-19-70/63232	Wooden Bowl Inner	Sarawak, Borneo, Malaysia	Brown. Crumbly.
PBH018	51-33-70/3224	Stone Adze	Cooper Creek, SA	Blackish brown. Friable.
PBH019	22-29-70/D1696	Stone Axe	Kimberley, WA	Blackish brown. Friable.
PBH020	23-47-70/D1798.1	Wooden Comb	Santa Cruz, Solomon Islands	Blackish brown. Friable.
PBH021	23-47-70/D1798.2	Wooden Comb	Santa Cruz, Solomon Islands	Dark brown. Friable.
PBH022	23-47-70/D1798.3	Wooden Comb	Santa Cruz, Solomon Islands	Dark brown. Flakey.
PBH023	07-30-70/72470	Comb	San Cristobal Isle, Soloman Islands	Dark brown. Friable.
PBH024	64-18-70/4471	Amber-like Stone	Papua (West New Guinea)	Yellow amber colour. Brittle, aromatic.
PBH025	2004.1.620	Handle Fragments	Australia	Reddish brown. Friable (leaves stain).
PBH026	2004.1.631	Handle of Stone Knife	Australia	Medium brown. Crumbly.
PBH027	26-53-70/D2690	Stone Knife	Kimberley, WA	Dark brown. Crumbly.
PBH028	2004.1.633	Resin Residue on Knife	Kimberley, WA	Blackish brown. Flakey.

Sample Number	Accession Number	Item Description	Origin	Resin Description
PBH029	2004.1.273	Shells in Resin – Black Resin	Oceania	Yellowish black. Glassy, brittle.
PBH030	2004.1.273	Shells in Resin – Yellow Resin	Oceania	Yellow. Opaque, friable.
PBH031	99-29-70/56075	Shell Pendants	PNG	Brown. Flakey.
PBH032	2004.1.577	Tusk Ornament	PNG	Blackish brown. Flakey.
PBH033	32-68-70/D4027	Paper Bark Bucket Seam	Kimberley, WA	Reddish brown. Crumbly.
PBH034	32-68-70/D4027	Paper Bark Bucket Rim	Kimberley, WA	Blackish brown. Crumbly.
PBH035	32-68-70/D4027	Paper Bark Bucket Inner	Kimberley, WA	Probably not resin, just bark?
PBH036	12-4-70/84534	Knife/Sword	Borneo, Malaysia	Dark brown. Friable.
PBH037	51-32-70/3295	Firesticks in Sheath - Sheath	Far North, Qld	Blackish brown. Soft.
PBH038	51-32-70/3295	Firesticks in Sheath – Ball (Abrus Seeds)	Far North, Qld	Dark brown. Fairly Soft.
PBH039	51-32-70/3289	Spearthrower Tip	Far North, Qld	Blackish brown. Friable.
PBH040	51-32-70/3289	Spearthrower Handle	Far North, Qld	Yellowish brown. Brittle.
PBH041	51-32-70/3289	Spearthrower Base Shell Adhesive	Far North, Qld	Brown. Friable, with sand inclusions.
PBH042	30-54-70/D3473	Spearthrower Tip	Arnhem Land, NT	Brownish black. Brittle.
PBH043	30-54-70/D3473	Spearthrower Base	Arnhem Land, NT	Pale brown. Probably not resin – mud/cement?
PBH044	51-32-70/3270	Spearhead Point	Darwin, NT	Brown. Friable with smoothed surface and plant fibres throughout.
PBH045	30-54-70/D3449.1	Ground Hafted Axe	Arnhem Land, NT	Dark, reddish brown. Very friable.
PBH046	43-5-70/2247	Stone Knife	Central North, NT	Dark brown with red surface (ochre?). Plant fibre inclusions.
PBH047	36-122-70/568	Stone Knife with Sheath - Knife	Tennant Creek, NT	Brown. Friable with plant fibre inclusions.
PBH048	36-122-70/568	Stone Knife with Sheath - Sheath	Tennant Creek, NT	Brownish white (white pigment?)
PBH049	36-122-70/572	Stone Knife with Wooden Handle	Tennant Creek, NT	Brown. Plant fibre inclusions (red and yellow ochre)
PBH050	967-71-70/4658	Wooden Adze	West Qld	Brownish black. Fairly brittle.
PBH051	08-36-70/74411	Bani Gum.	Luzon, Philippines	Yellowy amber colour. Brittle, small stone inclusions throughout.
PBH052	25-46-70/D2441	Spearthrower Base	Laverton. WA	Medium brown. Semi-brittle.
PBH053	25-46-70/D2425	Spearthrower Tip	Kimberley, WA	Brown. Plant fibre inclusions.
PBH054	32-68-70/D3961	Spearthrower Tip	South-West, WA	Dark brown. Fairly friable.

Sample Number	Accession Number	Item Description	Origin	Resin Description
PBH055	32-68-70/D3961	Spearthrower Base	South-West, WA	Reddish brown. Friable.
PBH056	32-68-70/D3942.1	Stick/Club Tip	South-West, WA	Reddish brown. Some plant inclusions.
PBH057	32-68-70/D3942.1	Stick/Club Base (smaller end)	South-West, WA	Reddish brown. Glassy, brittle.
PBH058	15-14-70/86042	Stone-headed Club	PNG	Yellow. Glassy, brittle with shell inclusions.
PBH059	52-4-70/3575	Arrow – Resin Coating over Hafting Binding	Kundiawa, PNG	Reddish brown (very red on top – ochre? Poss a mixture of resins, some brown some red). Soft.
PBH060	64-18-70/4556.6	Arrow	Papua (West New Guinea)	Black. Brittle.
PBH061	47-73-70/2801.1	Arrow – Thin Black Coating (all over)	Upper Sepik River, PNG	Black (scrapings from coating).
PBH062	40-63-70/1974	War Club (painted red and white)	Fiji	Brown (under the red paint). Flakey.
PBH063	39-17-70/1292	Arrow – Black Coating over Hafting Binding	Sainke Doek, West Papua	Black. Flakey.
PBH064	39-17-70/1278	Two-pronged Arrow with Black Coating on Prongs and Binding – resin from prong insert seal	Sainke Doek, West Papua	Black. Friable.
PBH065	39-17-70/1283	Arrow with Black Coating – resin from where prong is inserted into bamboo shat and sealed with black resin	Sainke Doek, West Papua	Black. Friable.
PBH066	58-55-70/3875	Painted Bark Bucket Rim	Melville Islands, NT	Brown. Soft.
PBH067	35-92-70/323	Sword (pieces of resin fallen onto paper)	Sarawak, Borneo, Malaysia	Yellow. Opaque, friable.
PBH068	51-32-70/3260	Boomerang – Smear of Black Resin in Centre	Barrows Creek, NT	Black. Very thin and brittle.
PBH069	51-32-70/3259	Boomerang – Smear of Black Resin on End	Daly Waters, NT	Black. Fairly soft.
PBH070	25-46-70/D2419	Hafted Axe	Kimberley, WA	Ch8
PBH071	974-52-70/5536	Adze	Ontong Java, Solomon Islands	Dark brown. Friable.
PBH072	970-29-70/4762	War Club “Subi”	Solomon Islands	Brown. Friable, cracked and flakey.
PBH073	2004.1.276	Basket – Resin coating and filling of gaps of basket weave	Oceania	Brown. Friable.
PBH074	04-19-70/63130	Sculpture of Hornbill – adhesive holding hairs in eyespace (button missing)	Borneo, Malaysia	Brown. Shiny surface.
PBH075	47-72-70/2754	Staff Inlaid with Shell - Cement	Ysabel Isle, Solomon Islands	Reddish brown. Friable.
PBH076	970-29-70/4760	War club “Kaetau” – Cement for shell inlay	North Malaita, Solomon Islands	Orange. Glassy, brittle.
PBH077	47-54-70/2520	Carved Club – Adhesive for eyes of shell?	Ambrym Isle, Malampa Province, Vanuata	Dark brown on surface, white underneath.

Sample Number	Accession Number	Item Description	Origin	Resin Description
PBH078	48-56-70/3077	Stone-headed Club (sampled from bag of loose bits)	New Britain, PNG	Reddish brown. Glassy.
PBH079	996-22-70/5726	Spear	Melville Islands, NT	Blackish brown. Slightly soft, slightly flakey.
PBH080	47-54-70/2524	Bamboo Arrow Haft	Nikaura, Epi, Vanuatu	Dark, reddish brown. Thin, shiny.
PBH081	47-54-70/2524	Bamboo Arrow Residue	Nikaura, Epi, Vanuatu	Pale brown. Crumbly, matte.
PBH082	01-7-70/566761	Bamboo Arrow	Cairns, Northeast Qld	Dark brown. Slightly friable.
PBH083	40-12-70/1812.1	Bamboo Arrow	Bougainville Isle, PNG	Yellowish brown. Very thin, very smooth. (Very small amount)
PBH084	46-78-70/2387	Bamboo Arrow Haft	Soloman Islands	Dark brown. Smooth, thin.
PBH085	46-78-70/2387	Bamboo Arrow - Residue on Tip	Soloman Islands	Black. Grainy, thick, flakey.
PBH086	91-6-70/50645.1	Bamboo Arrow - Resin under/inserted into cane – wrapping around the outside.	Niue, Cook Islands, NZ (Polynesia)	Pale yellow. Shiny, transparent, brittle.
PBH087	40-12-70/1797	Bamboo Arrow - Resin at end of base, joining string to wood –very solid.	Bougainville Isle, PNG	Black. Slightly friable, quite hard.
PBH088	23-46-70/D1727	Medical Bone – Resin in one end of bone.	Kimberley, WA	Red. Hard, slightly brittle.
PBH089	23-68-70/D4006	Mourning Nose Stick	Mt Keith, WA	Black. Shiny, brittle.
PBH090	23-46-70/D1751.1	Cowrie Medicine Shell	Kimberley, WA	Black. Brittle, fairly smooth (apart from fingerprints).
PBH091	23-46-70/D1751.2	Cowrie Medicine Shell	Kimberley, WA	Black. Brittle, fairly smooth (apart from fingerprints).
PBH092	23-46-70/D1751.3	Cowrie Medicine Shell	Kimberley, WA	Black. Brittle, fairly smooth (apart from fingerprints).
PBH093	32-68-70/D4049.2	Women's Medicinal Headband (2 of 10)	NT, Australia	Brick red. Soft, friable, probably not resin.
PBH094	32-68-70/D4049.6	Women's Medicinal Headband (2 of 10)	NT, Australia	Brick red. Soft, friable, probably not resin.
PBH095	26-53-70/D2692	Shell Resin Pendant	North West Kimberley, WA	Dark, blackish brown. Shiny, friable.
PBH096	36-122-70/588	Body Ornament – Four lumps	Northern Qld	Looks like spinifex. Some red on inner joins.
PBH097	46-78-70/2312	Axe or Hammer	South Western, WA	Slightly reddish brown. Fairly friable, occasional small stone inclusions.
PBH098	51-32-70/3277	Ceremonial Stone Axe	North Australia	Pale, reddish brown. Slightly friable.
PBH099	967-71-70/4676	Bone Pointer	Australia	Brown. Shiny, quite brittle.

Sample Number	Accession Number	Item Description	Origin	Resin Description
PBH100	30-54-70/D3444	Iron Wood Resin on a Stick	Arnhem Land, NT	Dark red. Shiny, brittle.
PBH101	20-42-70/D1310	Axe Handle	Kimberley, WA	Reddish black. Very shiny and friable. Possibly kino or gum.
PBH102	32-68-70/D4028	Black Gum Used for Fixing Spearheads	South West, WA	Reddish black. Very shiny and brittle.
PBH103	25-46-70/D2420	Lump of Gum 'Cagera'	Kimberley, WA	Brown. Friable with lots of inclusions.
PBH104	23-46-70/D1734	Unrefined Spinifex Gum 'Cuyallie'	Kimberley, WA	Reddish brown. Friable with plant material inclusions.
PBH105	30-54-70/D3455.3	Spearthrower – black resin on peg haft	Arnhem Land, NT	Dark brown. Soft, sticky.
PBH106	30-54-70/D3455.3	Spearthrower – red resin on peg haft	Arnhem Land, NT	Light red. Soft, friable with plant material inclusions.
PBH107	96-25-70/49482.1	Throwing Club	Qld	Dark brown. Thin coating, friable.
PBH108	30-54-70/D3438.1	Flaked Stone Spearhead? With Bitumen?	Arnhem Land, NT	Dark brown. Smooth, slightly brittle.
PBH109	23-46-70/D1748.3	Emu Feathers	Kimberley, WA	Brown. Friable with plant fibres.
PBH110	23-46-70/D1748.4	Emu Feathers	Kimberley, WA	Brown. Friable.
PBH111	32-68-70/D3944	Chisel/Ceremonial Throwing Stick	Kimberley, WA	Mid-brown. Friable with plant fibres.
PBH112	96-25-70/49474.1	Spearthrower	Qld	Brown. Matte on outside. Slightly yellow and glassy on inside. Brittle.
PBH113	967-91-70/4651	Concave Spearthrower	River Murray, SA	Brown. Slightly brittle.
PBH114	30-54-70/D3421	Smoking Pipe - End	Arnhem Land, NT	Brown. Slightly friable.
PBH115	30-54-70/D3421	Smoking Pipe - Hole	Arnhem Land, NT	Brown. Very thin.
PBH116	30-54-70/D3421.1	Smoking Pipe – Inside coating	Arnhem Land, NT	Brown. Friable (falling out).
PBH117	20-42-70/D1309.1	Kimberley Spear with Glass Point	Kimberley, WA	Brown underneath the yellow pigment. Slightly brittle.
PBH118	20-42-70/D1309.2	Kimberley Spear with Glass Point	Kimberley, WA	Brown underneath the yellow pigment. Slightly brittle.
PBH119	20-42-70/D1309.3	Kimberley Spear with Glass Point	Kimberley,WA	Brown underneath yellow pigment. Slightly brittle.
PBH120	22-29-70/D1694.1	Kimberley Spear with Stone Point	Kimberley, WA	Brown underneath yellow pigment. Slightly brittle, very hard.
PBH121	22-29-70/D1694.2	Kimberley Spear with Stone Point	Kimberley, WA	Brown underneath yellow pigment. Slightly brittle, very hard.
PBH122	22-29-70/D1694.3	Kimberley Spear with Stone Point	Kimberley, WA	Brown underneath yellow pigment. Slightly brittle, very hard.

Sample Number	Accession Number	Item Description	Origin	Resin Description
PBH123	30-54-70/D3482.1	Hunting and war spear - Haft	Arnhem Land, NT	Reddish brown Fairly friable.
PBH124	30-54-70/D3482.1	Hunting and war spear - Base End	Arnhem Land, NT	Very dark brown. Fairly brittle.
PBH125	30-54-70/D3486	2-pronged fishing spear	Arnhem Land, NT	Reddish brown. Friable.

Pitt Rivers Museum

Sample Number	Accession Number	Item Description	Origin	Resin Description
PRM01	1886.1.1168	Kauri gum specimen, a piece of amber-coloured resin. [El.B DDF Body Arts Project 2010/2011 30/09/2010]	North Island, New Zealand	Amber-coloured
PRM02	1932.13.6	Kauri gum resin.	Great Barrier Island, New Zealand	Amber-coloured
PRM03	1933.40.32		New Zealand	Amber-coloured
PRM04	1933.51.61	Piece of kauri gum, an amber-coloured resin used for making tattooing pigment. [El.B DDF Body Arts Project 2010/2011 30/09/2010]	New Zealand	Amber-coloured
PRM05	1925.23.66	Lump of amber-coloured resin used for making tattooing pigment. [El.B DDF Body Arts Project 2010/2011 29/09/2010]	New Zealand	Amber-coloured
PRM06	1923.87.192 .2	Piece of plant resin used for making tattooing pigment. [El.B DDF Body Arts Project 2010/2011 30/09/2010]	North Island, New Zealand	Amber-coloured
PRM07	1923.87.193		North Island, New Zealand	Amber-coloured
PRM08	1923.87.194		North Island, New Zealand	Amber-coloured
PRM09	1923.87.195		North Island, New Zealand	Amber-coloured
PRM10	1923.87.196		North Island, New Zealand	Amber-coloured
PRM11	1923.87.197		North Island, New Zealand	Amber-coloured
PRM12	1923.87.199		North Island, New Zealand	Amber-coloured
PRM13	1923.87.200		North Island, New Zealand	Amber-coloured
PRM14	1923.87.201		North Island, New Zealand	Amber-coloured
PRM15	1923.87.202		North Island, New Zealand	Amber-coloured
PRM16	1923.87.203		North Island, New Zealand	Amber-coloured
PRM17	1923.87.204		North Island, New Zealand	Amber-coloured
PRM18	1923.87.205	Piece of orange coloured plant resin used for making tattooing pigment. [SM 17/11/2008]	North Island, New Zealand	Amber-coloured

Sample Number	Accession Number	Item Description	Origin	Resin Description
PRM19	1923.87.206	Piece of plant resin used for making tattooing pigment. [El.B DDF Body Arts Project 2010/2011 30/09/2010]	North Island, New Zealand	Amber-coloured
PRM20	1923.87.207		North Island, New Zealand	Amber-coloured
PRM21	1923.87.192 .1		North Island, New Zealand	Amber-coloured
PRM22	1931.86.320	Specimen of plant resin. [El.B DDF Body Arts Project 2010/2011 29/09/2010]	New Zealand	Amber-coloured
PRM23	1914.38.3	Xanthorrhea gum from the base of a burnt grass-tree stem.	Blue Mountains, NSW	
PRM24	1898.75.53	Round lump of gum.	Touranna Plains, WA	
PRM25	1924.63.11	Cowrie filled with spinifex gum, used by the TAKETA (doctor) for rubbing over the affected part.	Sherlock River, WA	
PRM26	1924.33.42(1924.63.12)			
PRM27	1908.70.93 .1-4	4 lumps of bees wax [.1-.4].	Oro Province, PNG	
PRM28	1908.70.94 .1-4	4 lumps of bee's wax or resin used as an adhesive.	Oro Province, PNG	
PRM29	1931.86.335	Gum from the canarium almond tree. Mixed with tobacco to make a cool smoke. In a native packet of palm leaf. [DCF Court Team 9/1/2003]	Bougainville Kurtachi, PNG	

Appendix C

Sample preparation protocol

All resin sub-samples were weighed to under 2mg, to avoid overloading the GC column. Sample preparation involved solvent extraction, derivitisation via methylation using (trimethylsilyl)diazomethane (TMS-DAM), and re-dilution in dichloromethane, by the following method:

Resin sample preparation for GC-MS analysis

1. Place the solid resin sample in a small vial
2. Add 2 drops DCM (and one drop methanol), or until dissolved
3. Reduce to dryness (blow down under nitrogen)
4. Mix 1 part methanol (e.g. 2mL) to 4 parts toluene (e.g.8mL) in a separate beaker – for 12-15 samples
5. Add 10μL TMS-DAM to every 1 mL toluene:MeOH (e.g. 100 μL to above)
6. Add the TMS-DAM:toluene:MeOH dropwise to the sample until in excess (until the yellow colour remains)
7. Leave the vial to stand in the fumehood for 1 hr
8. Quench the reaction by adding acetic acid until the mixture turns colourless
9. Reduce to dryness (blow down under nitrogen)
10. Add 10 drops DCM
11. Transfer into sterile (or wash 3 times with DCM) GC-MS vial inserts
12. Wash syringe 3 times with DCM (or replace disposable tips) in between samples
13. Run in GC-MS

Work on aluminium foil when dealing with solid samples, work under fumehood when using chemicals, wear protective glasses and gloves.

Only make just enough TMS-DAM:toluene:MeOH and use it all, drench any excess with acetic acid.

Remember to prepare and run a method blank (do everything except put a resin sample in the vial)

Make sure reagent is fresh.

Appendix D

Mass spectral data for conifer diterpenoid resin samples (Ch3)

Araucariaceae

Peak	RT	m/z (base peak in bold)	M+	Compound ID	References
a	21.24	55, 81, 91. 105, **121**, 133, 161, 189, 241, 259, 274	-	Unknown	-
b	21.22 (21.80)	55, 91, **121**, 159, 188, 213, 229, 246, 288	-	Unknown	-
c	22.02	**257**, 273, 288	-	Unknown	-
d	21.53 (22.10)	55, 67, **81**, 95, 109, 114, 121, 135, 191, 215, 230, 289	-	Unknown	-
tCA	21.72	79, 81, 93, 105, **121**, 134, 147, 161, 175, 201, 241, 257, 301, 316	316	trans-Communic acid, methyl ester	NIST11; NIST Chemistry WebBook, SRD 69
SA	21.79	91, 105, **121**, 133, 180, 181, 241, 257, 301, 316	316	Sandaracopimaric acid. Methyl ester	NIST11; NIST Chemistry WebBook, SRD 69
e	22.13	55, 81, **121**, 133, 161, 188, 257, 288, 316	-	Unknown	-
f	22.36	93, **135**, 257, 301, 316	-	Unknown	-
DDHA	22.42	91, 115, 141, 165, 197, 209, **237**, 253, 312	312	Didehydroabietic acid, methyl ester	NIST11
g	21.89 (22.43)	55, 67, 81, 95, 114, **123**, 135, 163, 191, 230, 289	-	Unknown	-
h	22.64	55, 79, 91, 107, 121, **135**, 257, 315, 330	-	Unknown	-
j	22.15 (22.72)	55, 81, 93, 107, **121**, 133, 161, 188, 241, 257, 287, 301, 316	-	Unknown	-
AbA	22.97	55, 79, 91, 105, **121**, 136, 195, 213, 241, 256, 273, 301, 316	316	Abietic acid, methyl ester	NIST11; NIST Chemistry WebBook, SRD 69
k	23.00 (23.58)	55, 67, 81, 93, **114**, 121, 133, 149, 161, 175, 189, 207, 227, 246, 273, 288, 302	-	Unknown	-
AtA	23.026	59, 91, 141, 155, 167, 197, **237**, 253, 297, 312	312	6,8,11,13-Abietatetrene-18-oic acid methyl ester	
DHA	23.085	55, 91, 141, 197, **239**, 255, 299, 314	314	Dehydroabietic acid, methyl ester	NIST11
m	23.29	55, 128, 181, **237**, 297, 312, 332	-	Unknown	-
n	23.44	55, 79, 91, **110**, 121, 181, 231, 290, 371	-	Unknown	-
o	23.44	55, 79, 91, 110, **121**, 181, 231, 290, 371	-	Unknown	-
p	23.83	162, 195, **237**, 253, 312, 330	-	Unknown	-
q	23.29 (23.87)	55, 67, 81, 93, **114**, 121, 133, 149, 161, 175, 189, 207, 227, 246, 273, 288, 302	-	Unknown	-
r	23.91	55, 81, 107, **121**, 281, 355, 429	-	Unknown	-
15-HDHA	24.03	59, 197, 237, 255, **315**, 330	330	15-Hydroxydehydroabietic acid, methyl ester	NIST11
AgA	24.11	55, 81, 170, **121**, 189, 249, 271, 302, 345, 362	362	Agathic acid, methyl ester	NIST11
s	24.31	55, 81, 107, **121**, 189, 241, 257, 301, 316	-	Unknown	-
7-Oxo-DHA	24.39	55, 187, 213, **253**, 269, 296, 313, 328	328	7-Oxodehydroabietic acid, methyl ester	NIST11
t	23.92 (24.49)	55, 67, 81, 93, 107, **114**, 121, 133, 147, 159, 173, 201, 219, 258, 289, 303	-	Unknown	-
u	24.49	55, 81, 109, 119, 135, 173, **188**, 216, 248, 281	-	Unknown	-
v	24.82 (25.40)	55, 81, 93, 107, 114, 121, **135**, 147, 161, 175, 189, 207, 241, 288, 303, 347	-	Unknown	-
w	25.43	57, 71, 85, 101, 117, **130**, 131, 190, 203, 267, 343, 399	-	Unknown	-
x	25.17 (25.72)	55, 81, 93, 107, 121, **135**, 147, 161, 175, 189, 203, 243, 303, 316, 361	-	Unknown	-
y	25.12 (25.73)	55, 81, 93, 107, 121, **135**, 147, 161, 175, 189, 207, 227, 243, 281, 303, 316, 361	-	Unknown	-
15-H-7-oxo-DHA	25.77	269, **329**, 344	344	15-Hydroxy-7-oxodehydroabietic acid, methyl ester	NIST11

Non-Araucariaceae (Cupressaceae, Podocarpaceae, miscellaneous)

Peak	RT	m/z (base peak in bold)	M+	Compound ID	References
A	21.84	55, 81, 91, **123**, 133, 257, 271, 286	-	Unknown	-
B	22.09	55, 81, 93, 109, **121**, 137, 161, 175, 201, 257, 316	-	Unknown	-
KA	22.2	55, 79, **91**, 105, 121, 133, 213, 241, 257, 273, 301, 316	316	Kaur-16-en-18-oic acid, methyl ester	
tCA	22.33	79, 81, 93, 105, **121**, 134, 147, 161, 175, 201, 241, 257, 301, 316	316	trans-Communic acid, methyl ester	NIST11; NIST Chemistry WebBook, SRD 69
SA	22.41	91, 105, **121**, 133, 180, 181, 241, 257, 301, 316	316	Sandaracopimaric acid, methyl ester	NIST11; NIST Chemistry WebBook, SRD 69
C	22.58	55, 81, 91, 121, **257**, 273, 288	-	Unknown	-
D	22.64	55, 79, 91, 105, **121**, 134, 147, 161, 175, 201, 241, 257, 301, 316	-	Unknown	-
IPA	22.76	55, 79, 91, 105, 119, 133, 187, 201, **241**, 257, 287, 301, 316	316	Isopimaric acid, methyl ester	NIST11; NIST Chemistry WedBook, SRD 69
CalA	22.8	55, 91, 115, 129, 141, 159, 173, 197, **239**, 255, 299, 314	314	Calitrisic acid, methyl ester (Mass spectrally similar t	NIST11; Gough 1968
E	22.92	55, 159, 171, 185, 199, **202**, 213, 227, 269, 284	-	Unknown	-
F	22.98	55, 69, 91, 115, 128, 149, 159, 175, 189, 201, 271, **286**	286	Ferriginol	NIST11
G	23.08	55, 199, 205b, **229**, 298, 314, 316	-	Unknown	-
H	23.74	55, 91, 115, 173, **189**, 203, 229, 257, 285, 300, 316, 372	-	Unknown	-
J	23.99	55, 91, 109, 115, 128, 203, 217, 231, 245, 271, 286, **314**	-	Unknown	-
K	24.05	55, 69, 115, 128, 159, 173, 215, 243, 257, **285**, 300, 314	-	Unknown	-
L	24.08	59, 91, 115, 141, 128, 162, 195, **237**, 253, 287, 312, 330	-	Unknown	-
KA-13-H	24.26	55, 81, 91, 107, **121**, 135, 146, 173, 254, 273, 299, 314, 332	332	Kaur-16-en-18-oic acid, 13-hydroxy-, methyl ester	NIST11
M	24.34	59, 91, 115, 128, 141, 181, 197, **237**, 255, 297, 315, 330	-	Unknown	-
7-oxo-DHA	24.77	55, 187, 213, **253**, 269, 296, 313, 328	328	7-Oxodehydroabietic acid, methyl ester	NIST11
N	24.96	55, 91, 147, 213, **255**, 315, 330	-	Unknown	-
O	25.14	55, 69, 115, 128, 193, 219, 233, 245, 273, 315, **330**	-	Unknown	-
P	25.34	55, 69, 115, 163, 203, 217, 243, **285**, 300	-	Unknown	-
Q	25.65	55, 91, 128, 147, 175, 188, 227, **269**, 329, 344	-	Unknown	-
R	25.79	55, 91, 115, 128, 165, 203, 231, 245, 259, **275**, 301, 314, 329, 344	-	Unknown	-
15-MDHA	26.15	91, 203, 269, 313, **329**, 344	344	15-Methoxydehydroabietic acid, methyl ester	NIST11

Appendix E

Mass spectral data for non-conifer diterpenoid resin samples (Ch4)

Spinifex

Peak	Figure	RT	m/z (base peak in bold)	M+	Compound description	References
HCA	1a	10.88	51, 65, 77, 91, **104**, 133, 164	164	Hydrocinnamic acid, methyl ester	NIST11; NIST Chemistry WebBook
β-PLA	1b	12.22	51, 65, 77, **91**, 103, 121, 131, 162, 180	180	β-Phenyllactic acid, methyl ester	NIST11; NIST Chemistry WebBook
PA	1c	13.12	53, 63, 91, 121, **149**, 180	180	Piperonylic acid, methyl ester	NIST11; NIST Chemistry WebBook
	1d	14.05	51, 77, 91, 103, 131, **162**	162	Similar to cinnamic acid, methyl ester	NIST11; NIST Chemistry WebBook
	1e	15.24	53, 63, 91, 119, 147, **178**, 210	178	Similar to coumaric acid, methyl ester	NIST11; NIST Chemistry WebBook
	C1	21.37	55, 69, 91, 106, **110**, 119, 138, 152, 184, 189, 207, 318	-	Unknown	-
	1f	21.82	51, 65, 77, 91, 104, 105, 121, 131, **162**	-	Unknown	-
	A1	21.95	55, 69, 81, 95, 109, **123**, 129, 137, 165, 197, 290, 309	-	Unknown	-
	1g	22.61	59, 77, **91**, 103, 121, 131, 162, 179, 203, 216, 260	-	Unknown	-
	A2	22.91	55, 69, 81, 95, 109, **123**, 137, 165, 197, 207, 245, 321	-	Unknown	-
	A3	23.00	55, 69, 81, 95, 109, 125, 157, **179**, 194, 249, 291	-	Unknown	-
	1h	23.15	59, 77, 91, 107, 121, 131, 143, **162**, 203, 222, 289	-	Unknown	-
	1i	23.22	59, 71, 89, **91**, 125, 143, 165, 203, 229, 320	-	Unknown	-
	E1	23.30	55, 69, 95, 109, 121, 135, 163, **191**, 320	-	Unknown	-
	C2	23.37	55, 69, 95, **110**, 121, 135, 163, 191, 289, 320	-	Unknown	-
	C3	23.41	55, 69, 81, 109, **121**, 123, 137, 207, 239, 251, 261, 265, 293, 325, 336	-	Unknown	-
	E2	23.45	55, 69, 81, 95, 109, 121, 135, 174, **191**, 195, 209, 223, 255, 293, 325	-	Unknown	-
	A4	23.56	55, 69, 81, 95, 109, 123, 139, **207**, 261, 293, 334	-	Unknown	-
	C4	23.59	55, 69, 91, 110, 119, 138, **151**, 212, 315	-	Unknown	-
	A5	23.88	55, 69, 81, 95, 109, **123**, 154, 108, 186, 197, 207, 275, 305	-	Unknown	-
	A6	24.02	55, 69, 81, 95, 109, **123**, 139, 165, 207, 221, 281, 305, 336	-	Unknown	-
	D1	24.39	55, 69, 83, 95, 105, **110**, 118, 132, 159, 187, 207, 316	-	Unknown	-
	A7	24.50	55, 69, 109, 123, **135**, 205, 220, 233, 303, 334	-	Unknown	-
	D2	24.87	55, 69, 91, 105, 119, 133, **189**, 207, 281, 303, 318	-	Unknown	-
	B1	24.93	77, 94, 122, **137**, 207, 286, 328	-	Unknown	-
	A8	25.02	55, 69, 81, 95, 109, **123**, 135, 183, 207, 220, 253, 281, 346	-	Unknown	-
	D3, C5	25.28	55, 69, 95, 121, 135, **168**, 189, 217, 249, 346	-	Unknown	-
	E3	25.34	55, 95, 121, 168, **191**, 219, 251, 289, 334, 362	-	Unknown	-
	E4	25.45	55, 69, 81, 95, 109, **121**, 137, 161, 191, 203, 221, 265, 287, 306, 319, 348	-	Unknown	-
	E5	25.85	55, 69, 81, 95, 109, 121, 137, 149, 168, 191, 219, **251**, 289, 321, 348	-	Unknown	-
	B2	25.90	55, 77, 91, 137, 151, 202, 283, 311, **326**	-	Unknown	-
	D4	26.11	55, 69, 95, 105, 121, 133, 147, 161, 175, **191**, 207, 221, 237 ,277, 319, 350	-	Unknown	-
	D5	26.29	55, 79, 95, 105, 119, 147, 163, **189**, 217, 249, 287, 319, 346, 360, 378	-	Unknown	-
	D6	26.69	55, 69, 91, 107, **122**, 133, 147, 161, 175, 203, 209, 221, 257, 281, 314, 332, 350, 429	-	Unknown	-
	B3	27.33	65, 77, 91, 124, 145, 161, 177, **192**, 344	-	Unknown	-
	B4	27.39	65, 77, 91, 145, 151, 161, 175, **192**, 206, 273, 358	-	Unknown	-
	B5	28.45	77, **137**, 151, 167, 193, 208, 222, 273, 358	-	Unknown	-
	1j	28.96	51, 65, 77, 91, 105, 131, 148, **162**	-	Similar to 4-methoxycinnamaldehyde	NIST11

Ironwood

Peak	RT	m/z (base peak in bold)	M+	Compound description	References
5a	21.28	55, 67, 81, 95, 107, 121, 136, **161**, 179, 203, 221, 235, 253, 264, 296	-	Unknown	-
5b	21.61	55, 79, 91, 109, 124, 135, 147, 161, **189**, 205, 231, 278	-	Unknown	-
5c	21.78	55, 79, 91, 109, 122, **124**, 135, 147, 161, 189, 205	-	Unknown	-
5d	21.83	55, 69, 91, **106**, **110**, 119, 138, 152, 184, 212, 287, 318	-	Unknown	-
5e	22.1	55, 69, 81, **95**, 107, 121, 136, 149, 163, 175, **191**, 238, 277, 289, 305, 320	-	Unknown	-
5f	23.27	55, 69, 81, 95, **109**, 123, 137, 151, 163, 179, 189, 207, 251, 273, 288, 307	-	Unknown	-
5g	23.52	55, 69, 81, 91, 105, 119, 133, 147, 163, 178, 189, 241, **257**, 269, 285, 301, 316	-	Unknown	-
5h	23.57	55, 69, 81, 95, **109**, 123, 137, 149, 163, 189, 207, 223, 237, 321	-	Unknown	-
5i	24.38	55, 69, 81, 95, 109, 123, 137, 149 , 161, 177, 189, 207, **291**, 352	-	Unknown	-
5j	24.57	55, 69, 81, 95, 109, 123, 135, 149, 163, 179, **189**, 207, 251, 275, 289, 307, 339	-	Unknown	-
5k	24.74	55, 69, 83, 95, 109, 121, 135, 149, 163, 177, 189, **205**, 287, 303, 319, 334	-	Unknown	-
5l	24.96	55, 69, 83, 95, 109, 121, 123, **124**, 135, 149, 163, 177, 205, 250, 303, 316, 334	-	Unknown	-
5m	25.6	55, 69, 84, 95, 109, **123**, 137, 149, 163, 189, 207, 225, 300, 322, 354	-	Unknown	-
5n	25.85	55, 69, 95, 109, 121, 135, **168**, 189, 207, 217, 251, 281, 319, 346, 382	-	Unknown	-

Appendix F

Mass spectral data for triterpeniod resin samples (Ch5)

Triterpenoids

Peak	RT	m/z (base peak in bold)	M+	Compound ID	Common name	References
P	30.395	55, 69, 95, 109, 257, 271, **409**, 424	424	Lanosta-8,24-dien-3-one		
C	31.16	55, 133, 255, 269, 407, **422**	422	Ursa-9(11),12-dien-3-one		NIST11
D	31.28	55, 133, 255, 295, 391, **424**	424	Ursa-9(11),12-dien-3-ol		NIST11
E	31.6	55, 69, 95, 135, 189, 203, **218**, 409, 424	424	Olean-12-en-3-one	β-amyrone	NIST11; Lucero-Gómez 2014
d	31.68	55, 69, 81, 95, 107, 119, 135, 147, 161, 175, 189, 203, **218**, 255, 285, 355, 409, 424	424	Oleanane-type compound		Modugno et al. 2006; Lucero-Gómez 2014
B	31.98	55, 69, 81, 95, 107, 121, 135, 147, 161, 175, 189, 203, **218**, 257, 411, 426	426	Olean-12-en-3-ol	β-amyrin	NIST11
N	32.22	55, 67, 81, 95, 109, 123, 189, **205**, 245, 313, 409, 424	424	Lup-20(29)-en-3-one		NIST11
F	32.26	55, 69, 95, 135, 189, 203, **218**, 405, 424	424	Urs-12-en-3-one	α-amyrone	NIST11; Lucero-Gómez 2014
g	32.271	55, 69, 81, 95, 109, 122, 135, 148, 161, 189, 203, **218**, 409, 424	-	Unknown compound		-
h	32.39	55, 69, 81, 95, 107, 122, 135, 147, 161, 175, 189, 203, **218**, 257, 281, 411, 426	426	related to α-amyrin (possibly co-eluted)		Modugno et al. 2006; Lucero-Gómez 2014
A	32.64	55, 69, 81, 95, 107, 122, 135, 147, 161, 175, 189, 203, **218**, 257, 411, 426	426	Urs-12-en-3-ol	α-amyrin	NIST11
G	32.841	55, 69, 95, 109, 123, 145, 159, 173, 203, 255, 295, 313, 391, 406, **466**		Ursa-9(11),12-dien-3-yl acetate		NIST11
H	33.344	55, 69, 95, 109, 119, 135, 161, 175, 189, 203, **218**	468	12-Oleanen-3-yl acetate		NIST11
J	34.108	109, 122, 135, 161, 175, 189, 203, **218**	468	Urs-12-en-24-oic acid, 3-oxo-, methyl ester		NIST11
j	34.636	59, 85, 125, **143**, 205, 381, 399	-	Unknown compound		-
k	34.796	55, 69, 95, **109**, 123, 205, 313, 355, 424	-	Unknown compound		-
L	38.218	69, 95, 121, 135, 175, 232, **273,** 422, 482	482	11-Oxoolean-12-en-3-yl acetate		NIST11
M	39.149	69, 95, 119, 135, 175, 232, **273**, 422, 482	482	11-Oxours-12-en-3-yl acetate		NIST11

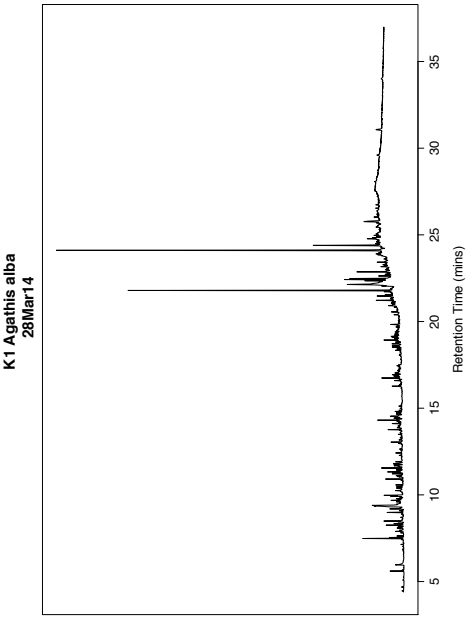
Appendix G

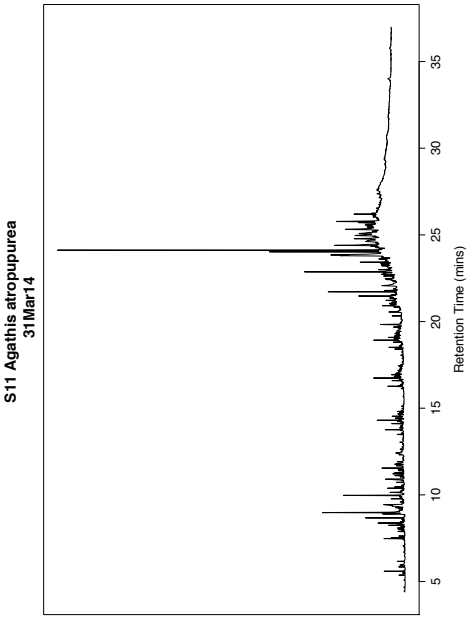
Mass spectral data for *Xanthorrhoea* phenolic resin samples (Ch6)

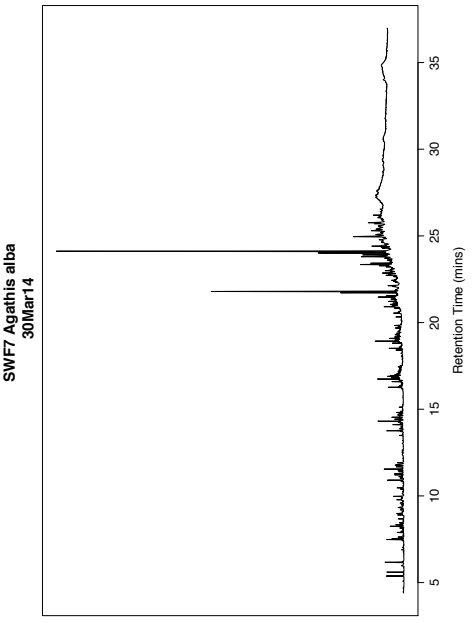
Peak	RT	m/z (base peak in bold)	M+	Compound ID	References
A	11.484	51, 77, 103, **131**	132	Cinnamaldehyde	NIST11
B	12.96	51, 77, 103, **131**, 162	162	Cinnamic acid, methyl ester	NIST11
C	14.07	55, 69, 94, 111, 125, **154**	154	Taxicatigenin	NIST11
D	14.2	51, 65, 77, 95, 119, 151, 165, **166**	166	Veratraldehyde	NIST11
VA	14.663	65, 108, 123, **151**, 167, 182	182	Vanillic acid, methyl ester	NIST11
E	16.5	51, 63, 77, 89, 118, 133, **161**, 192	192	4-Methoxycinnamic acid, methyl ester	NIST11
9	16.853	51, 77, **105**, 134, 161	-	Unknown	NIST11
F	17.3	51, 65, 91, 119, **147**, 178	178	4-Hydroxycinnamic acid, methyl ester	NIST11
1	18.24	51, 63, 77, 89, 105, 117, 133, 145, 177, **208**	208	Ferulic acid methyl ester	NIST11
a	18.99	77, 115, 127, 152, **185**, 214	-	Unknown	-
G	19.134	51, 65, 77, 91, **104**	240	Benzeneacetic acid, 2-phenylethyl ester	NIST11
b	19.64	63, 92, 115, 128, 152, **171**, 185, 200	-	Unknown	-
H	22.04	63, 76, 115, 152, 181, 213, **227**, 242	242	Benzocyclopentane, 4,6,7-triethyl-1- methyl-5-vinyl-	NIST11
5	22.087	51, 63, 76, 91, 102, 115, 152, 165, 178, 195, 209, 224, **240**	240	Benzene, 1,3-dimethoxy-5-[(1E)-2-phenylethenyl]-	NIST11
2	22.724	51, 63, 79, 107, 122, 150, 177, **254**	254	4H-1-Benzopyran-4-one, 2,3-dihydro-5,7- methoxy-3-phenyl-	NIST11
c	22.775	69, 115, 165, 191, 237. 253, 267, **268**	-	Unknown	-
3	23.479	51, 77, 108, 136, 163, **240**	240	5-Hydroxy-2-phenyl-4-chromanone	NIST11
J	23.56	51, 69, 95, 138, 166, **193**, 270	270	Pinostrobin chalcone	NIST11
K	23.59	51, 77, 91, 103, 115, 117, **131**, 193, 219, 264	264	Cinnamyl cinnamate	NIST11
4	23.865	51, 77, 103, 122, 151, 165, **177**, 237, 253, 254	454	1-(2-Acetoxy-4-methoxyphenyl)-2,3-dibromo-3-phenylpropanone	NIST11
L	24.22	51, 69, 78, 103, 104, 124, 152, 179, 238, **256**	256	5,7-Dihydroxyflavanone	NIST11
M	24.847	51, 77, 103, 137, 152, **180** ,207, 256, 284	284	5,7-Dimethoxyflavanone	NIST11
d	24.95	53, 77, 107, 120, **151**, 166, 181, 207, 242, 256, 272	-	Unknown	-
N	25.07	51, 65, 91, 108, 121, **134**, 151, 177, 241, 253, 269, 284	284	2-Hydroxy-4-methoxy-alpha-(p-methoxybenzylidene)acetophenone	NIST11
e	25.241	51, 69, 91, 95, 121, **134**, 166 193, 299, 300	-	Unknown	NIST11
P	25.576	51, 65, 79, 91, 107, 120. **151**, 164, 177, 253, 270	270	2-Hydroxy-alpha-(p-methoxybenzylidene)-4-methoxyacetophenone	NIST11
f	25.64	51, 65, 77, 91, 107, 120, 133, 138, 154, 167, **286**	-	Unknown	-
Q	25.83	51, 69, 91, 121, **134**, 166, 193, 286, 300	300	5-Hydroxy-4',7-dimethoxyflavanone	-
R	26.172	51, 69, 91, 107, 120, 133, 153, 165, 255, **272**	272	Naringenin	NIST11
S	26.4	69, 95, 120, 138, **167**, 180, 193, 286	286	Sakuranetin	NIST11
h	26.53	51, 65, 91, 117, **147**, 167, 186, 235, 286	-	Unknown	-
j	26.6	69, 91, 121, 142, 191, 225, 253, 269, **283**, 284	-	Unknown	-
6	26.986	65, 91, 120, 153, **166**, 194, 221, 272, 314	-	Unknown	-
7	27.061	53, 69, 91, 109, 120, 152, 181, 194, 272, **300**, 314	-	Unknown	-
k	27.246	51, 79, 122, 137, 151, 165, 167, 180, 207, 281, 299, 313, **330**	-	Unknown	-
8	27.598	65, 91, 120, 152, 180, 194, **300**	-	Unknown	-
m	27.38	77, 95, 107, 137, 150, 167, 193, 207, 273, 299, **316**	-	Unknown	-
n	28.135	51, 73, 123, **151**, 177, 207, 252, 281, 316	-	Unknown	-
o	29.041	51, 73, 95, 135, 153, 167, 193, **207**, 232, 253, 281, 315, 332	-	Unknown	-

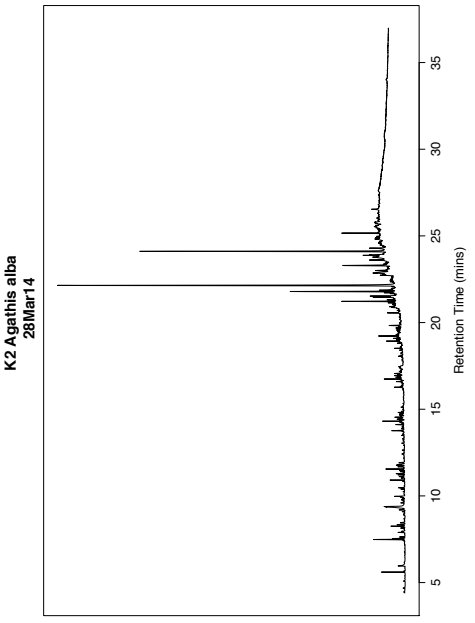
Appendix H

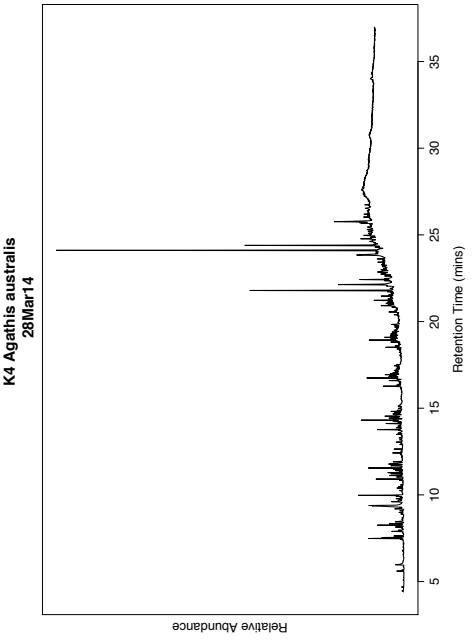
Total ion chromatograms (TIC) for Araucariaceae reference resins (Ch3)

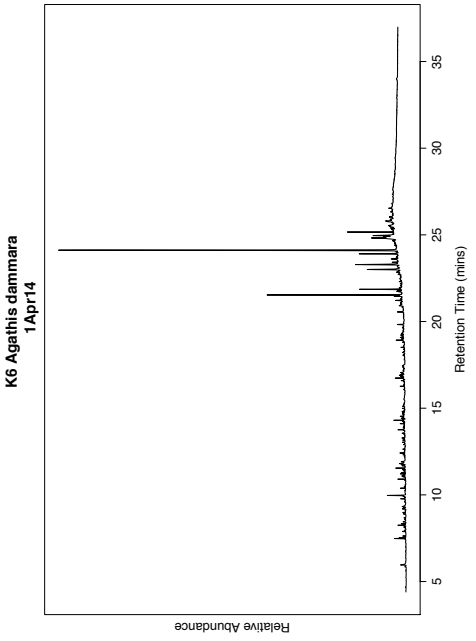

K1 Agathis alba
28Mar14
Relative Abundance
Retention Time (mins)
5
10
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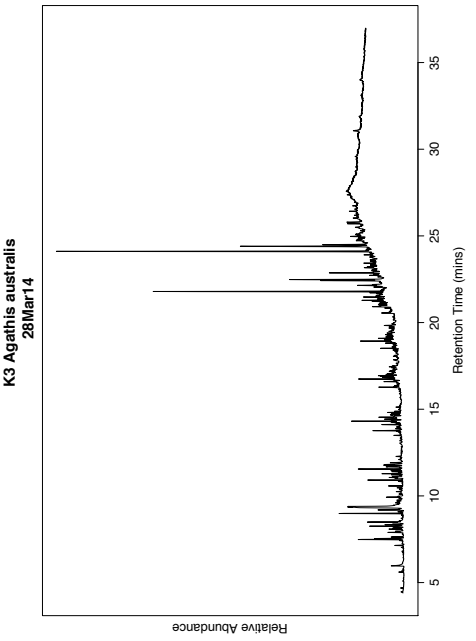

S11 Agathis atropupurea
31Mar14
Relative Abundance
Retention Time (mins)
5
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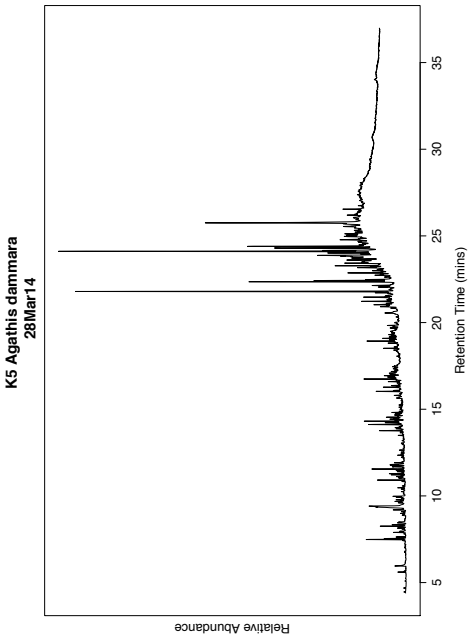

SWF7 Agathis alba
30Mar14
Relative Abundance
Retention Time (mins)
5
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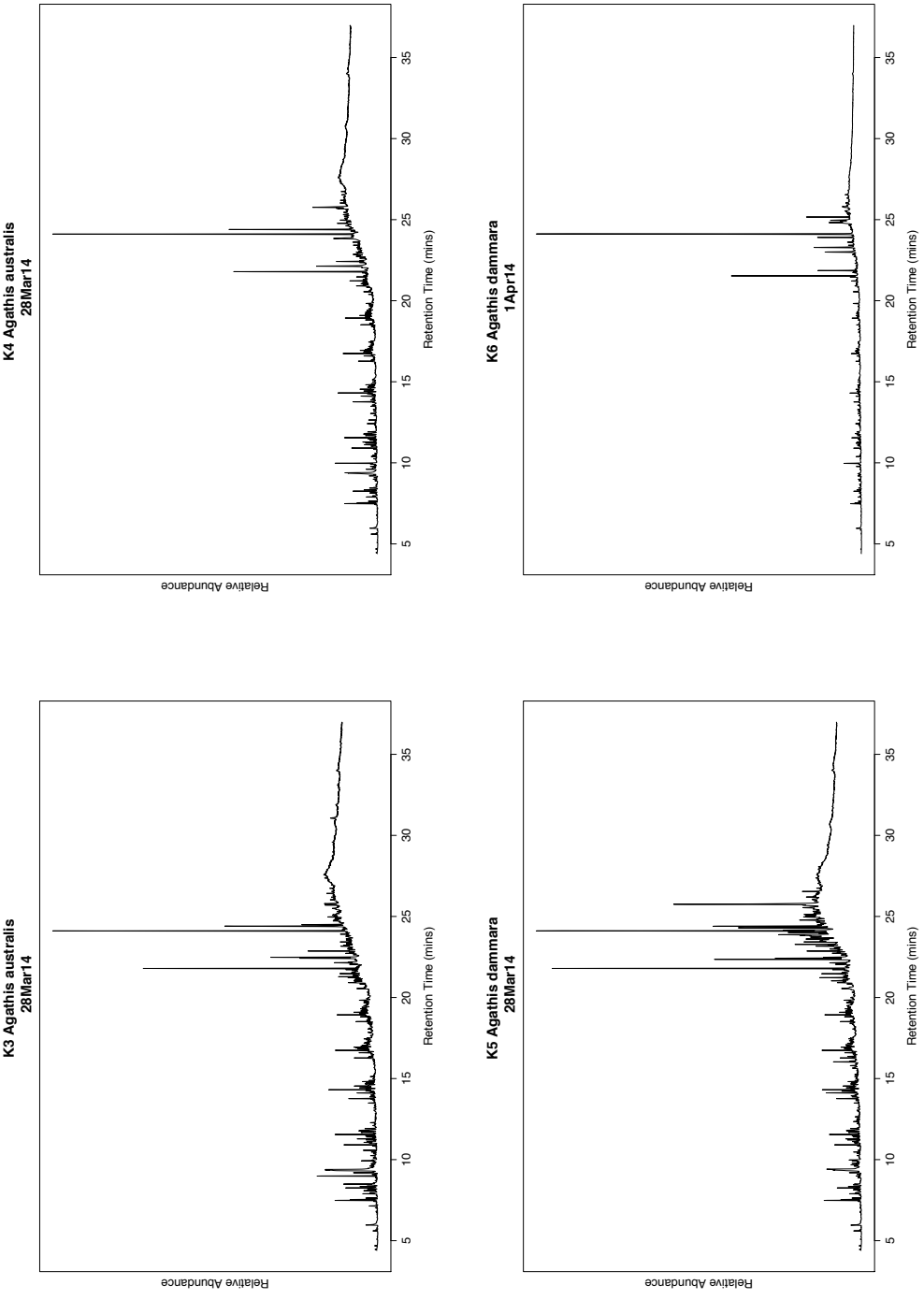

K2 Agathis alba
28Mar14
Relative Abundance
Retention Time (mins)
5
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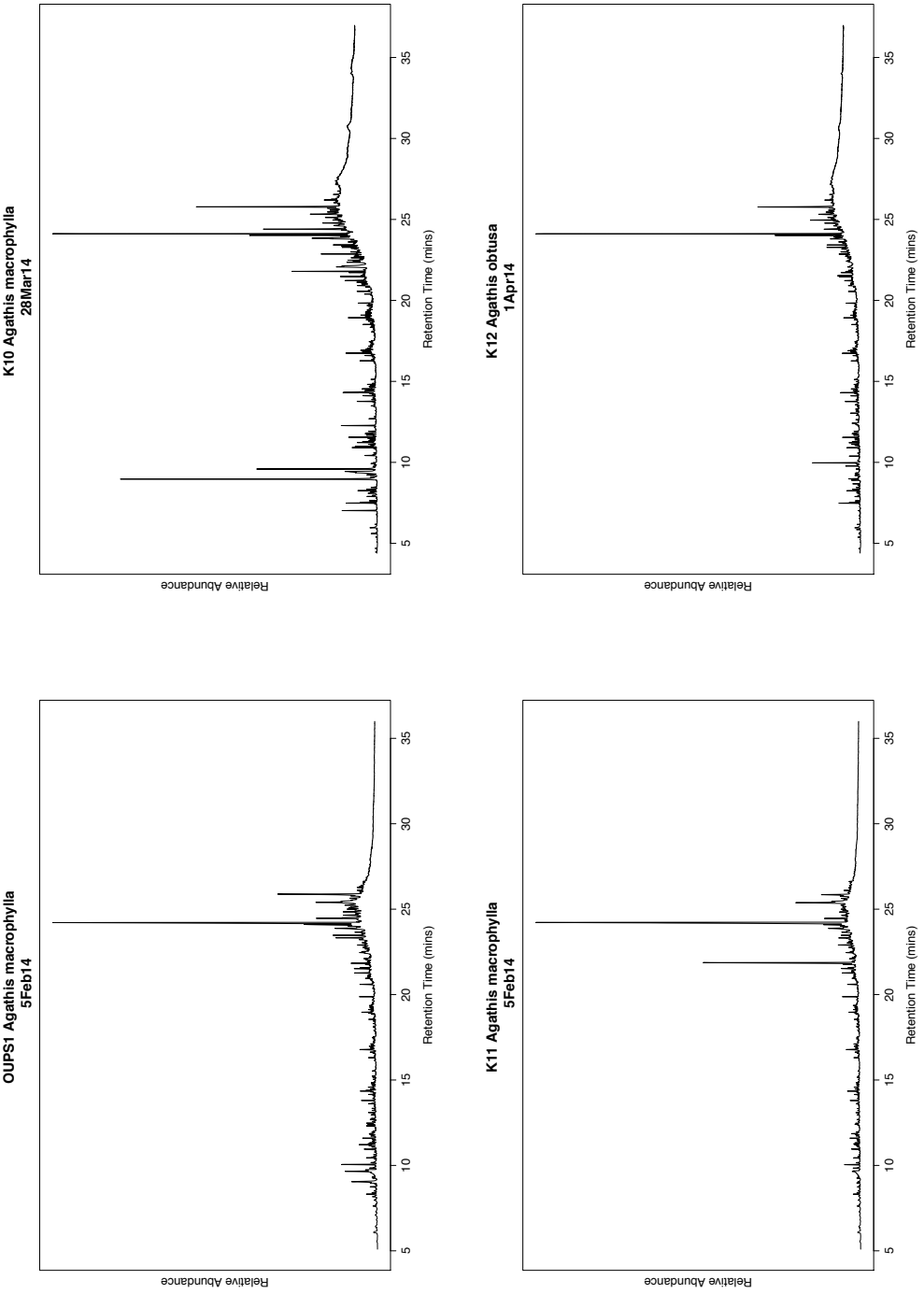

K4 Agathis australis
28Mar14
Relative Abundance
Retention Time (mins)
5
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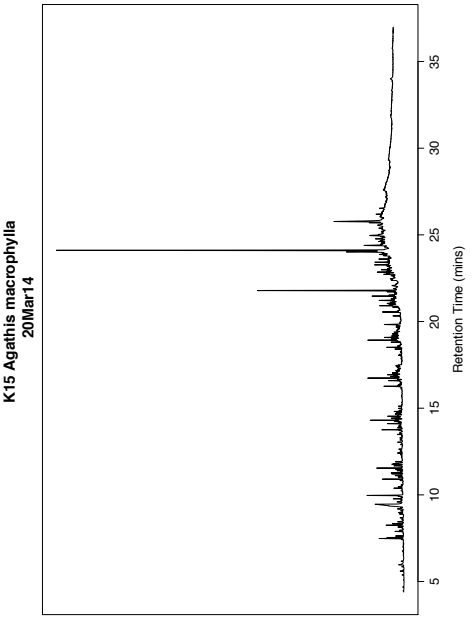

K6 Agathis dammara
1Apr14
Relative Abundance
Retention Time (mins)
5
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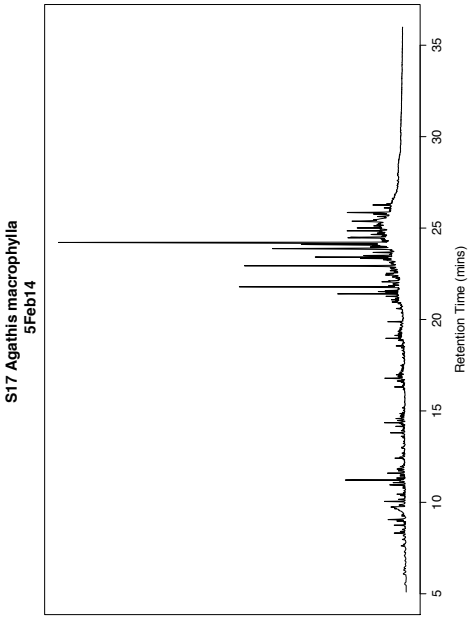

K3 Agathis australis
28Mar14
Relative Abundance
Retention Time (mins)
5
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20
25
30
35

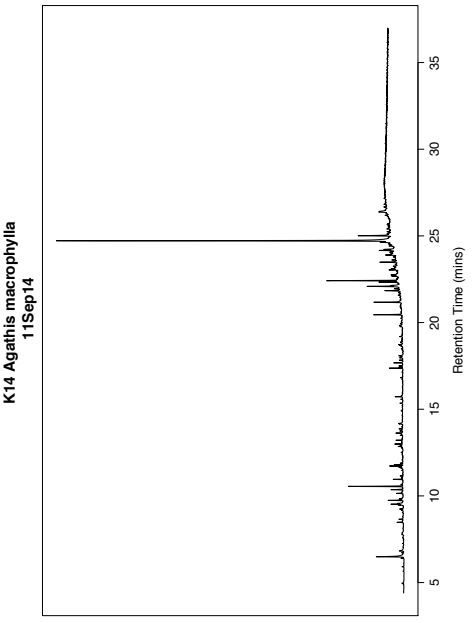

K5 Agathis dammara
28Mar14
Relative Abundance
Retention Time (mins)
5
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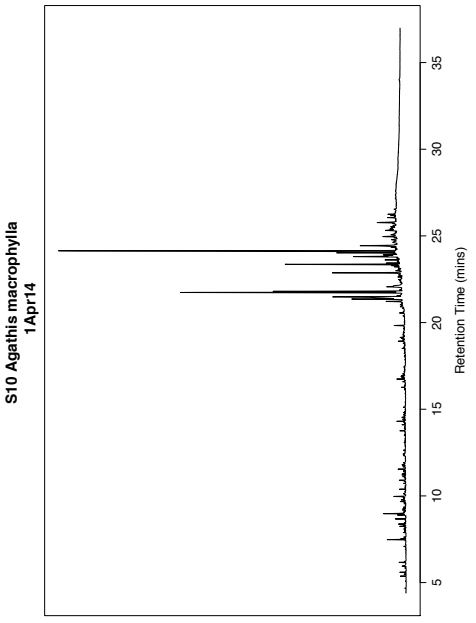

K4 Agathis australis
28Mar14
K6 Agathis dammara
1Apr14
K3 Agathis australis
28Mar14
K5 Agathis dammara
28Mar14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
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35

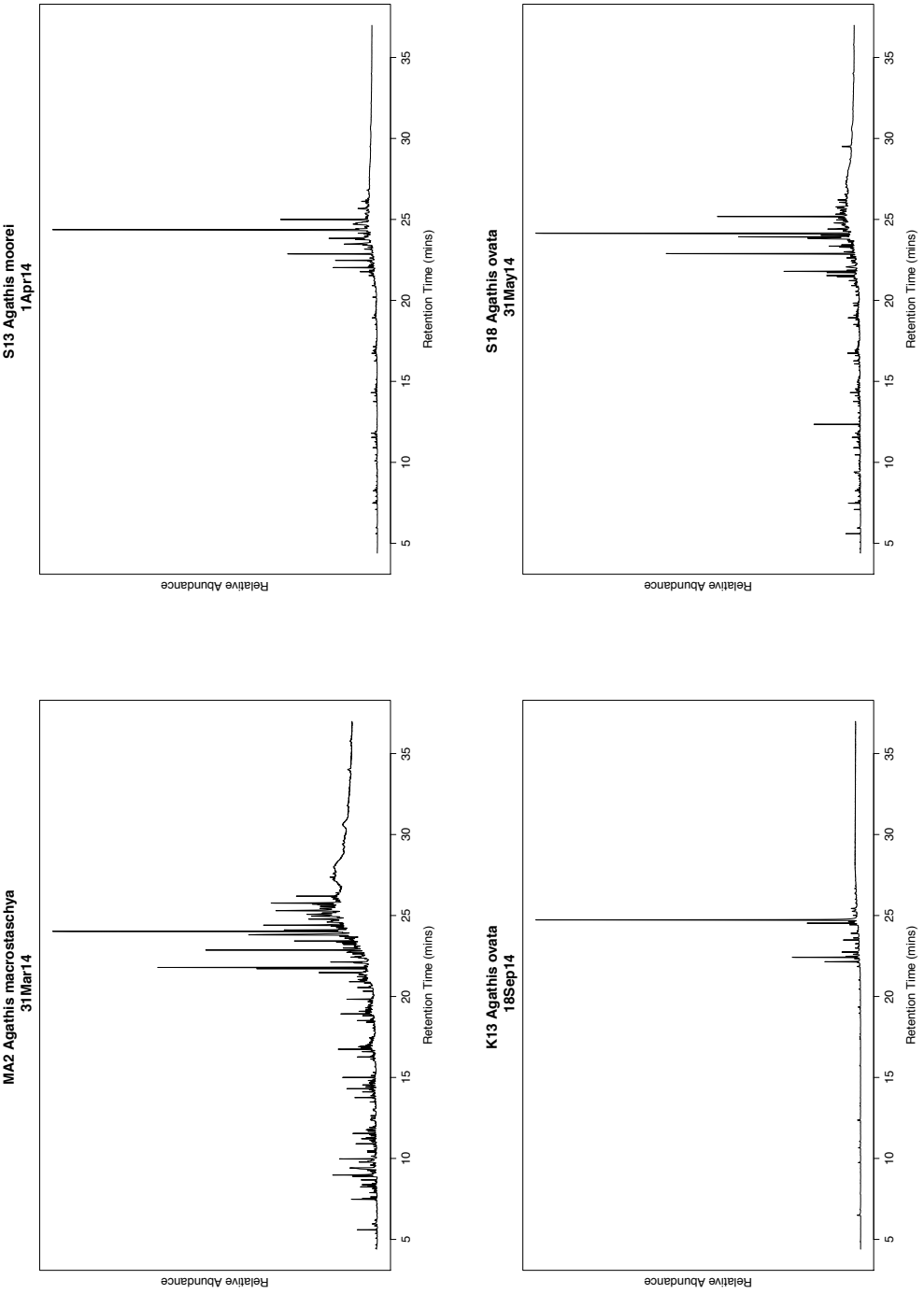

K10 Agathis macrophylla
28Mar14
K12 Agathis obtusa
1Apr14
OUPS1 Agathis macrophylla
5Feb14
K11 Agathis macrophylla
5Feb14
Relative Abundance
Retention Time (mins)
5
10
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25
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35

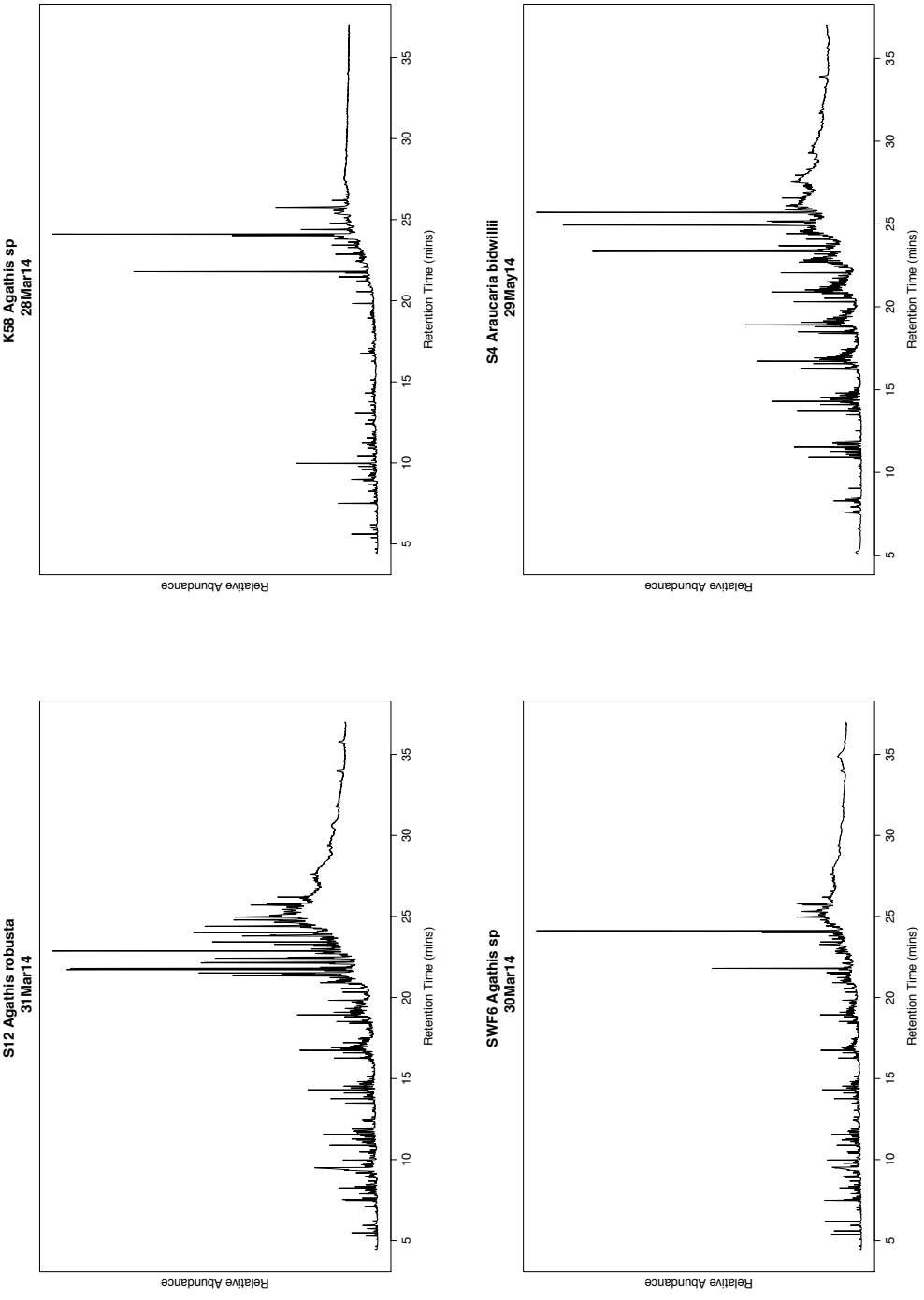

K15 Agathis macrophylla
20Mar14
Relative Abundance
Retention Time (mins)
5
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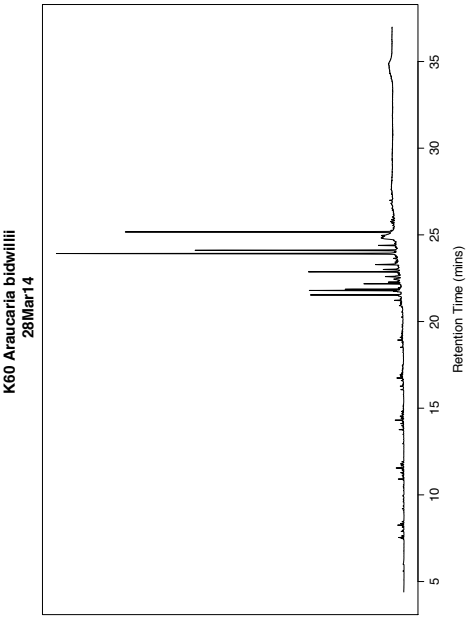

S17 Agathis macrophylla
5Feb14
Relative Abundance
Retention Time (mins)
5
10
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35

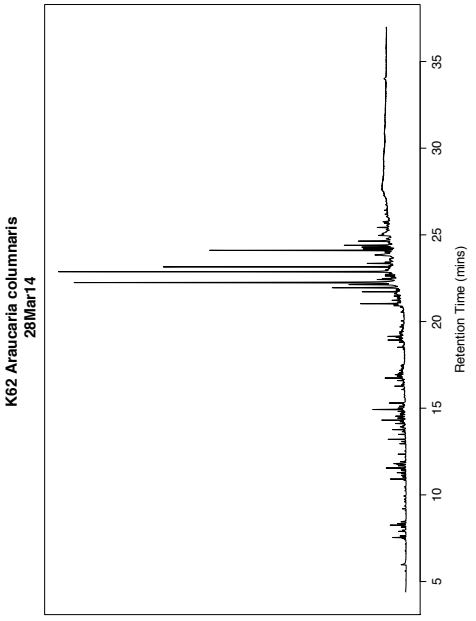

K14 Agathis macrophylla
11Sep14
Relative Abundance
Retention Time (mins)
5
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35

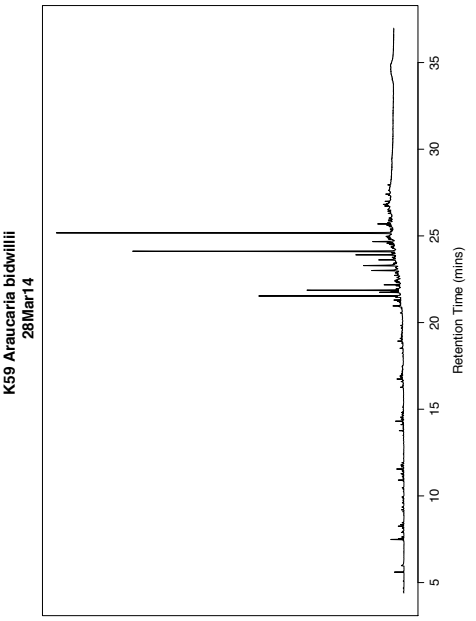

S10 Agathis macrophylla
1Apr14
Relative Abundance
Retention Time (mins)
5
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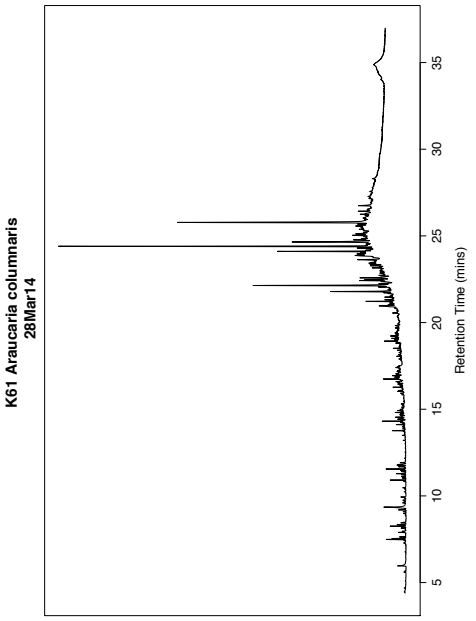

S13 Agathis moorei
1Apr14
S18 Agathis ovata
31May14
MA2 Agathis macrostaschya
31Mar14
K13 Agathis ovata
18Sep14
Relative Abundance
Retention Time (mins)
5
10
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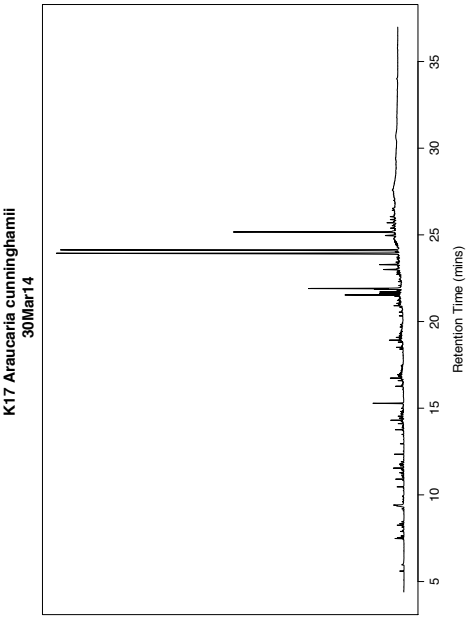

K58 Agathis sp
28Mar14
S4 Araucaria bidwillii
29May14
S12 Agathis robusta
31Mar14
SWF6 Agathis sp
30Mar14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
30
35

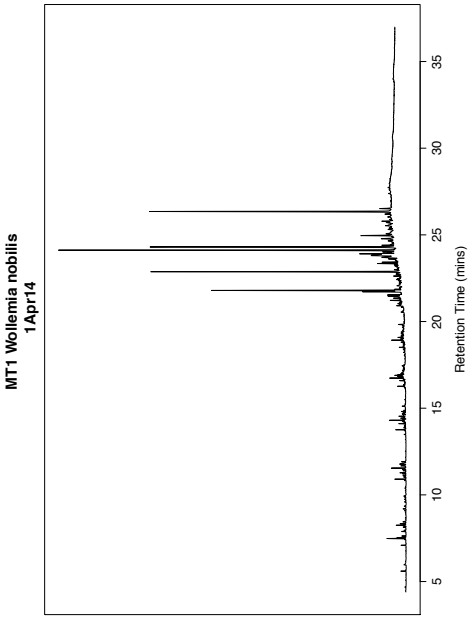

K60 Araucaria bidwillii
28Mar14
Relative Abundance
Retention Time (mins)
5
10
15
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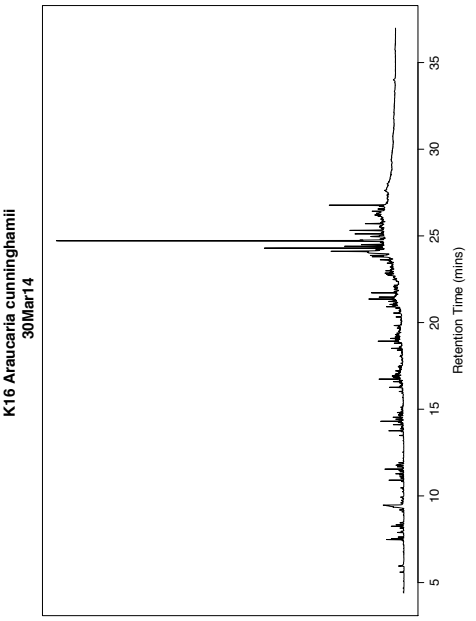

K62 Araucaria columnaris
28Mar14
Relative Abundance
Retention Time (mins)
5
10
15
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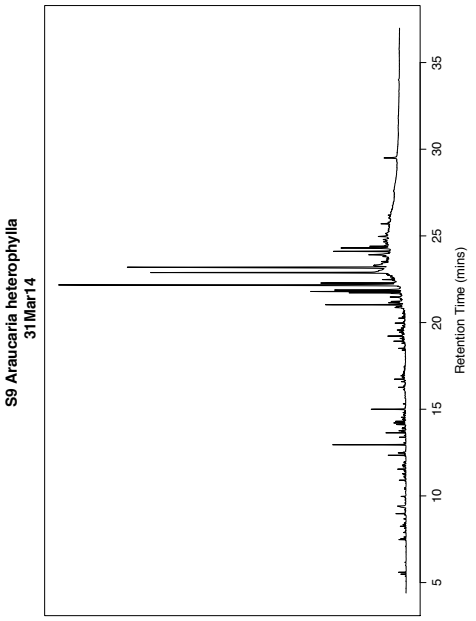

K59 Araucaria bidwillii
28Mar14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
30
35

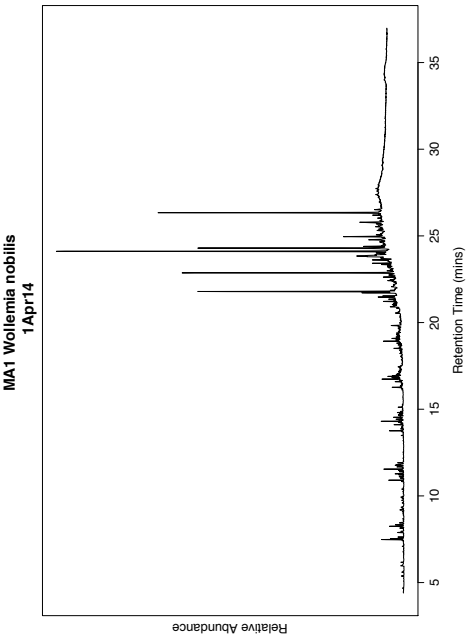

K61 Araucaria columnaris
28Mar14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
30
35


K17 Araucaria cunninghamii
30Mar14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
30
35


MT1 Wollemia nobilis
1Apr14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
30
35

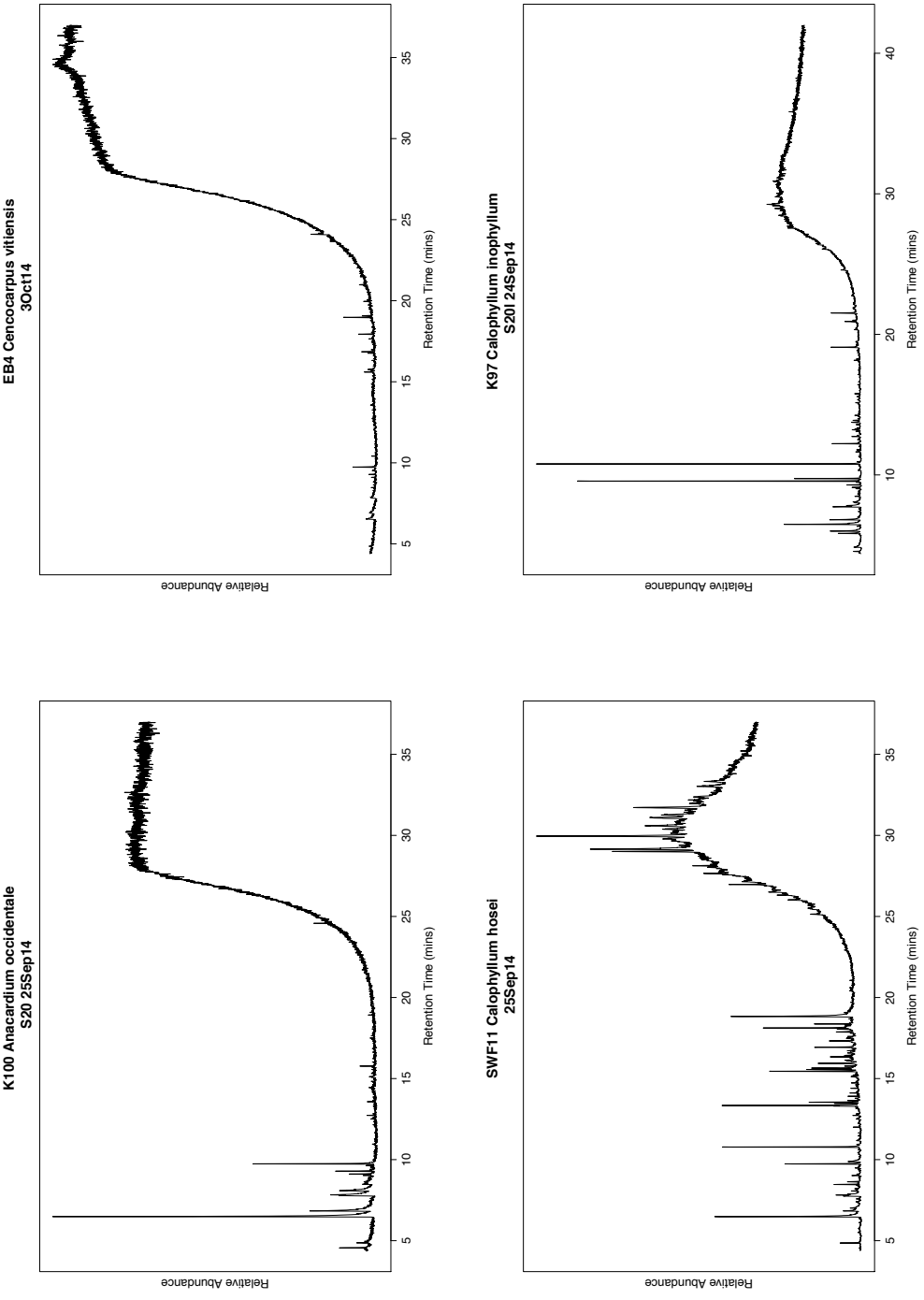

K16 Araucaria cunninghamii
30Mar14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
30
35

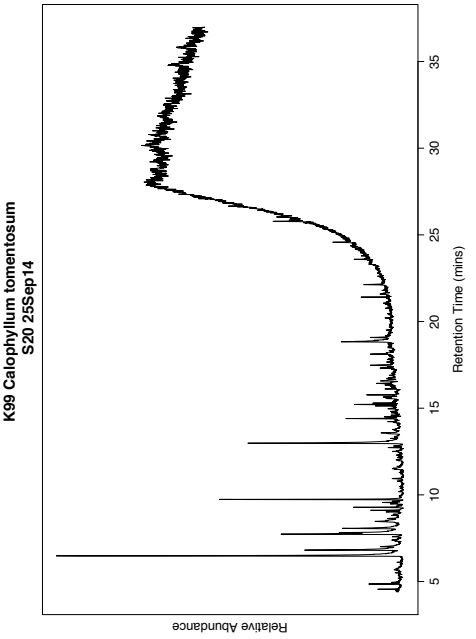

S9 Araucaria heterophylla
31Mar14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
30
35

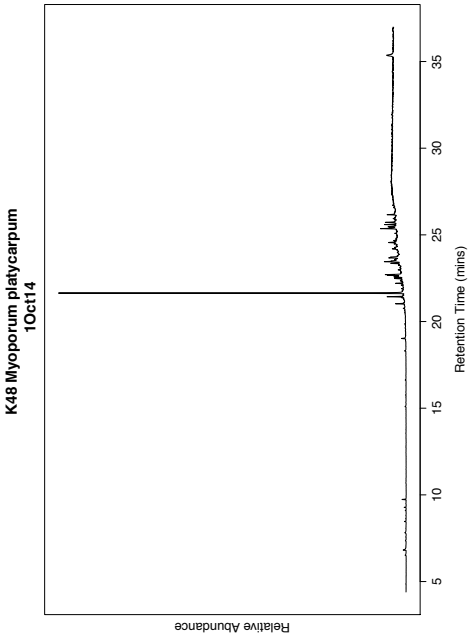

MA1 Wollemia nobilis
1Apr14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
30
35

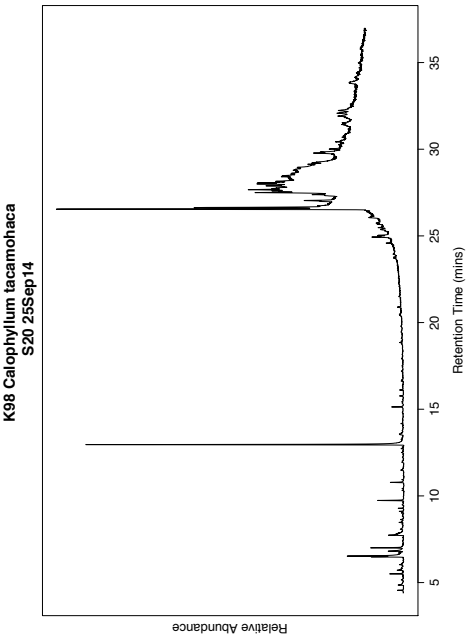
Appendix I

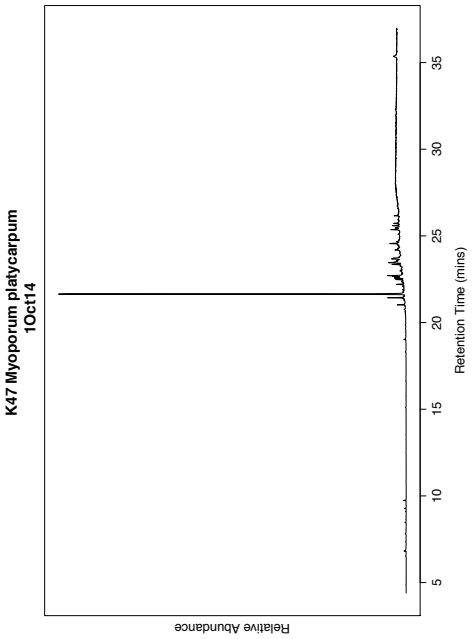
Total ion chromatograms (TIC) for Anacardiaceae, Clusiaceae and *Myoporum* reference resins (Ch5)


EB4 Cencocarpus vitiensis
3Oct14
K97 Calophyllum inophyllum
S20I 24Sep14
K100 Anacardium occidentale
S20 25Sep14
SWF11 Calophyllum hosei
25Sep14
Relative Abundance
Retention Time (mins)


K99 Calophyllum tomentosum
S20 25Sep14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
30
35

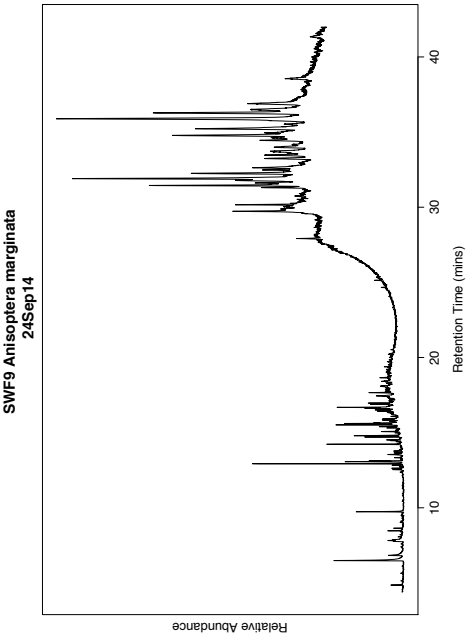

K48 Myoporum platycarpum
1Oct14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
30
35

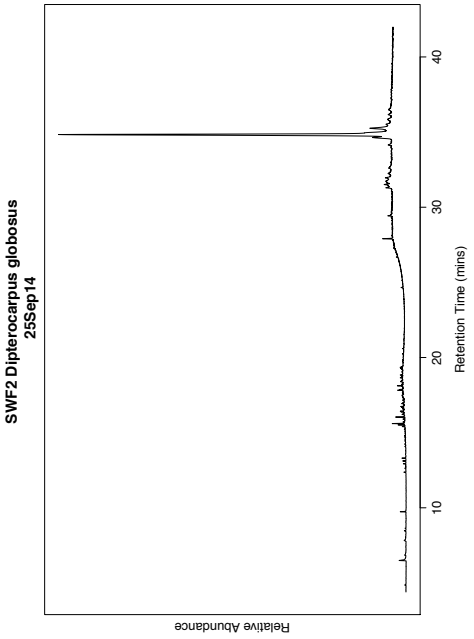

K98 Calophyllum tacamohaca
S20 25Sep14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
30
35

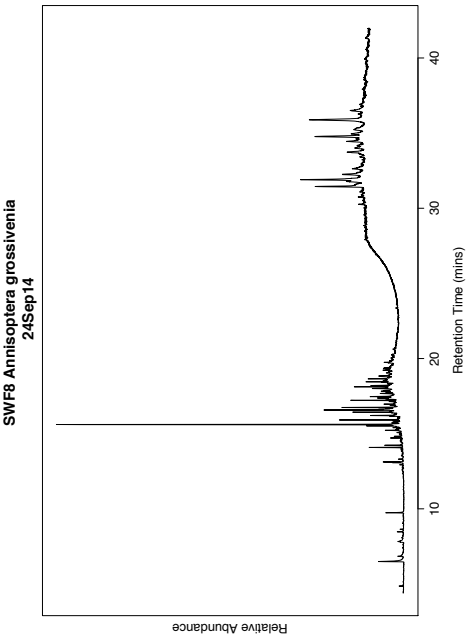

K47 Myoporum platycarpum
1Oct14
Relative Abundance
Retention Time (mins)
5
10
15
20
25
30
35

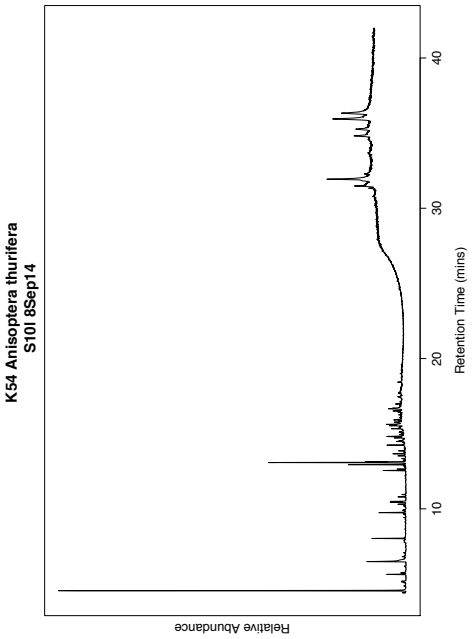
Appendix J

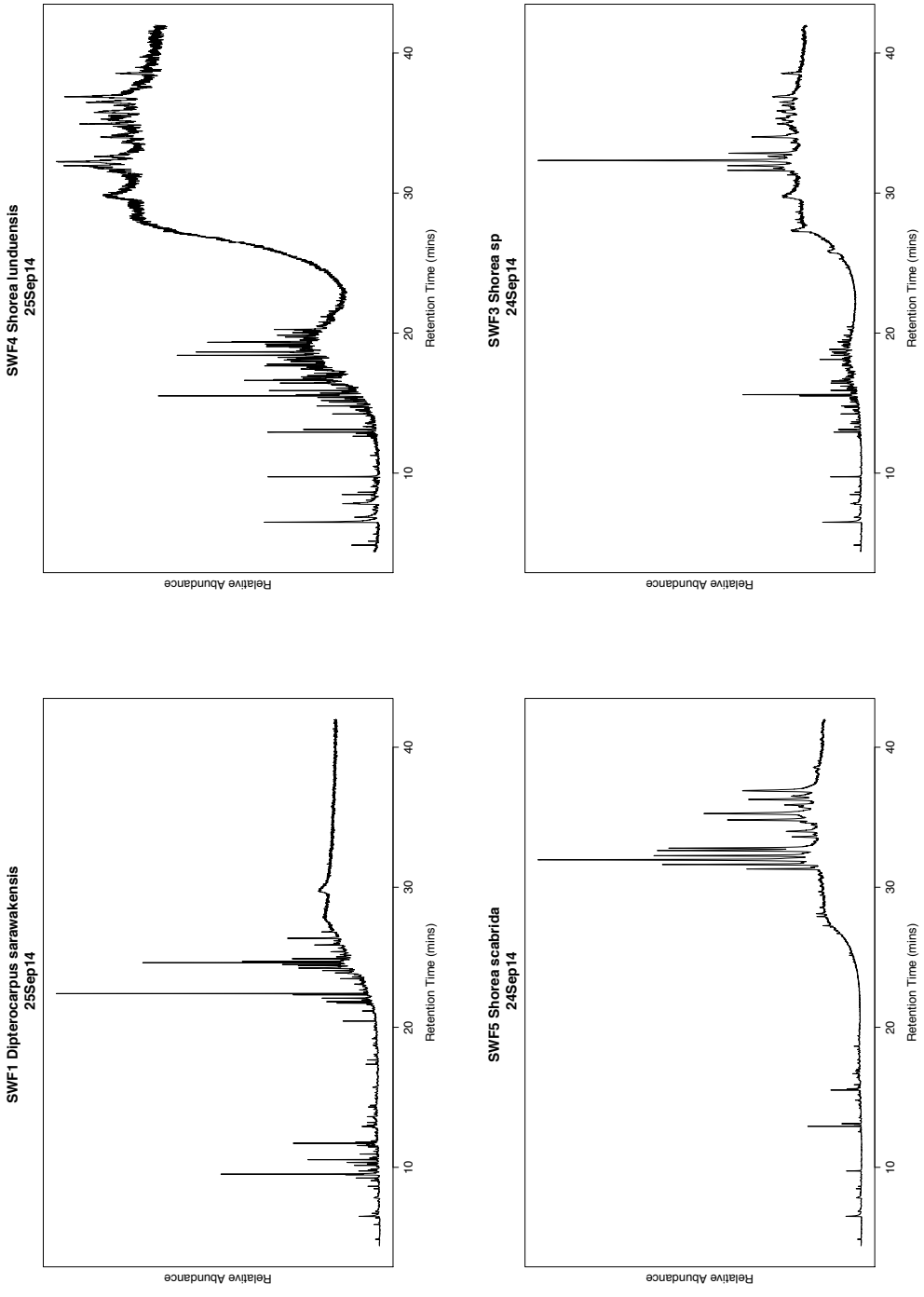
Total ion chromatograms (TIC) for Dipterocarpaceae reference resins (Ch5)

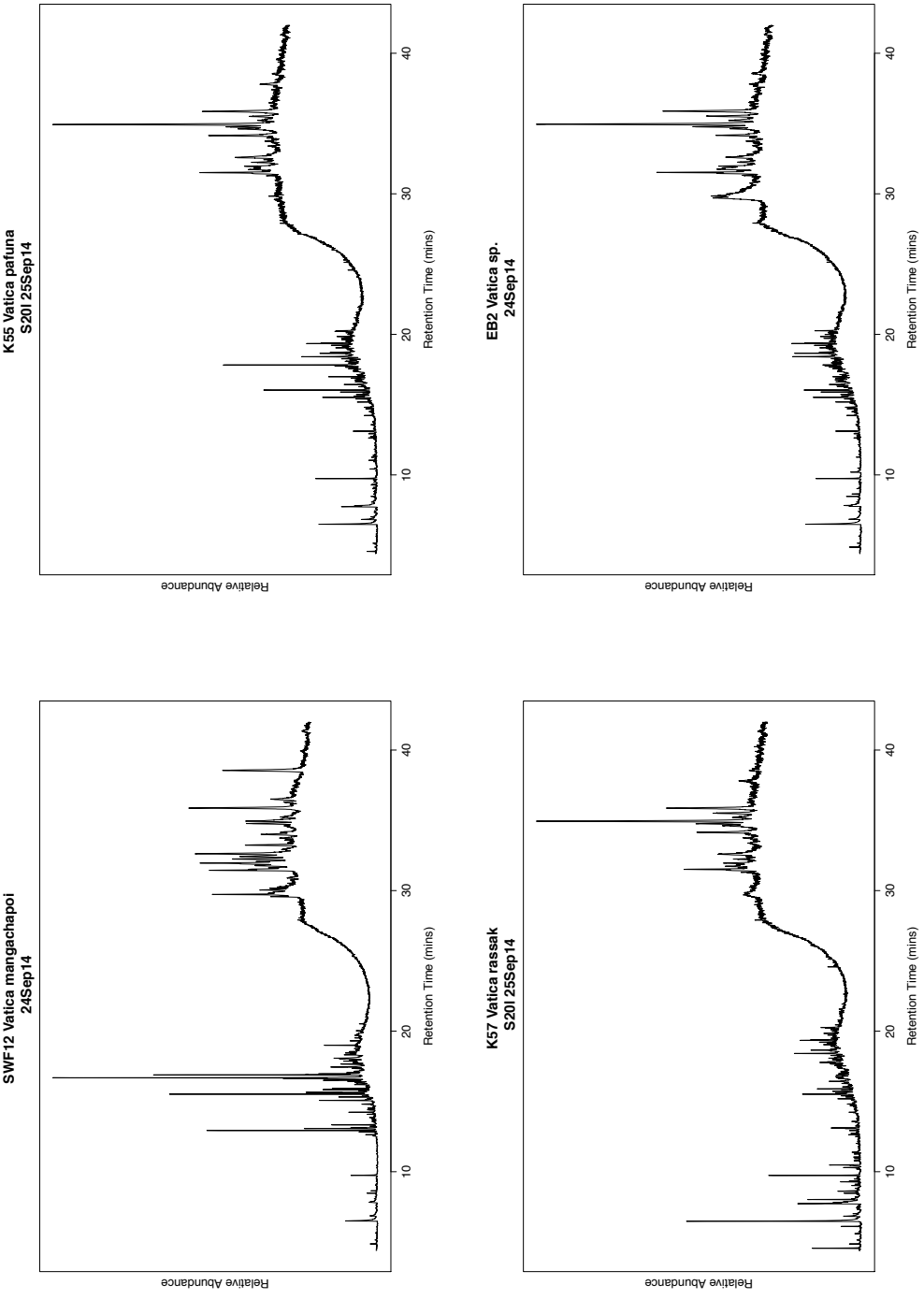

SWF9 Anisoptera marginata
24Sep14
Relative Abundance
Retention Time (mins)
10
20
30
40


SWF2 Dipterocarpus globosus
25Sep14
Relative Abundance
Retention Time (mins)
10
20
30
40


SWF8 Annisoptera grossivenia
24Sep14
Relative Abundance
Retention Time (mins)
10
20
30
40

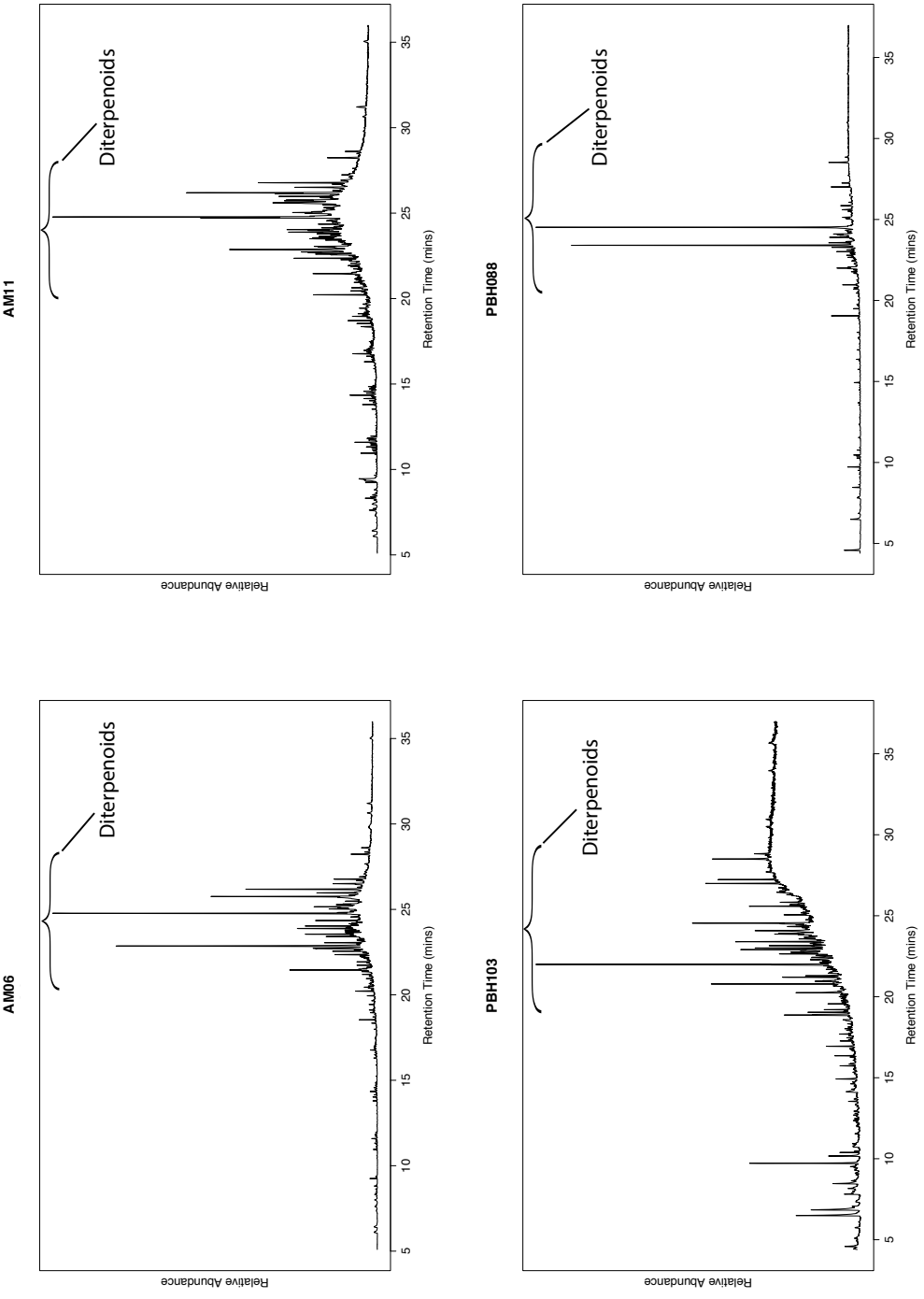

K54 Anisoptera thurifera
S10l 8Sep14
Relative Abundance
Retention Time (mins)
10
20
30
40

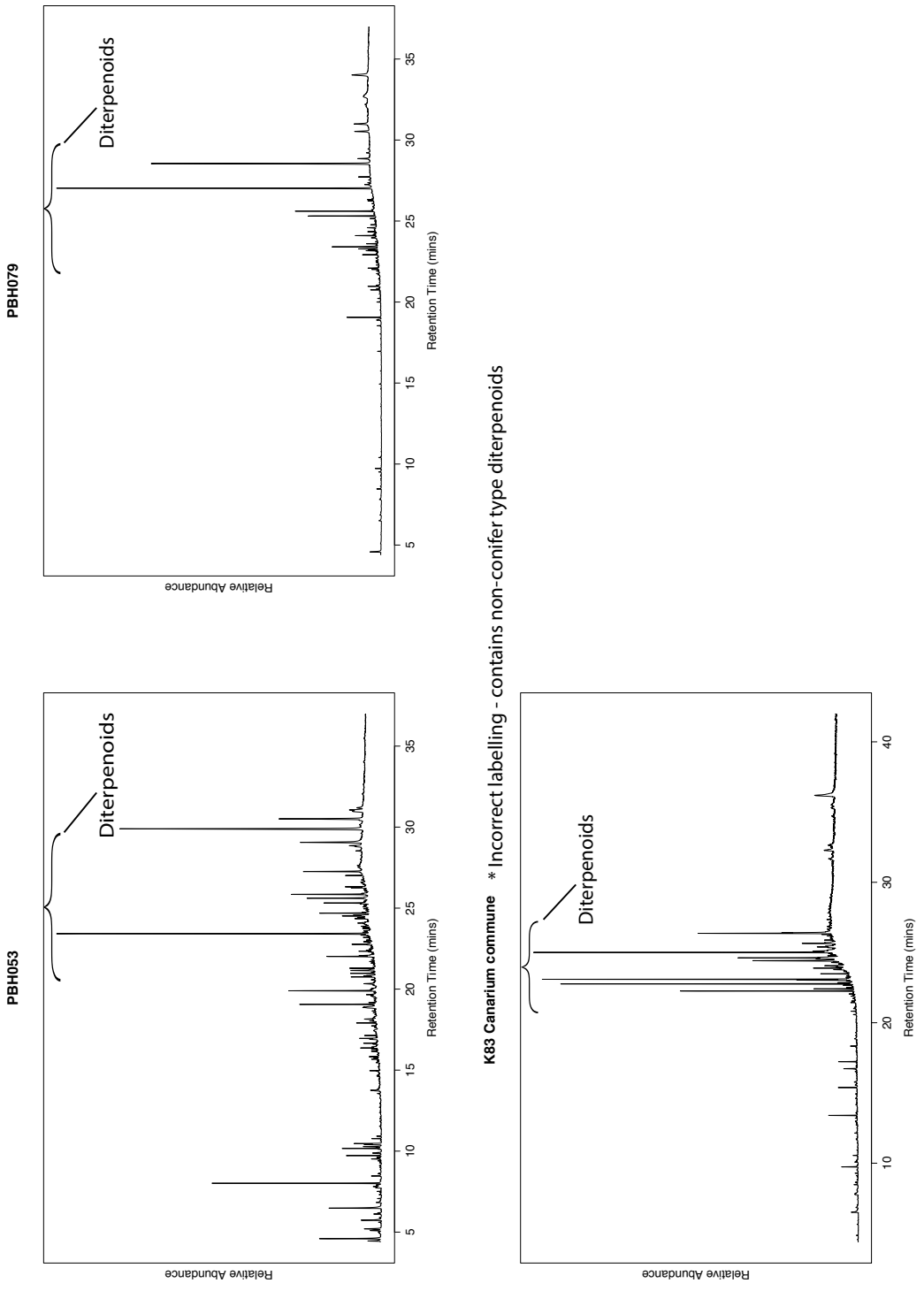

SWF4 Shorea lunduensis
25Sep14
SWF3 Shorea sp
24Sep14
SWF1 Dipterocarpus sarawakensis
25Sep14
SWF5 Shorea scabrida
24Sep14
Relative Abundance
Retention Time (mins)
10
20
30
40


K55 Vatica pafuna
S20I 25Sep14
EB2 Vatica sp.
24Sep14
SWF12 Vatica mangachapoi
24Sep14
K57 Vatica rassak
S20I 25Sep14
Relative Abundance
Retention Time (mins)
10
20
30
40

Appendix K

Total ion chromatograms (TIC) for ethnographic samples with non-conifer type diterpenoid resins that do not fit into the spinifex or ironwood groups (Ch4)

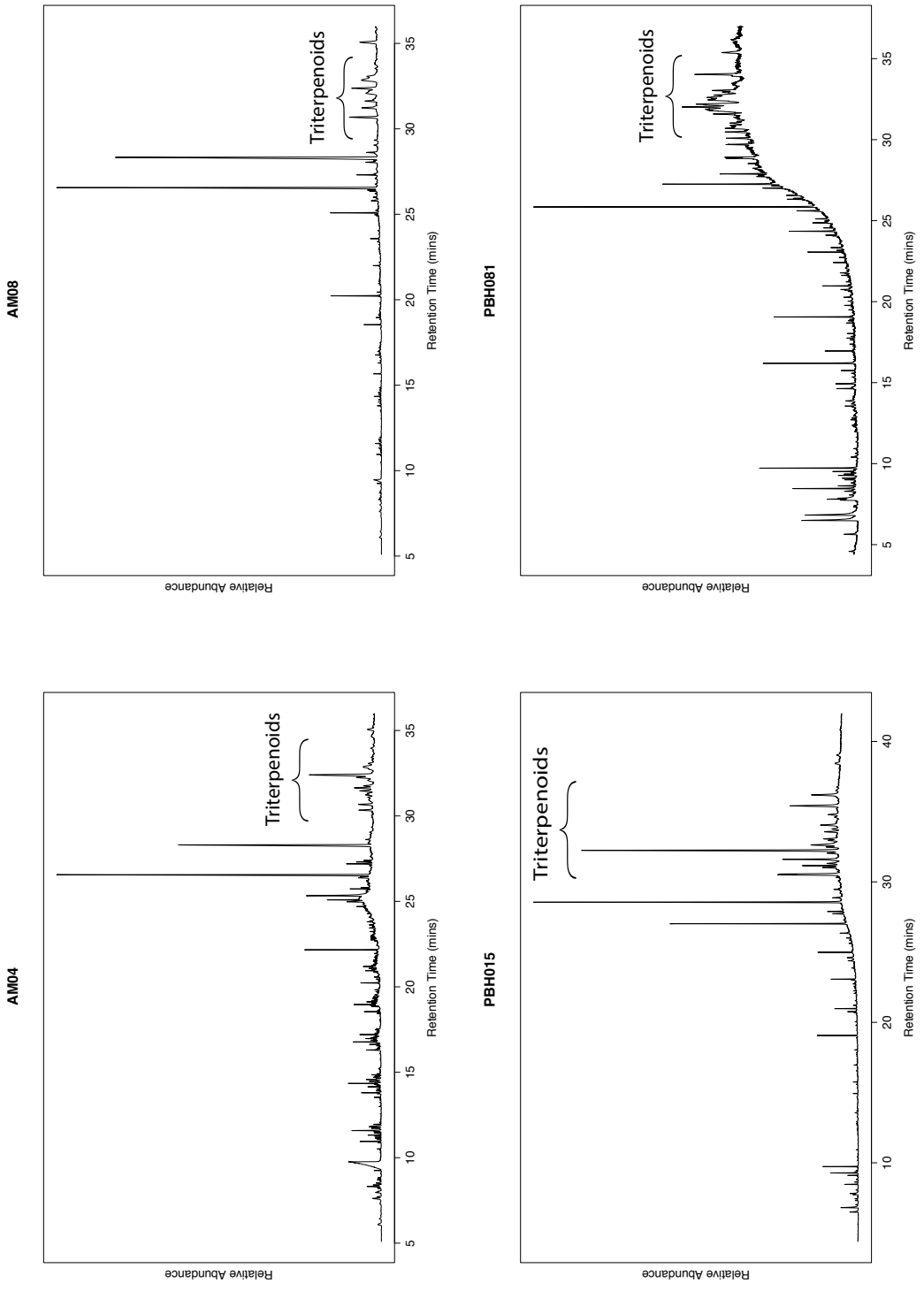

AM11
Diterpenoids
Relative Abundance
Retention Time (mins)
PBH088
Diterpenoids
Relative Abundance
Retention Time (mins)
AM06
Diterpenoids
Relative Abundance
Retention Time (mins)
PBH103
Diterpenoids
Relative Abundance
Retention Time (mins)


PBH079
Diterpenoids
Relative Abundance
Retention Time (mins)
PBH053
Diterpenoids
Relative Abundance
Retention Time (mins)
K83 Canarium commune * Incorrect labelling - contains non-conifer type diterpenoids
Diterpenoids
Relative Abundance
Retention Time (mins)

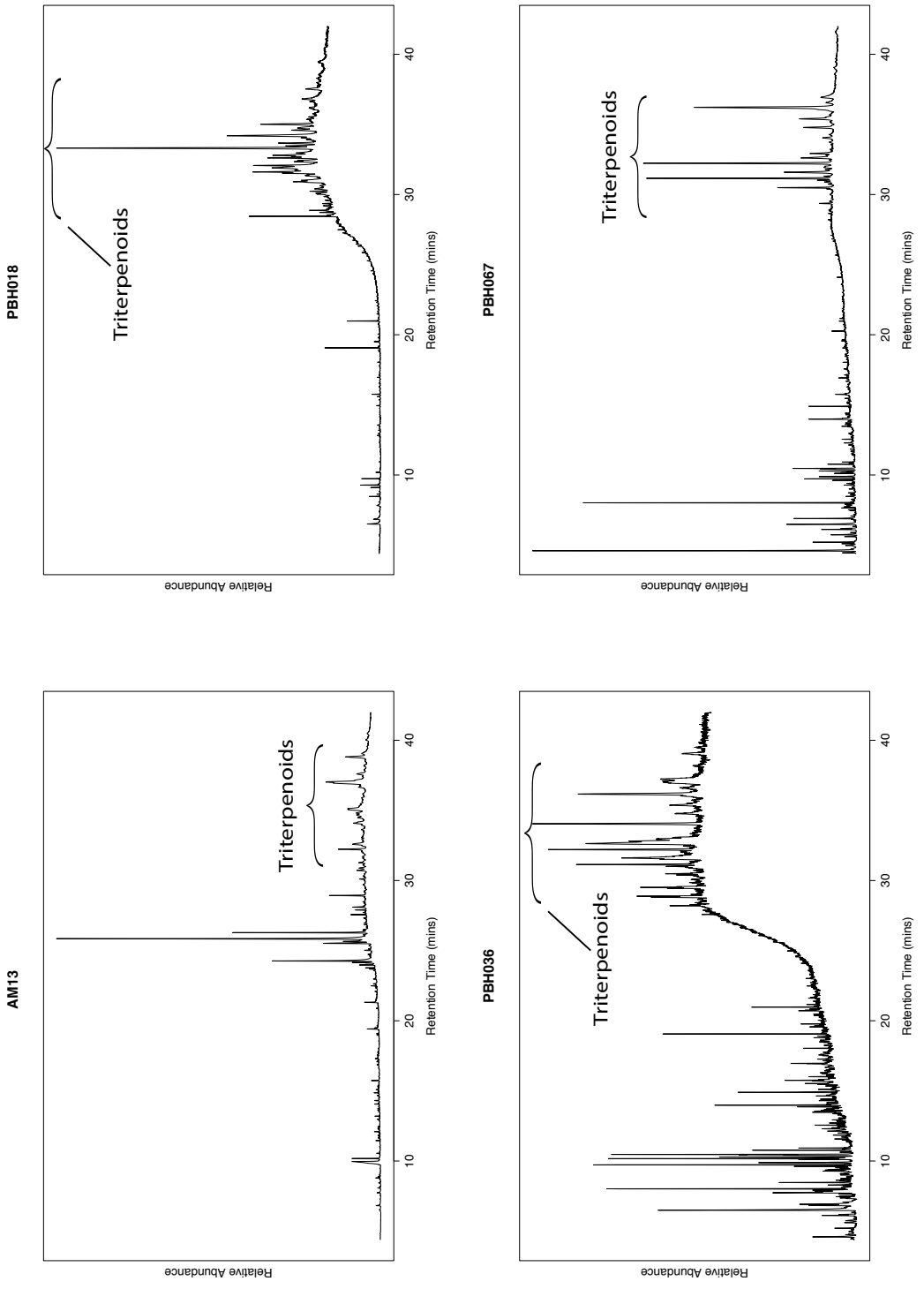
Appendix L

Total ion chromatograms (TIC) for ethnographic samples with lupane-type and dammarane-type triterpenoids (Ch5)

Samples containing lupane-type triterpenoids



Samples containing dammarane-type triterpenoids



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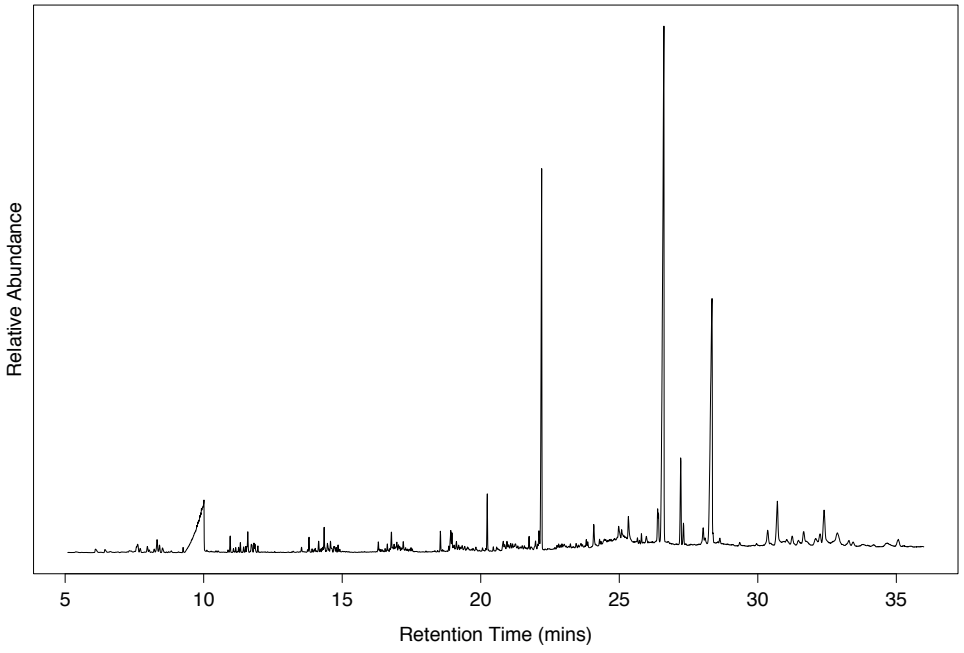
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Catalogue of ethnographic museum samples, with photographs and full chromatograms

Australian Museum

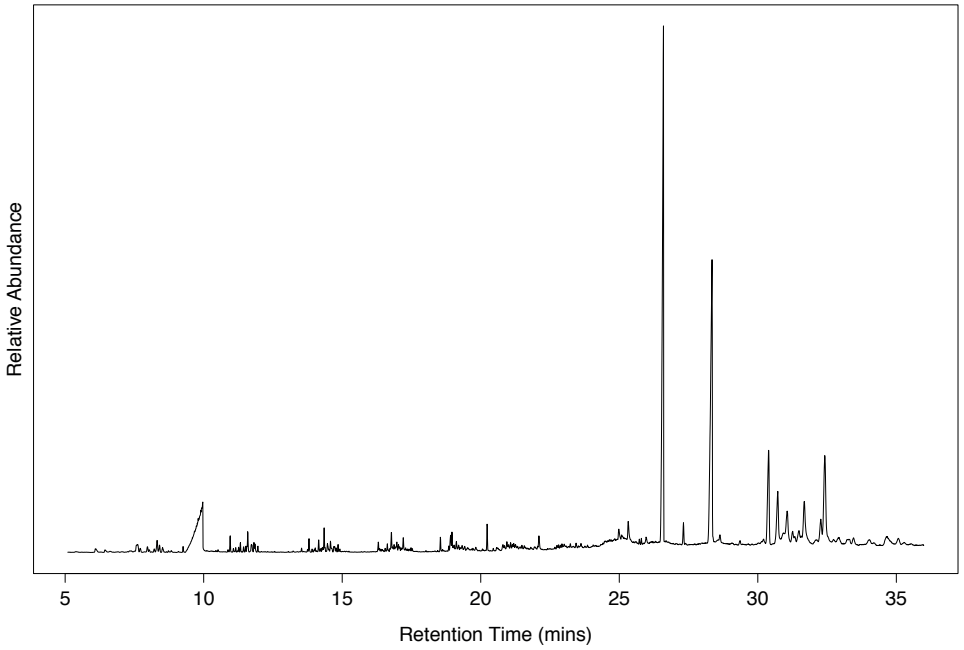
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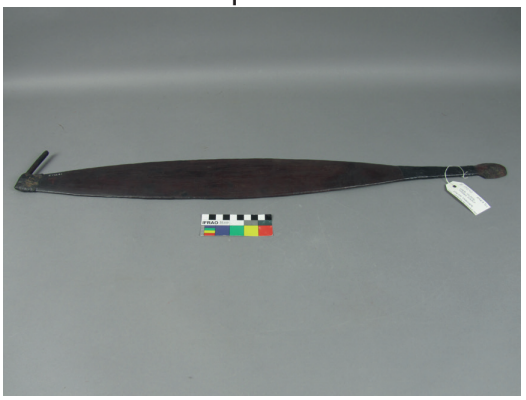

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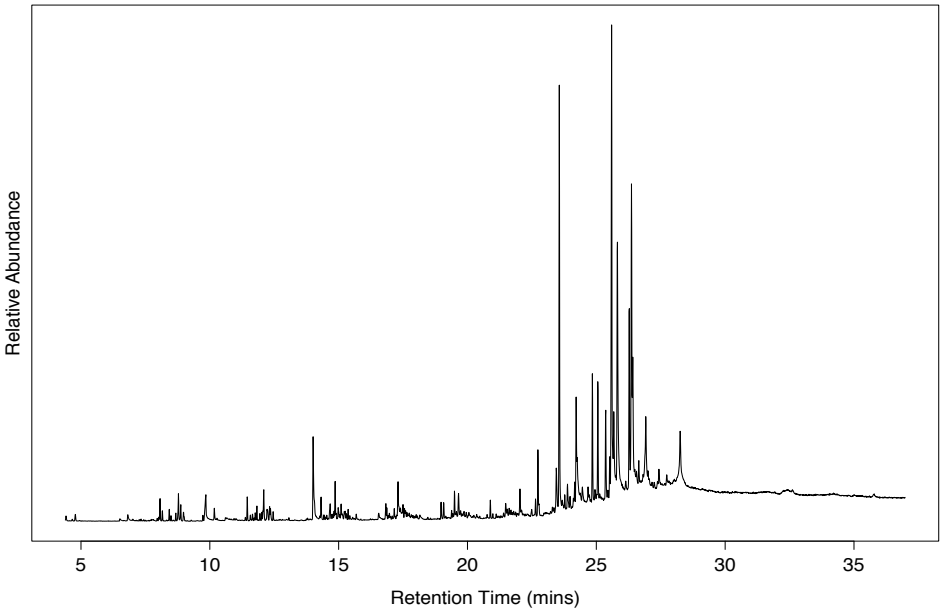

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AM03, AM04, AM05 | E17241

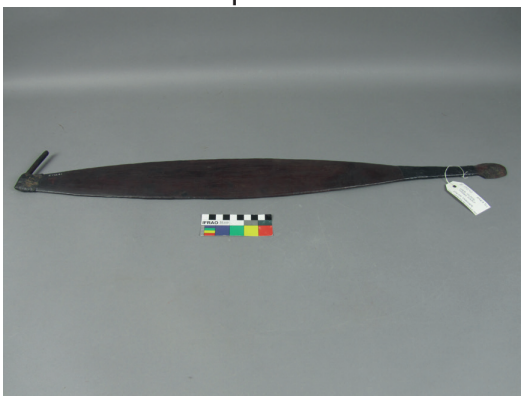


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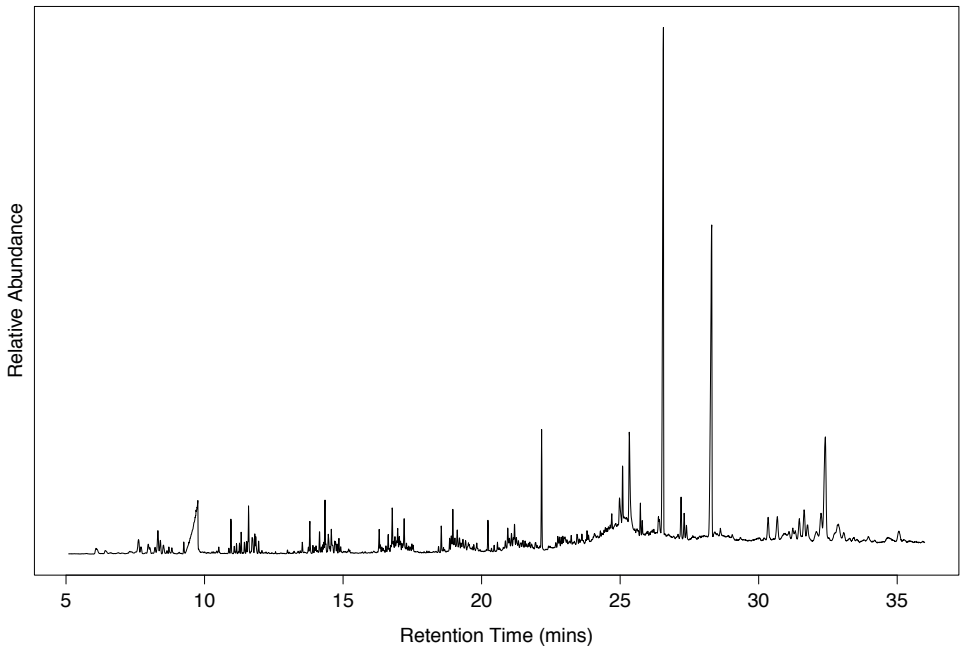


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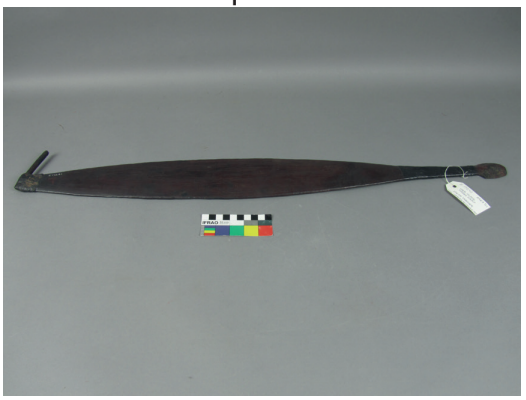


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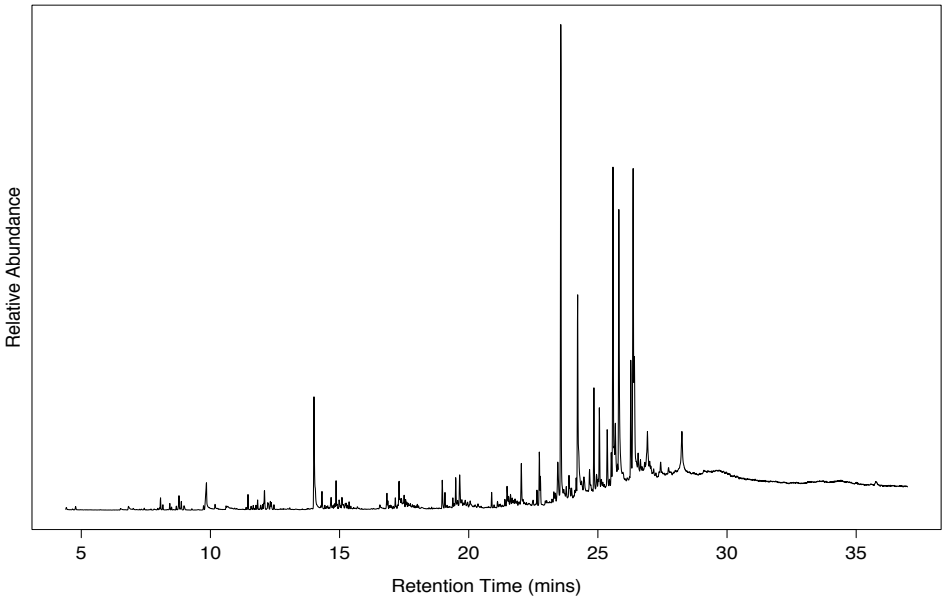


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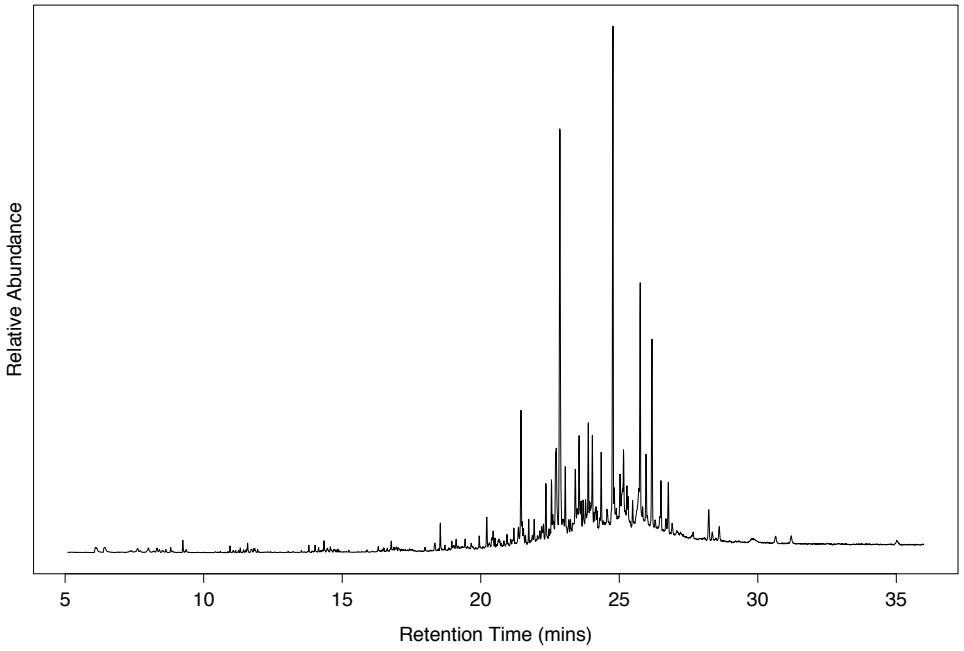
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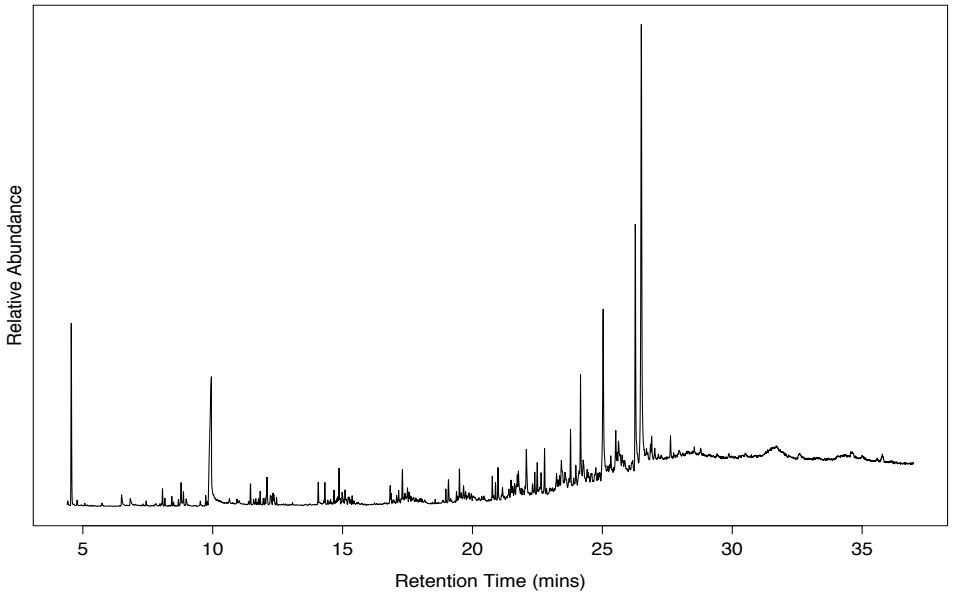
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IFRAO 10 cm


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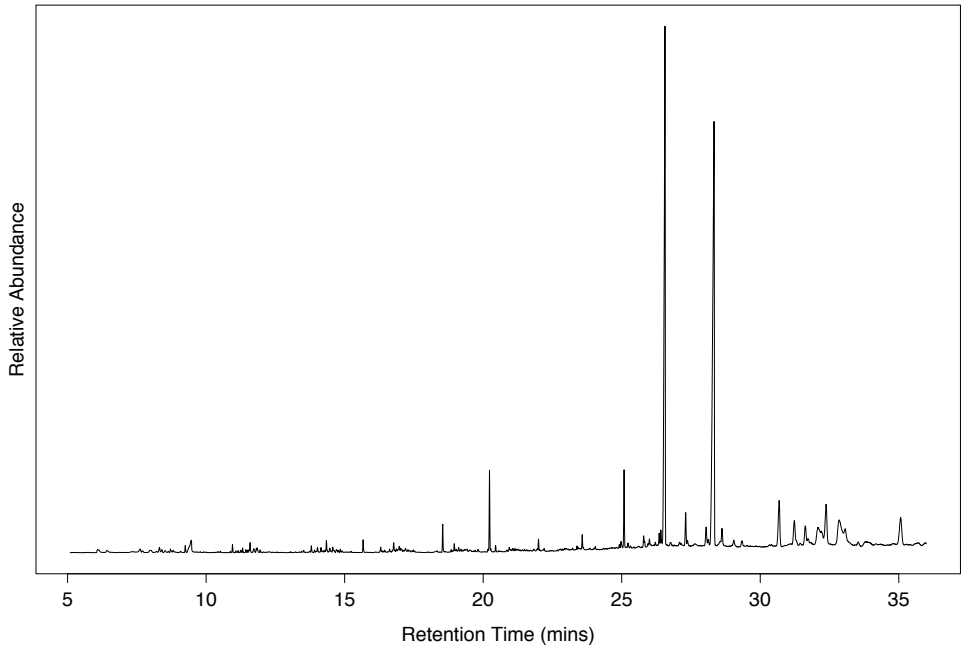
AM07 | E67922


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AM08 | E20705


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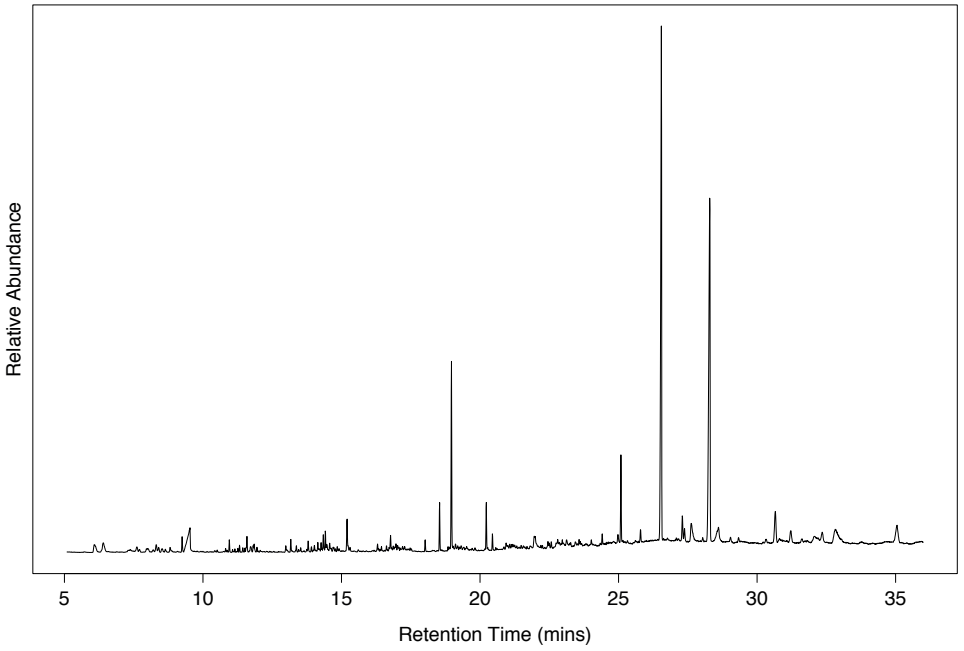

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AM09, AM10 | E74915



AM09 | E74915



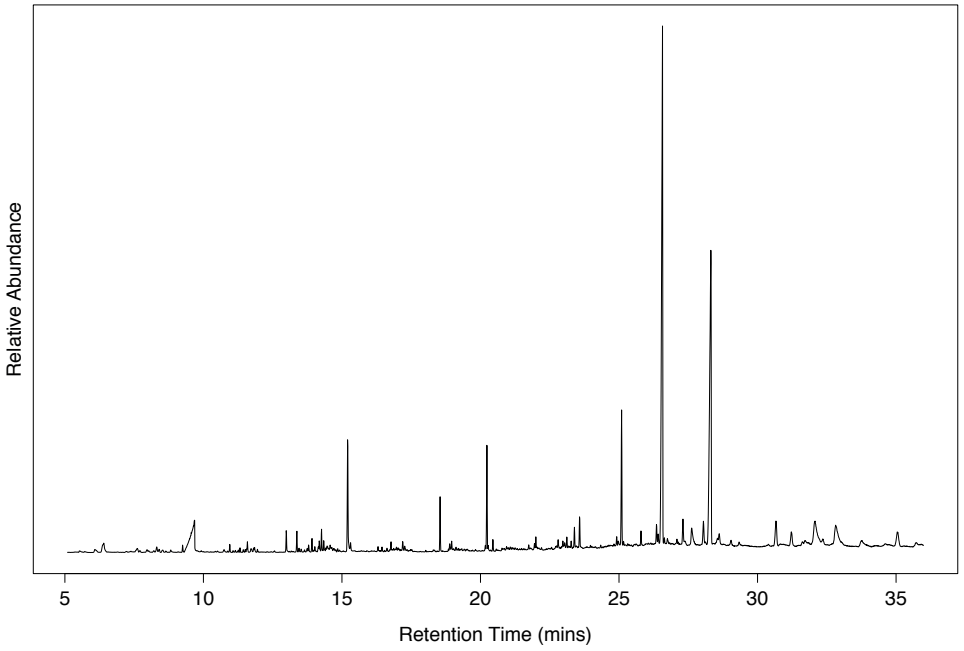


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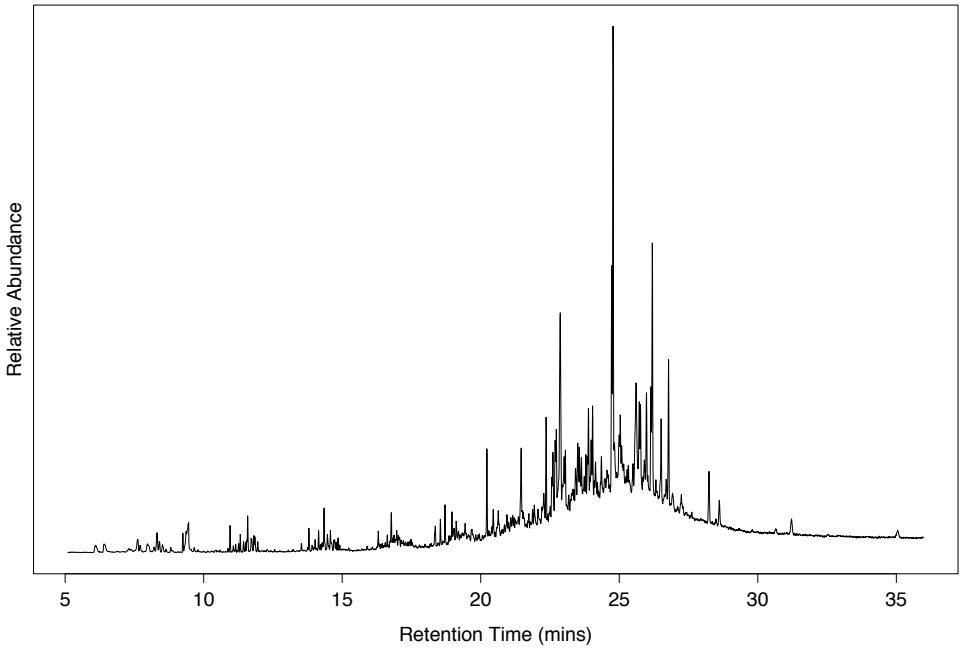
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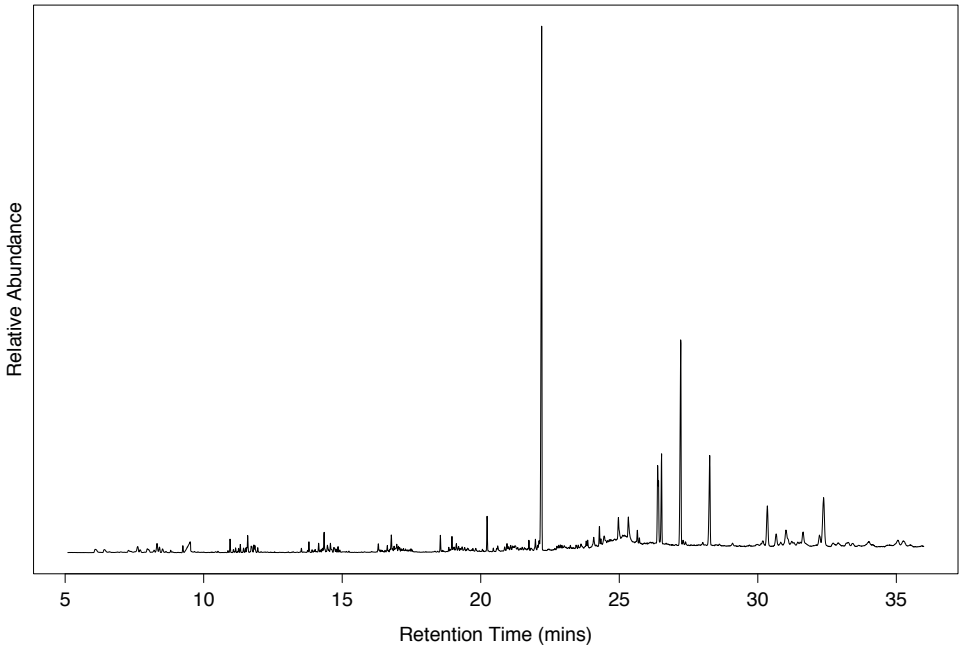
AM11 | E35571


IFRAO 10 cm
IFRAO 10 cm


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AM12 | AUR455


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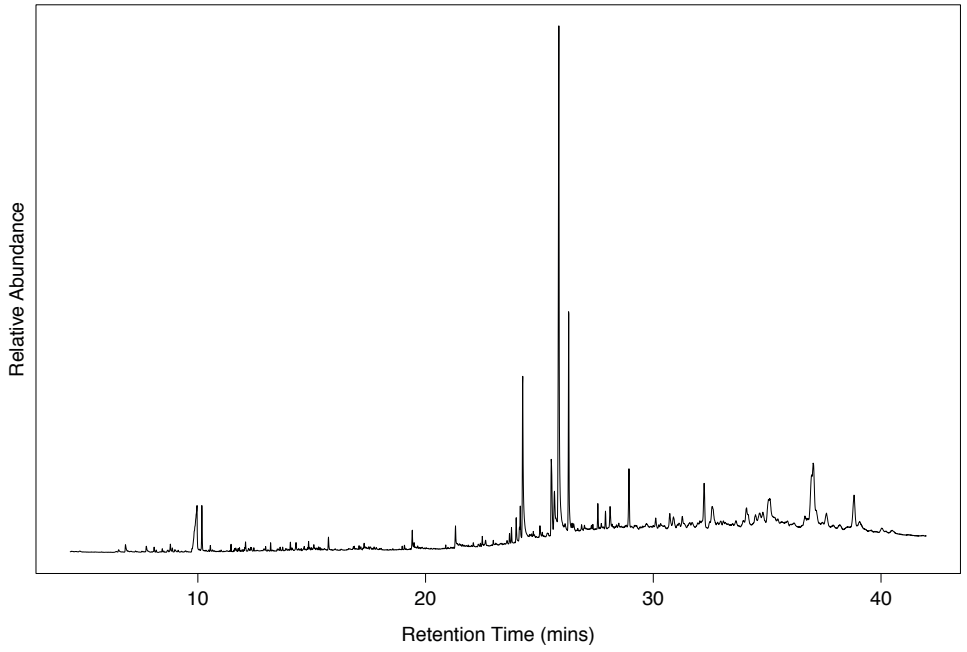

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AM13, AM14, AM15 | E13335



AM13 | E13335



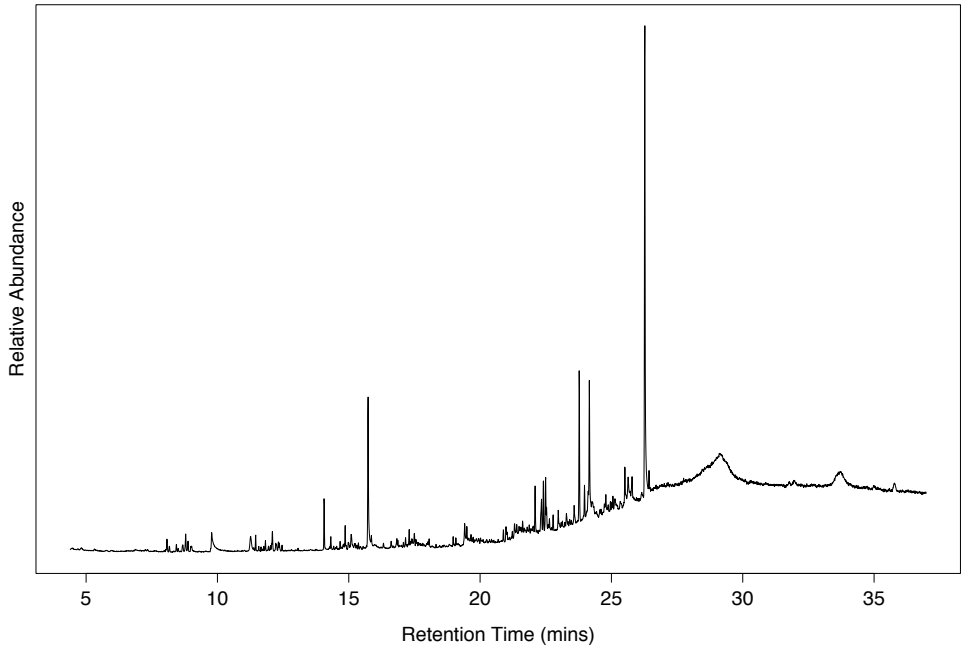


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AM14 | E13335



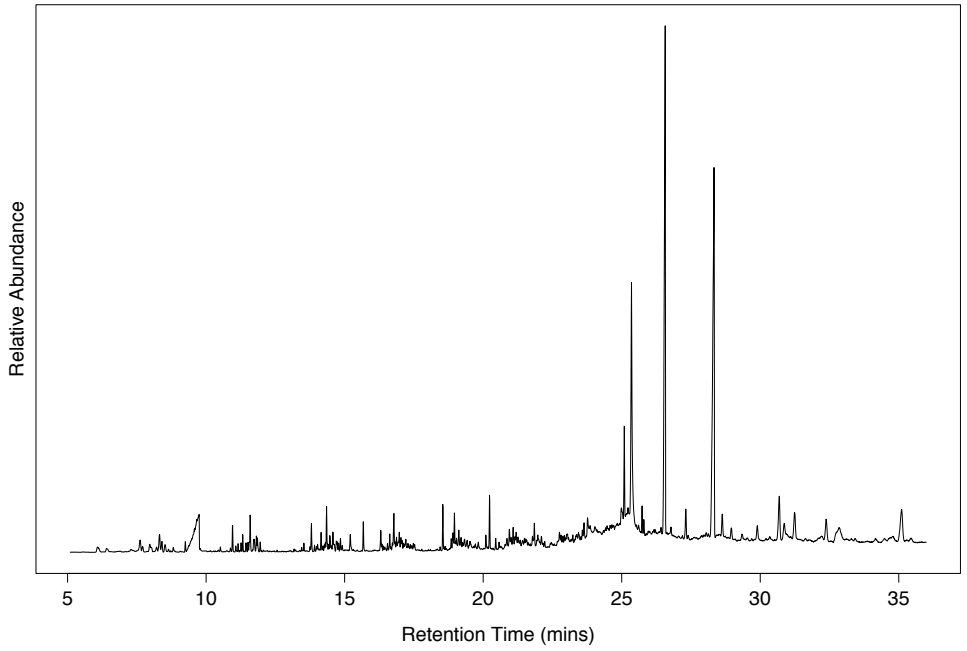


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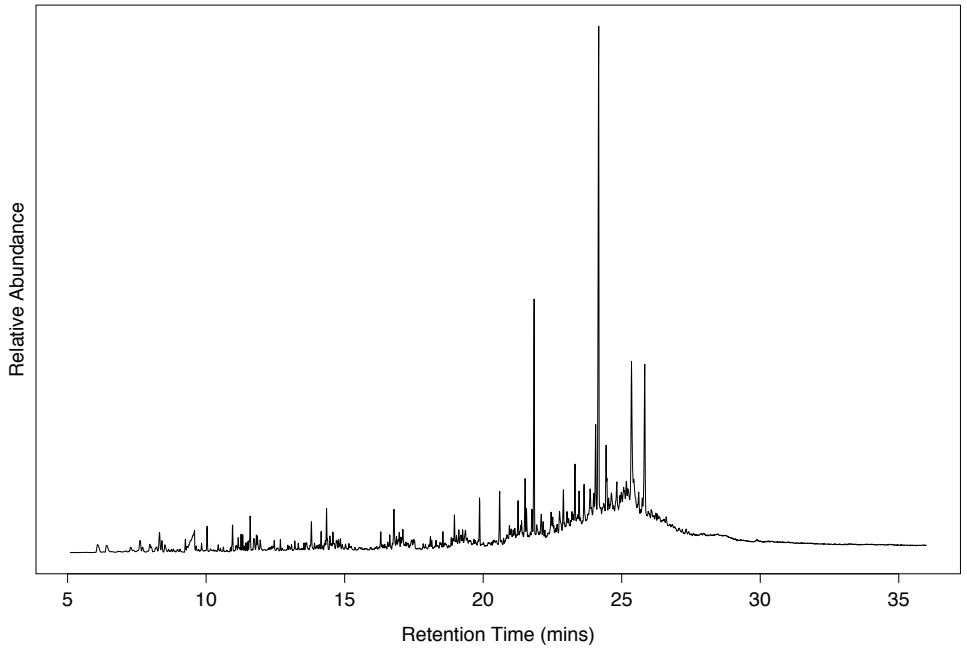
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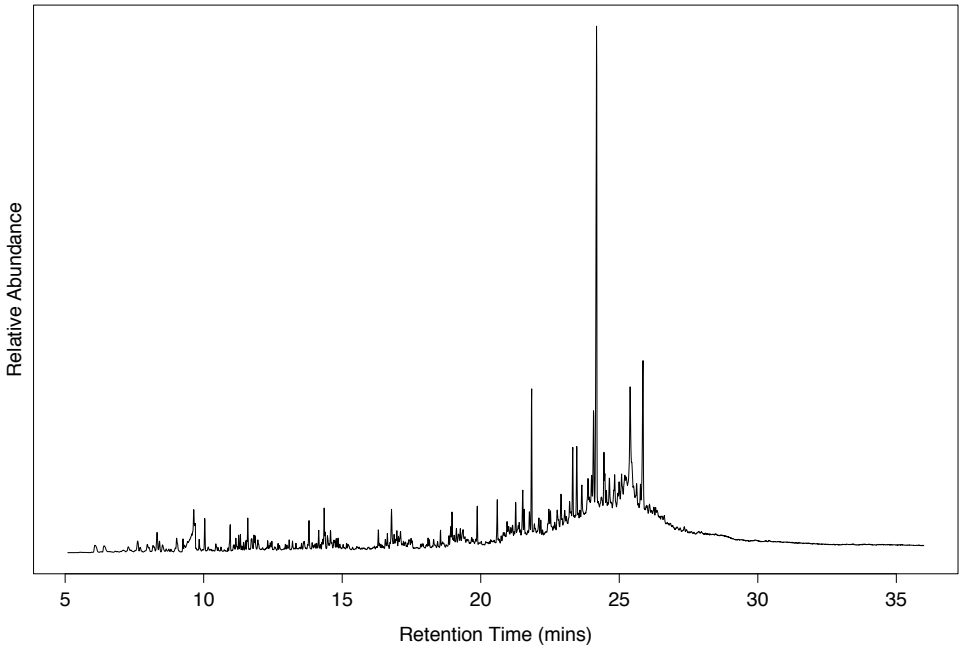
AM16 | E26007


IFRAO 10 cm


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35
Retention Time (mins)

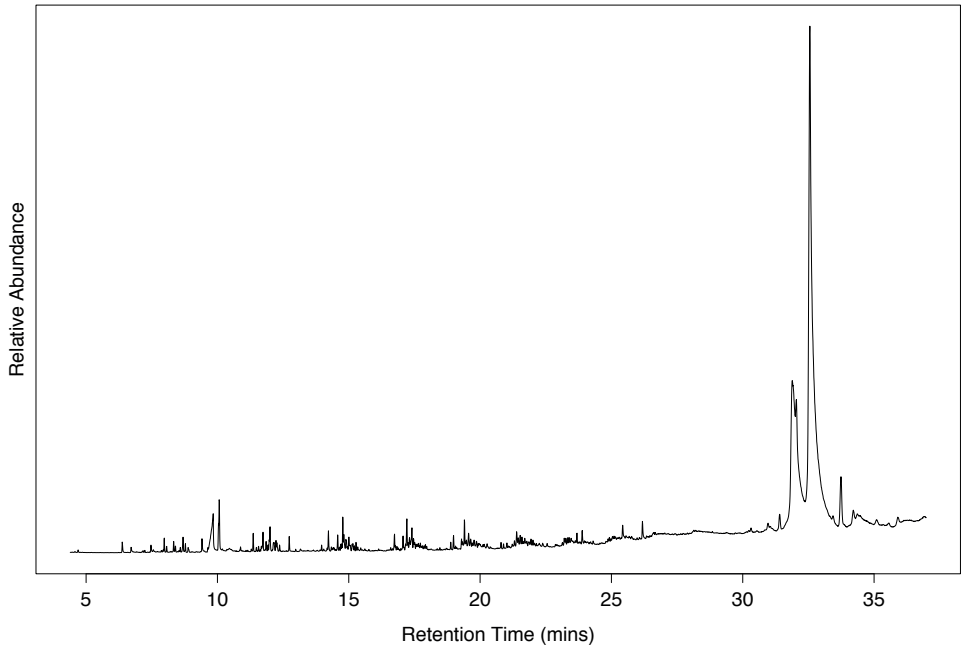
AM17 | E79383


IFRAO 10 cm
November 2001


Relative Abundance
5
10
15
20
25
30
35
Retention Time (mins)

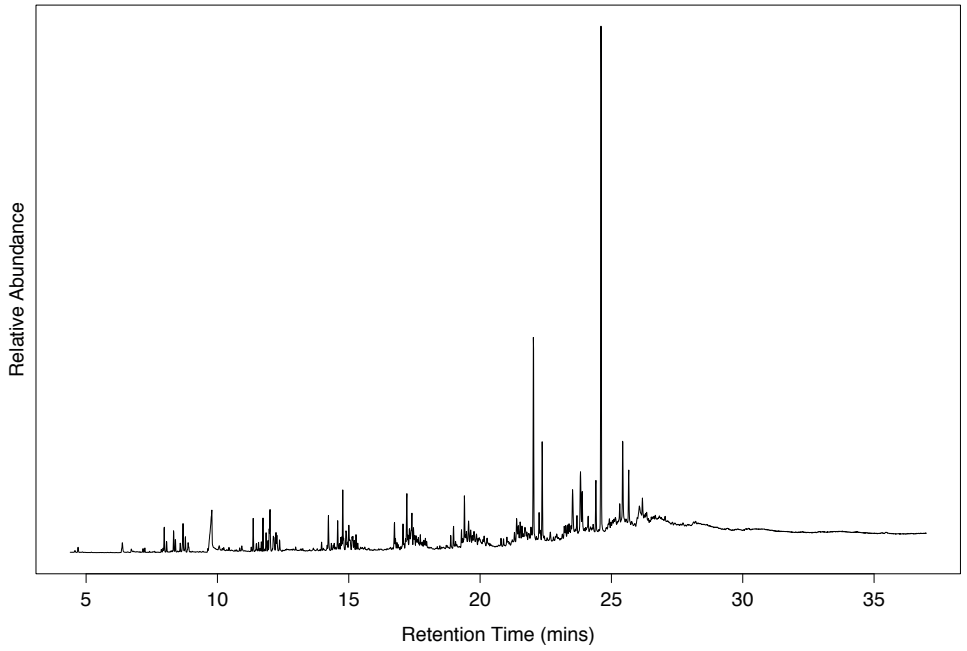
AM18 | E5349


IFRAO 10 cm
November 2001


Relative Abundance
5
10
15
20
25
30
35
Retention Time (mins)

AM19 | E78034

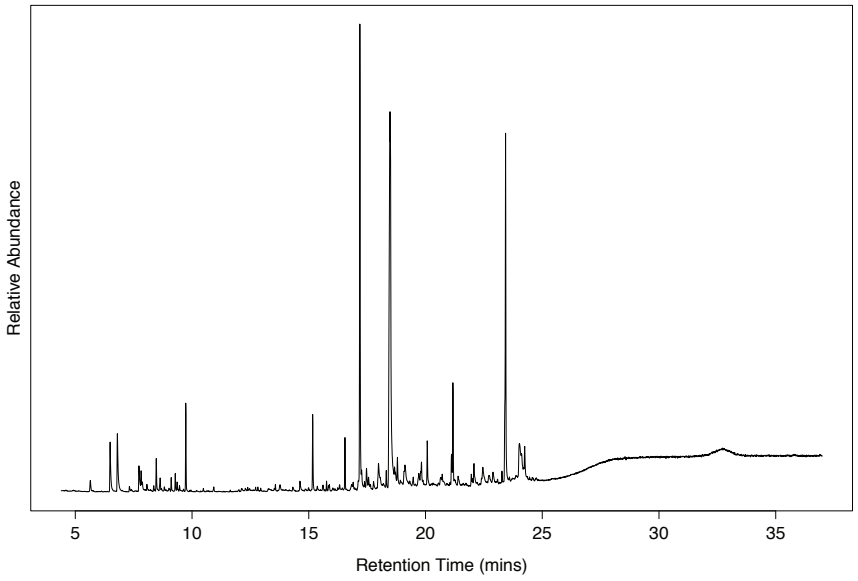

IFRAO 10 cm


Relative Abundance
5
10
15
20
25
30
35
Retention Time (mins)

Peabody Museum of Archaeology and Ethnology at Harvard University

PBH001 | 39-17-70/1393



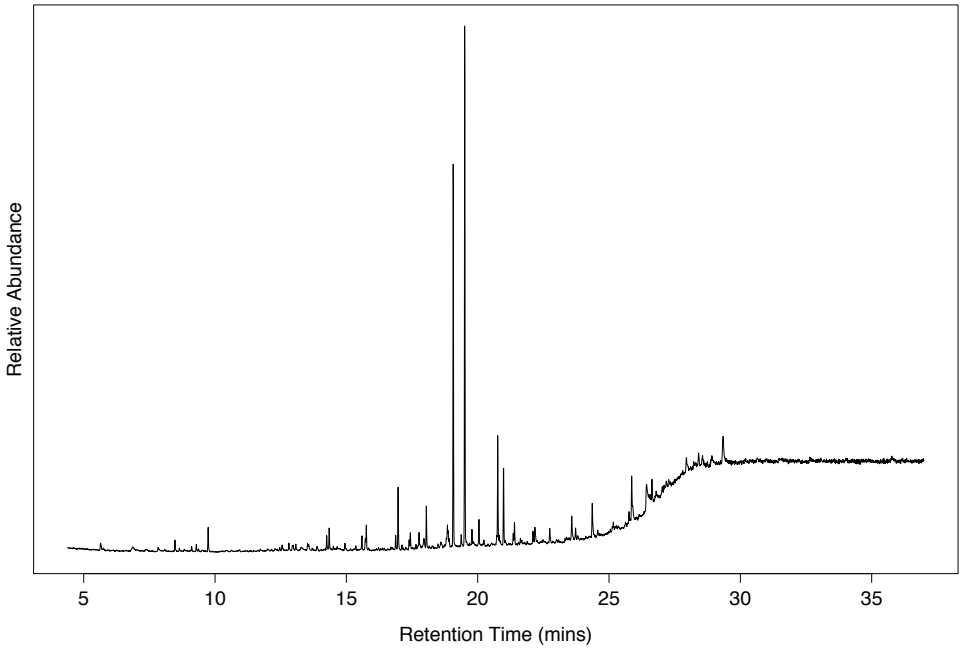


PBH002, PBH003 | 36-27-70/345



PBH002 | 36-27-70/345



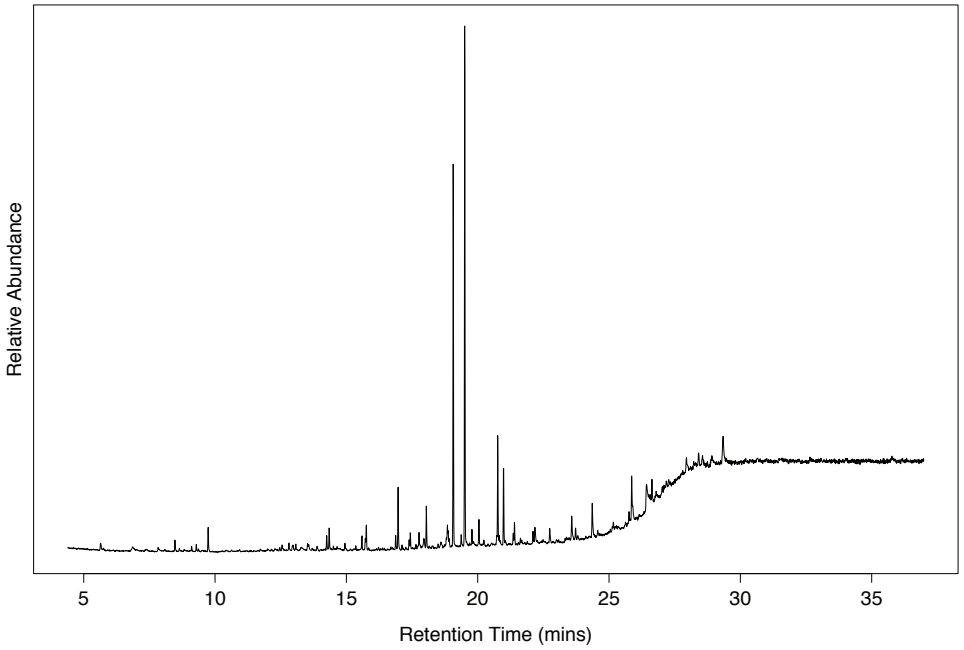


PBH002, PBH003 | 36-27-70/345



PBH003 | 36-27-70/345



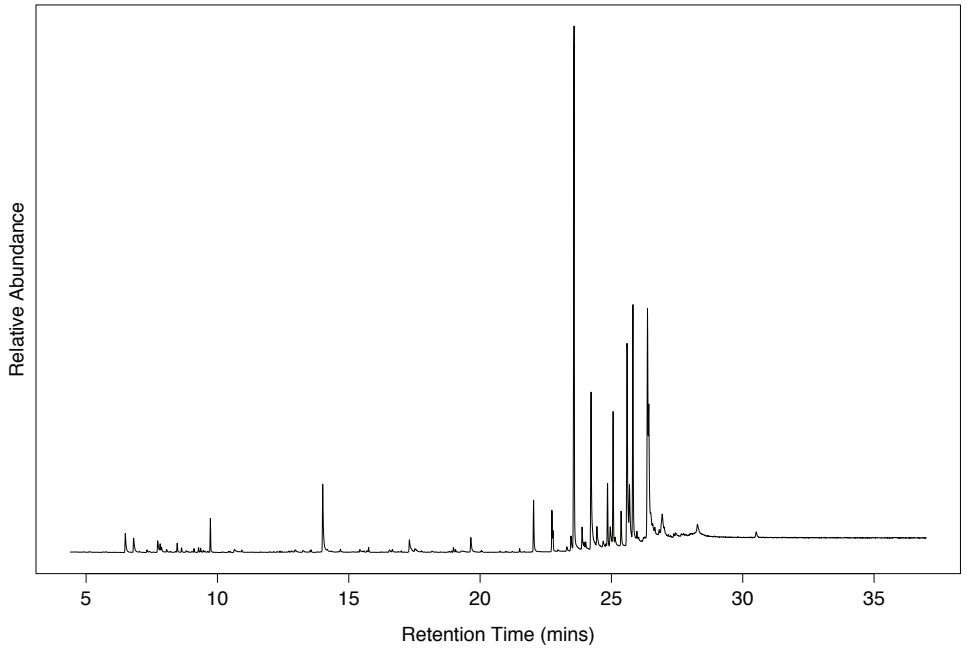


PBH004, PBH005, PBH006 | 51-32-70/3290



PBH004 | 51-32-70/3290



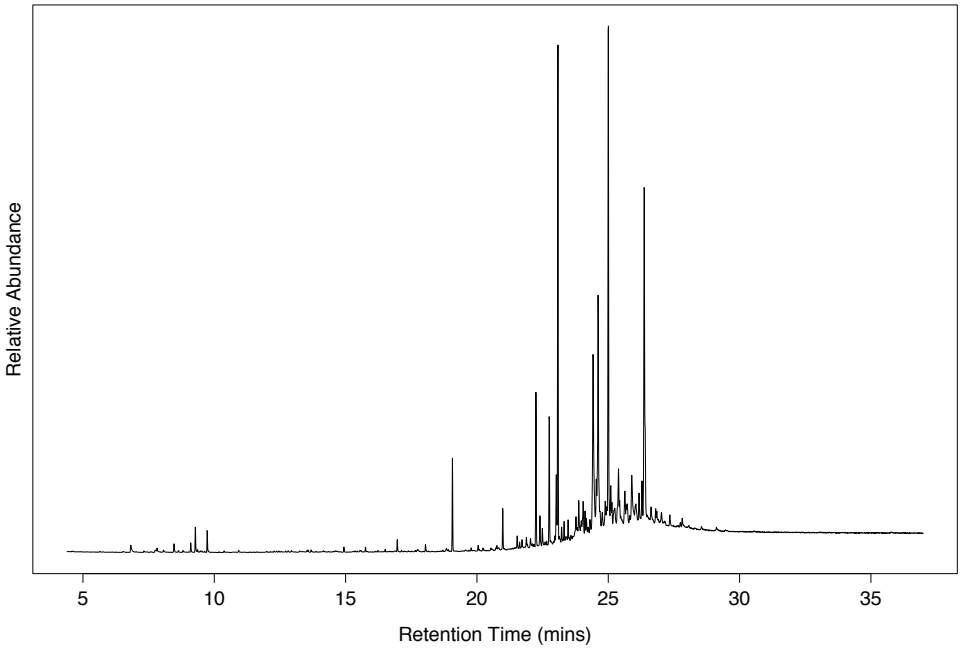


PBH004, PBH005, PBH006 | 51-32-70/3290



PBH005 | 51-32-70/3290



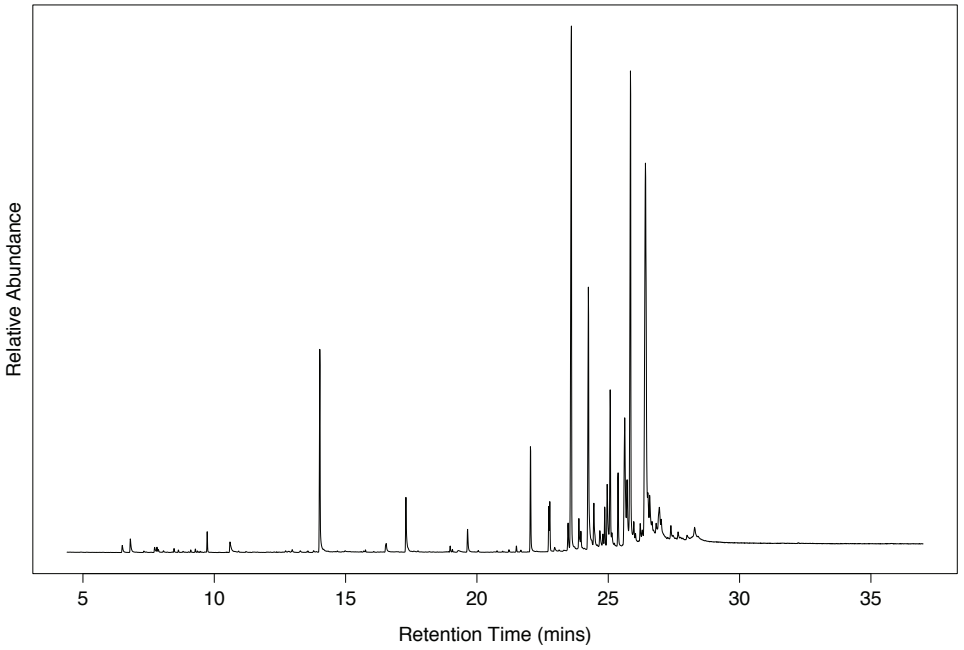


PBH004, PBH005, PBH006 | 51-32-70/3290

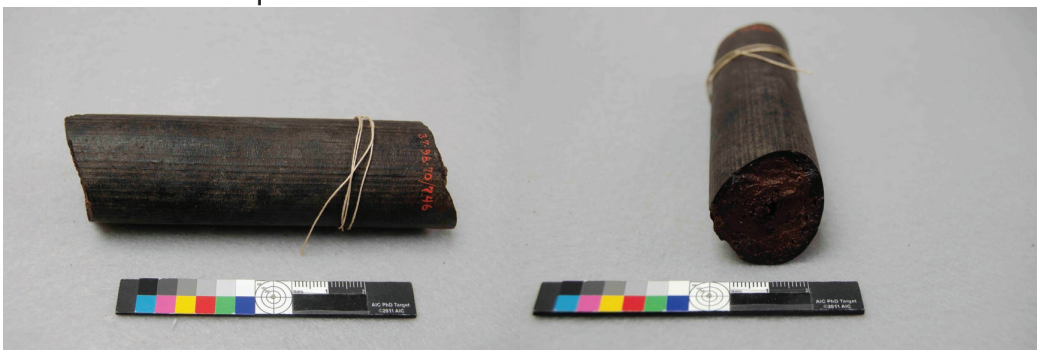


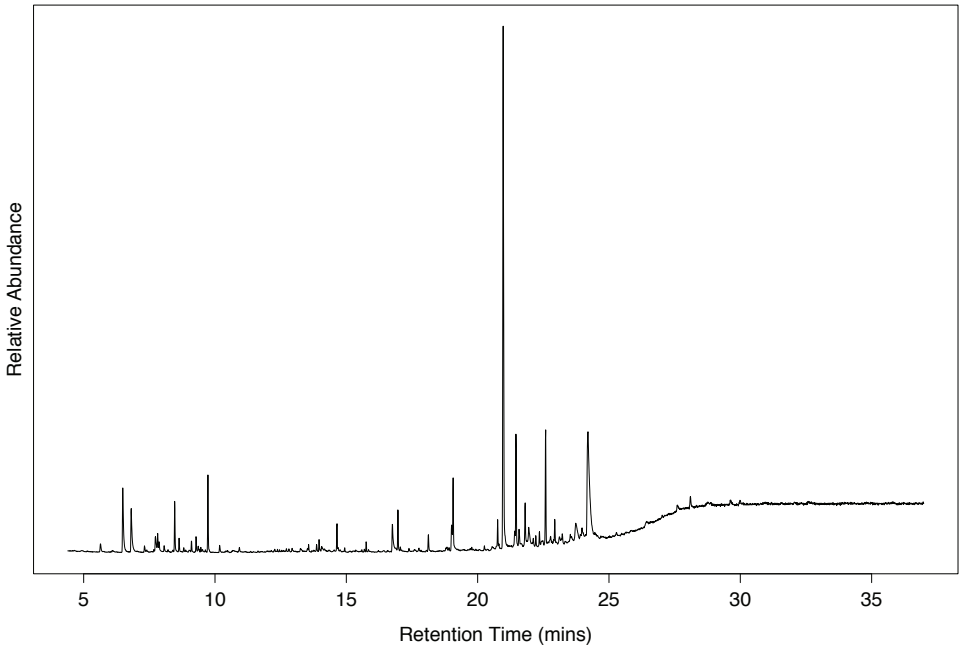
PBH006 | 51-32-70/3290





PBH007 | 37-98-70/746



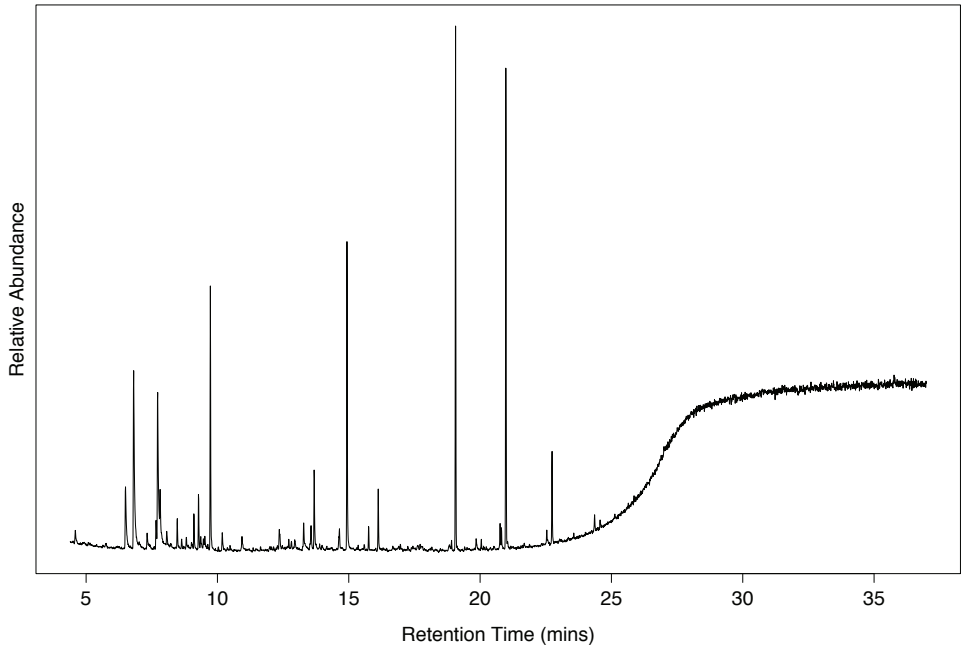


PBH008, PBH009 | 18-20-70/D-1224 (135383)



PBH008 | 18-20-70/D-1224 (135383)



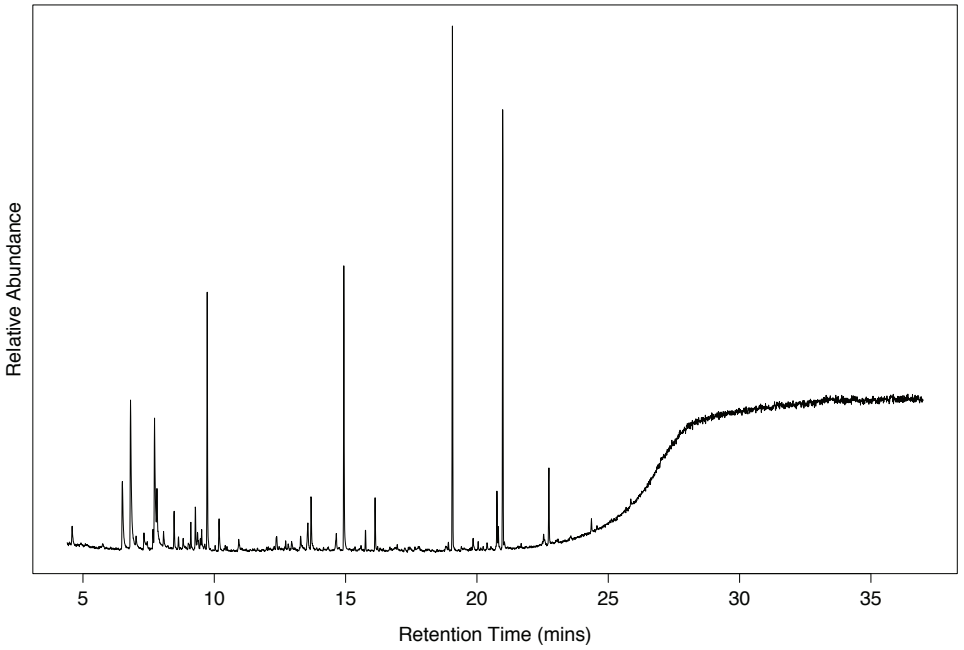


PBH008, PBH009 | 18-20-70/D-1224 (135383)

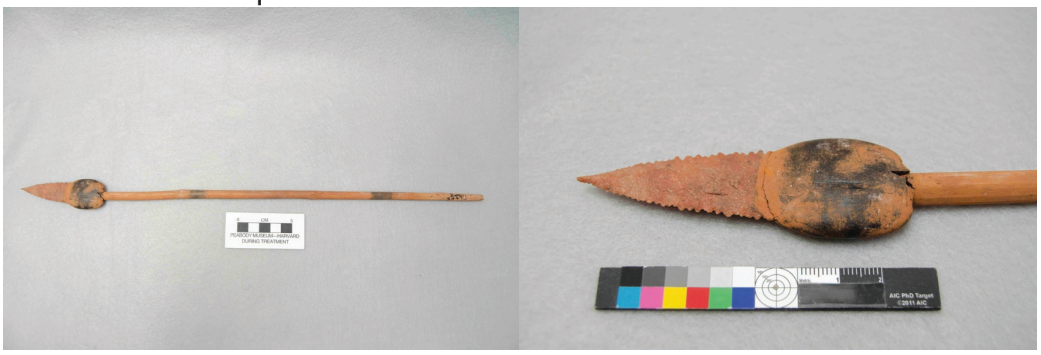


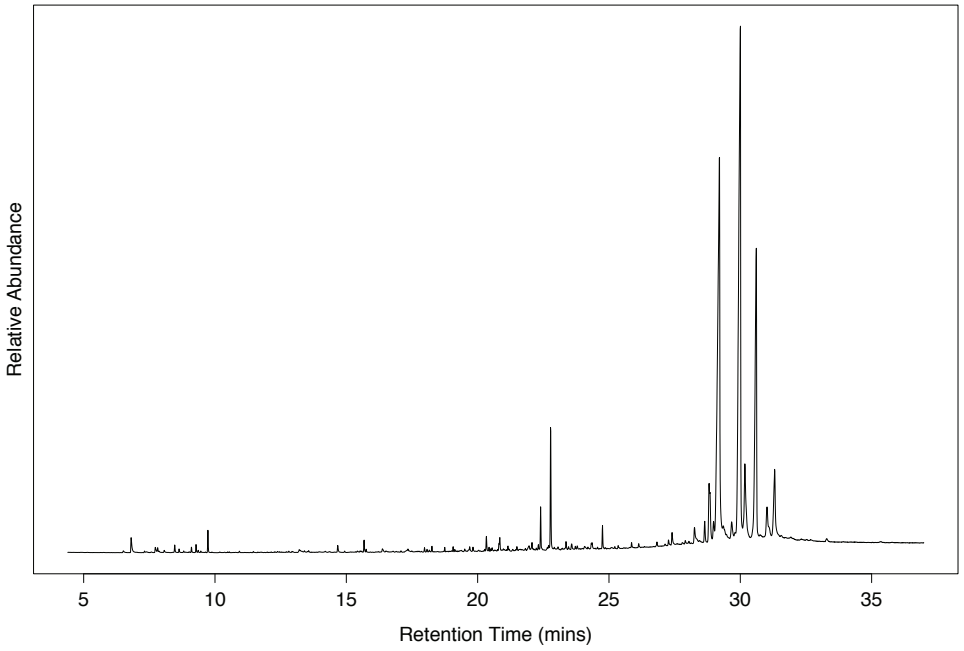
PBH009 | 18-20-70/D-1224 (135383)





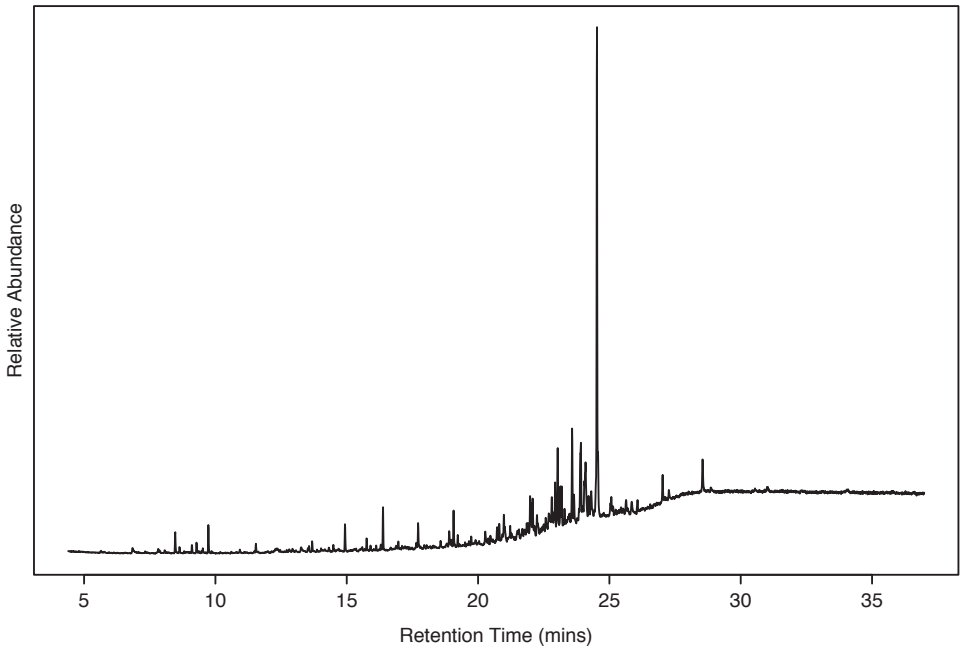
PBH010 | 32-68-70/D3947.1 5CR





PBH011 | 23-46-70/D-1735



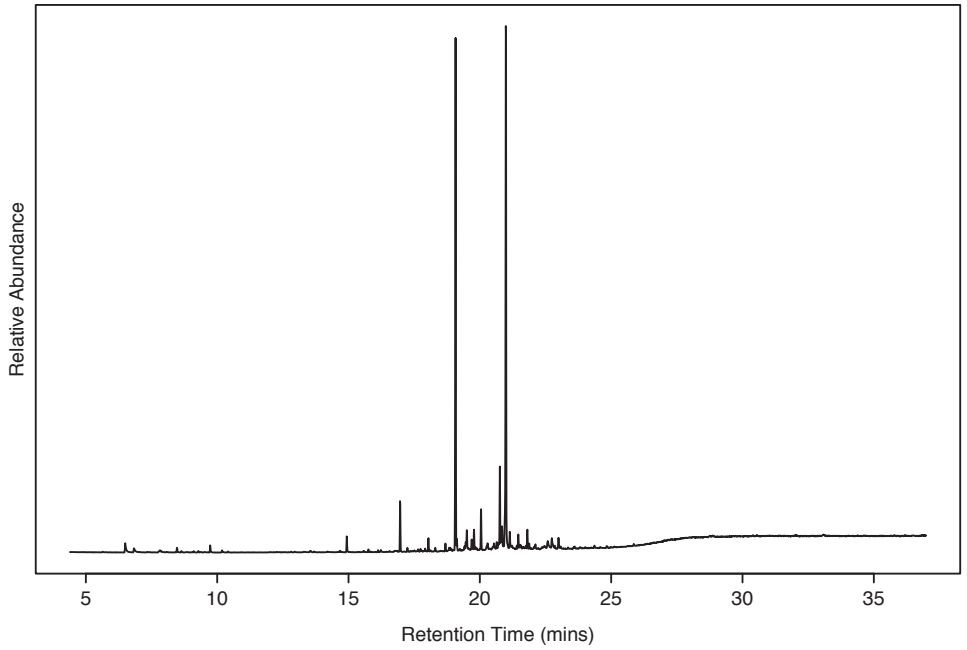


PBH012, PBH013 | 32-68-70/D-3962



PBH012 | 32-68-70/D-3962



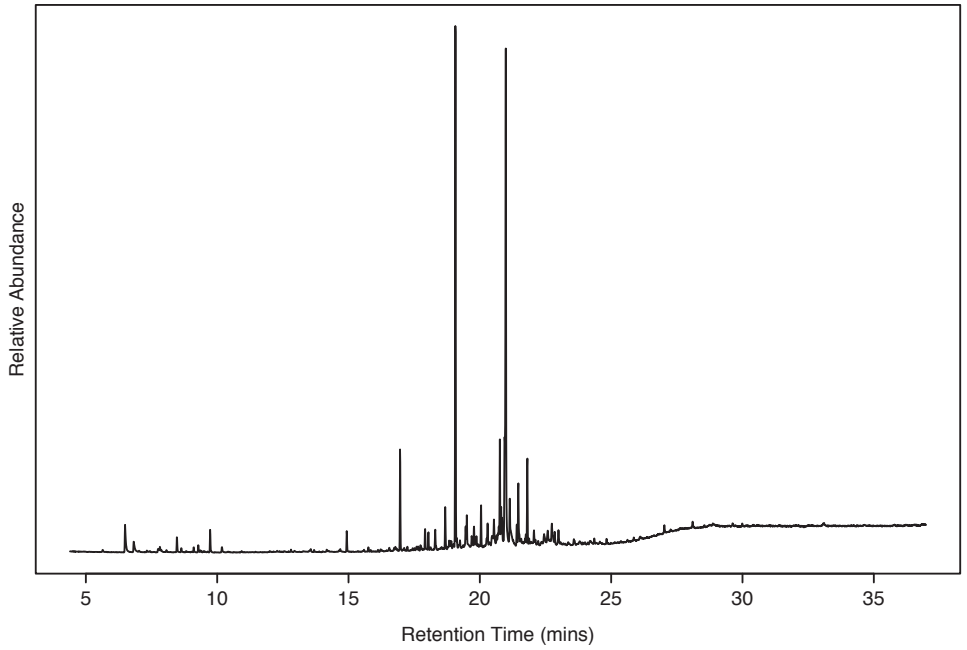


PBH012, PBH013 | 32-68-70/D-3962



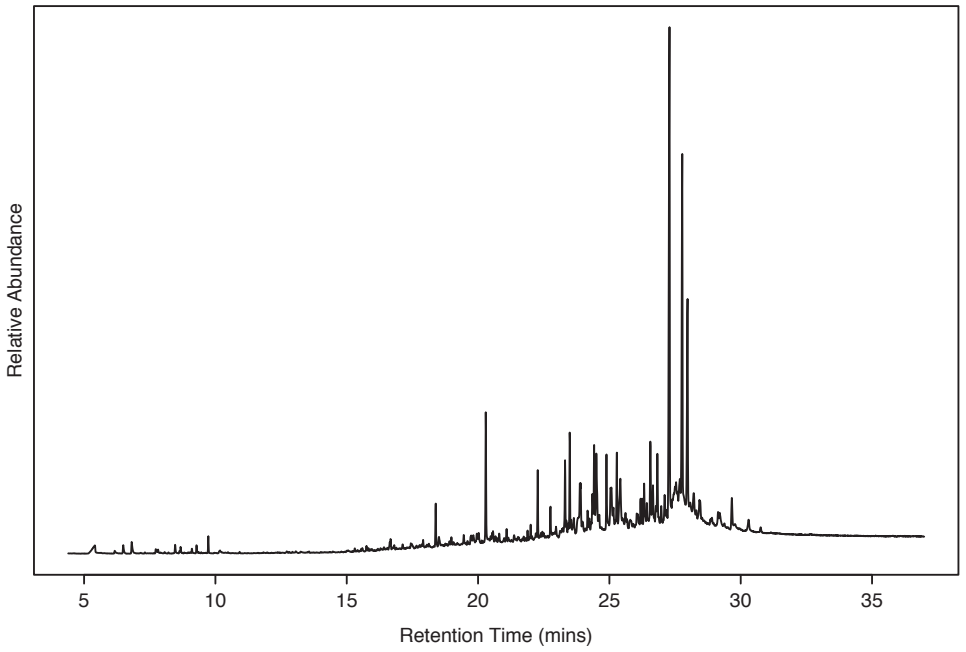
PBH013 | 32-68-70/D-3962





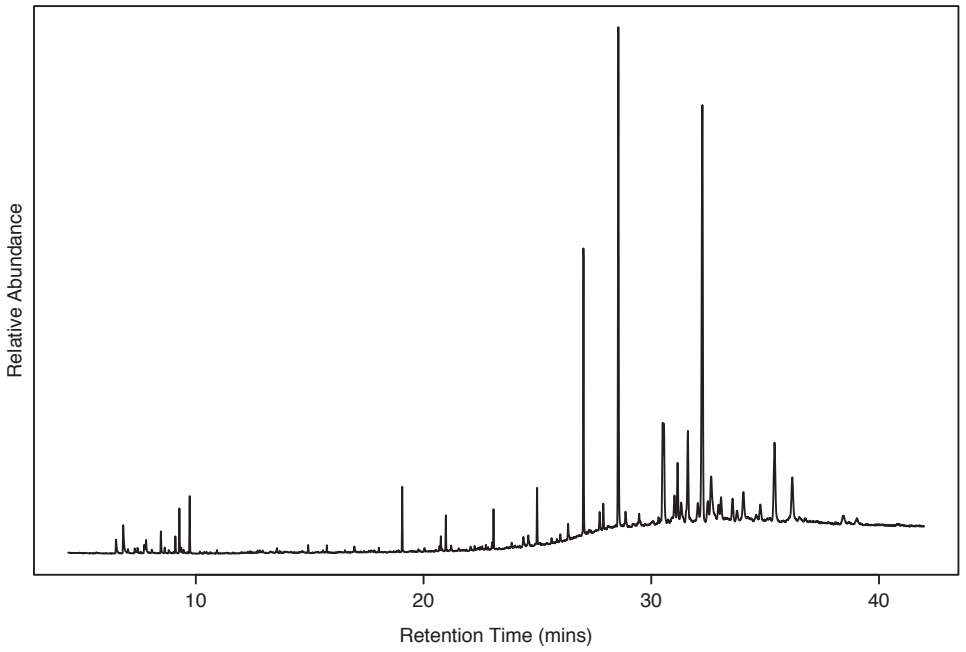
PBH014 | 67-10-70/249





PBH015 | 46-78-70/2400

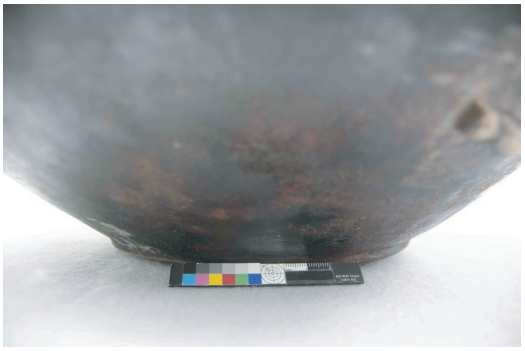


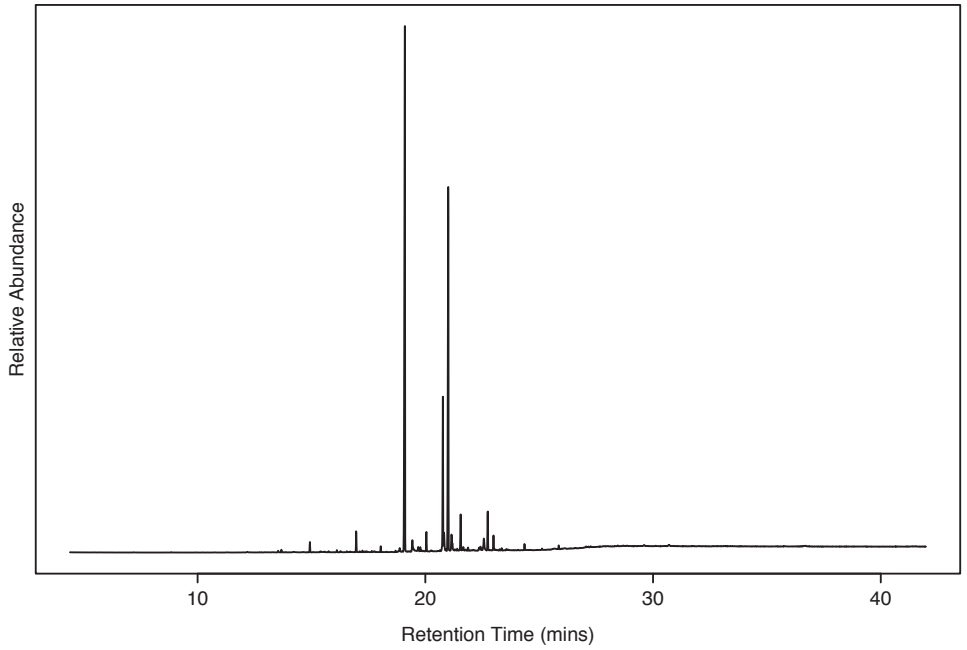


PBH016, PBH017 | 04-19-70/63232



PBH016 | 04-19-70/63232



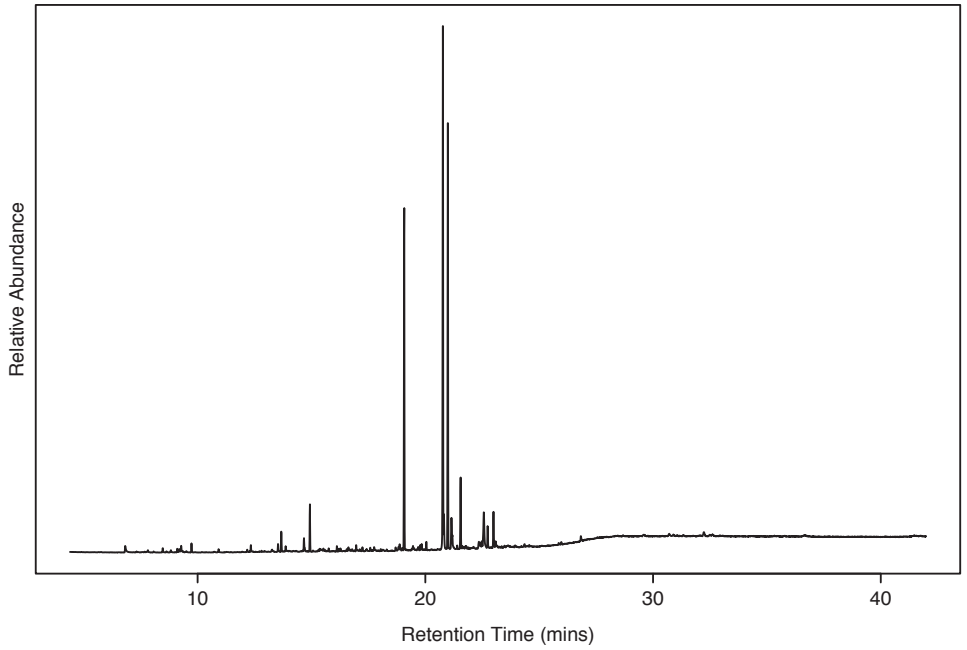


PBH016, PBH017 | 04-19-70/63232



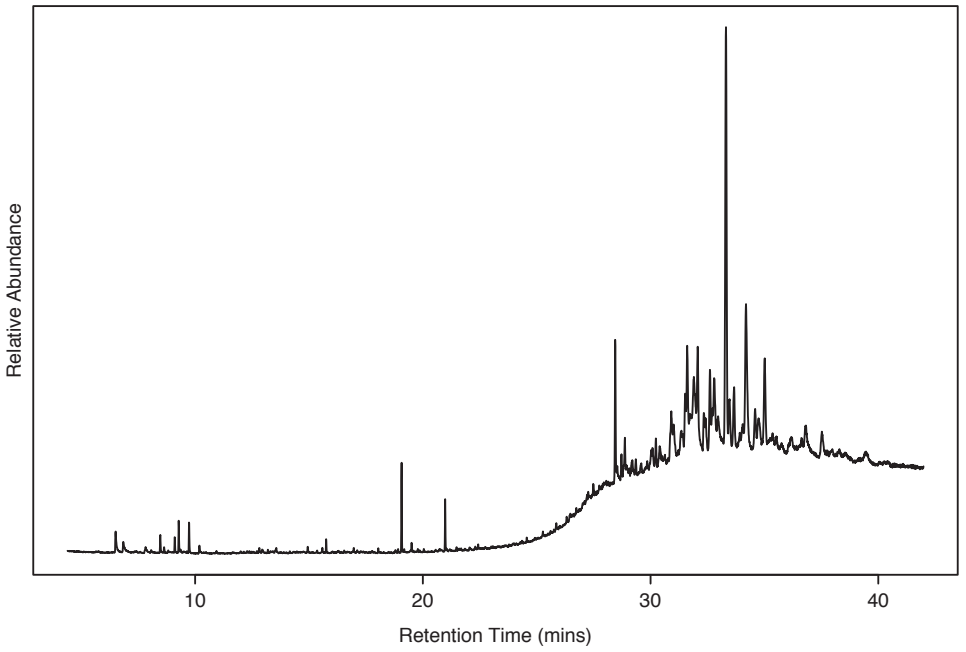
PBH017 | 04-19-70/63232





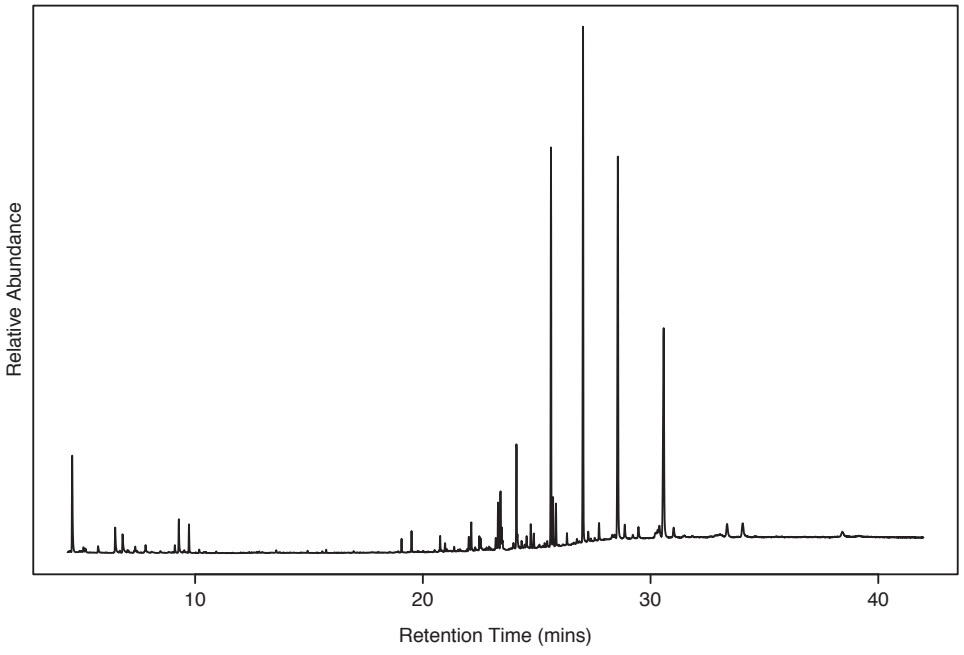
PBH018 | 51-33-70/3224





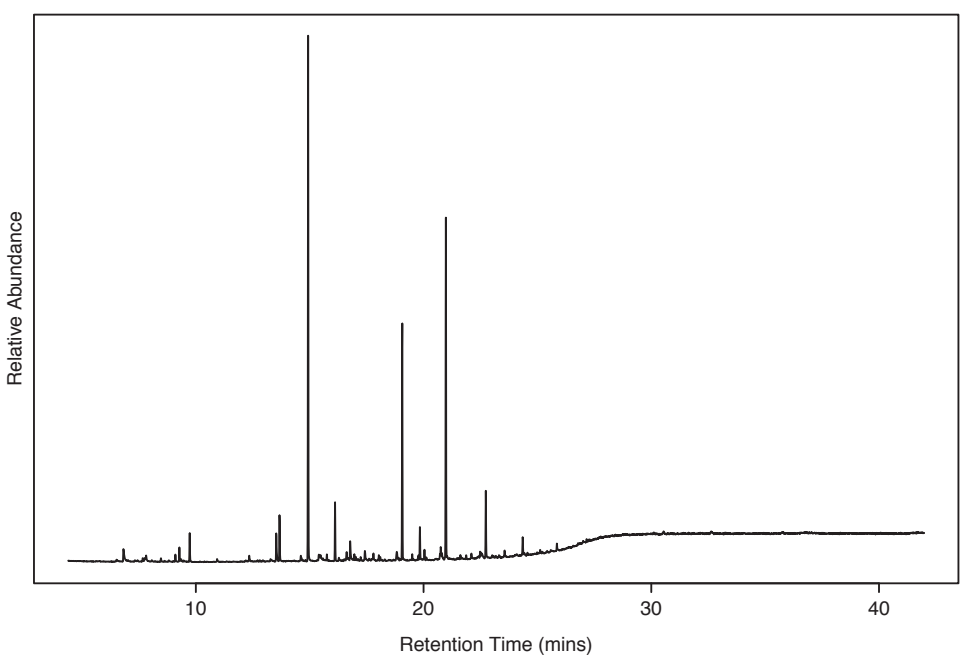
PBH019 | 22-29-70/D1696





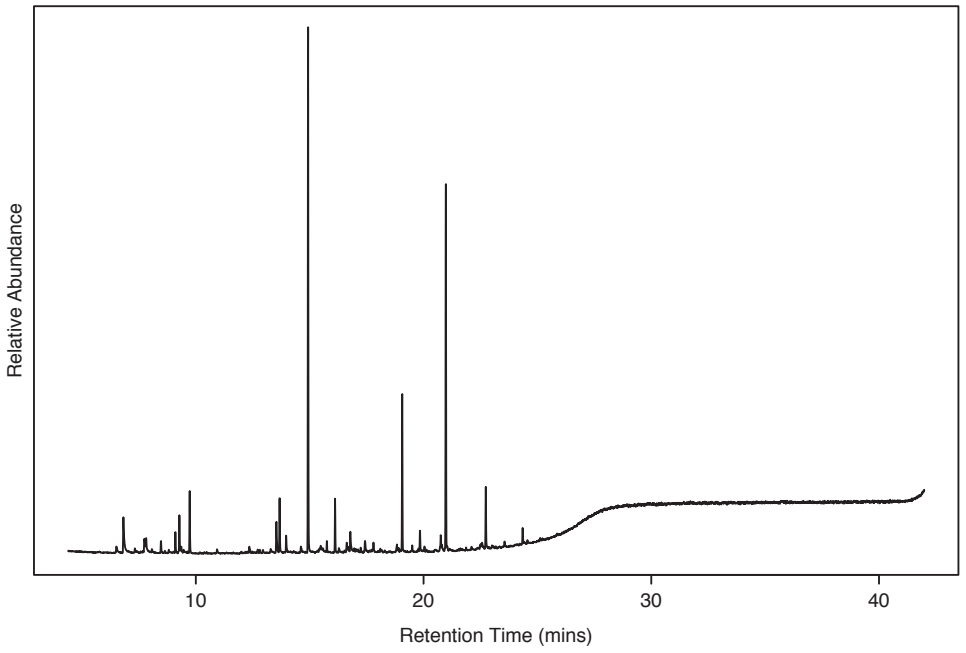
PBH020 | 23-47-70/D1798.1





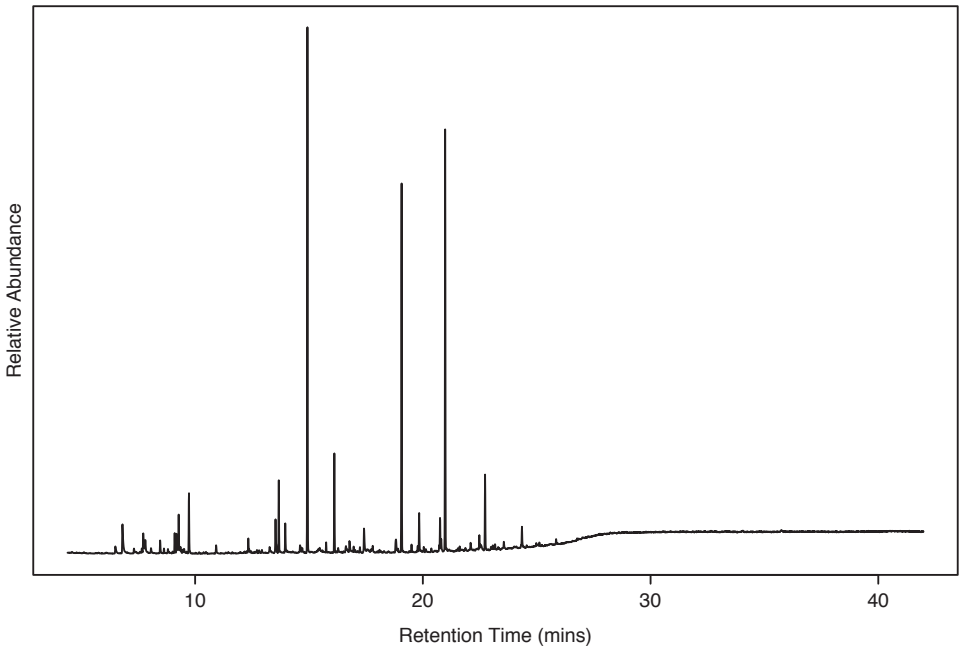
PBH021 | 23-47-70/D1798.2



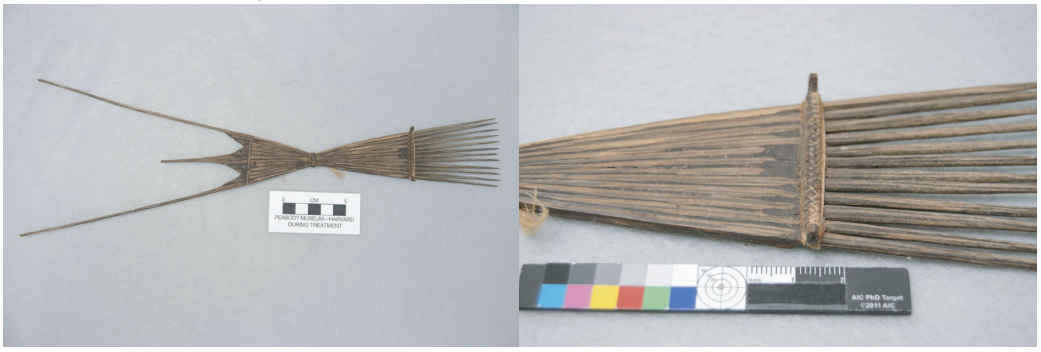


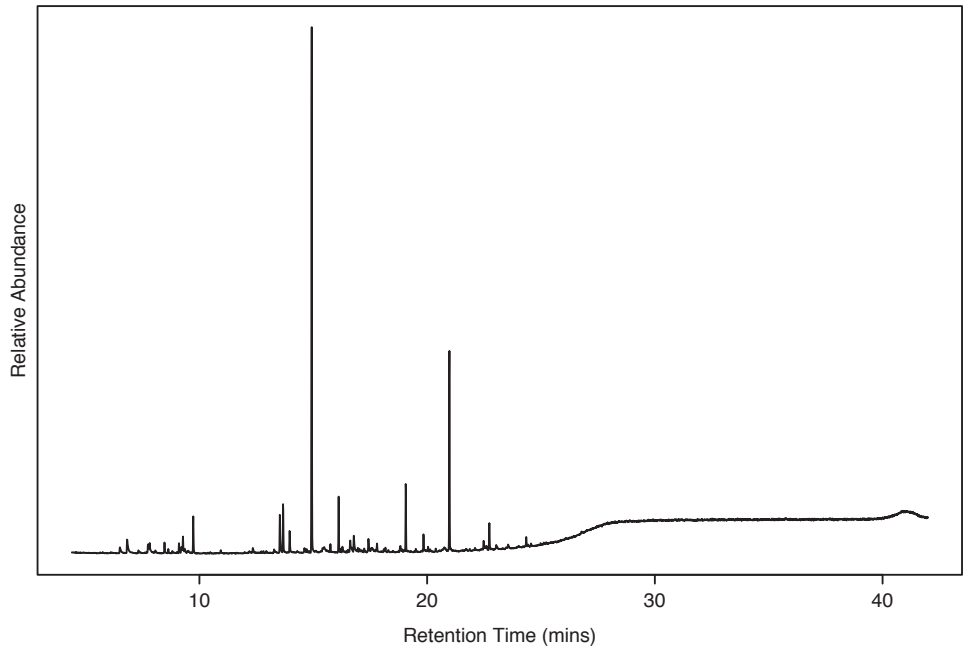
PBH022 | 23-47-70/D1798.3



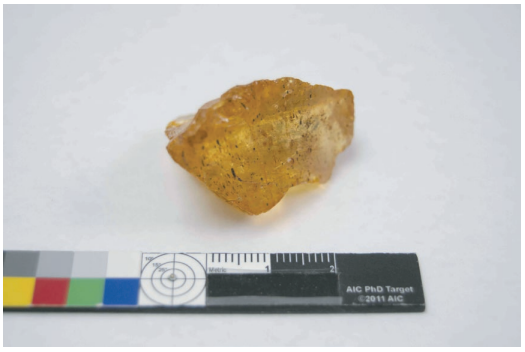


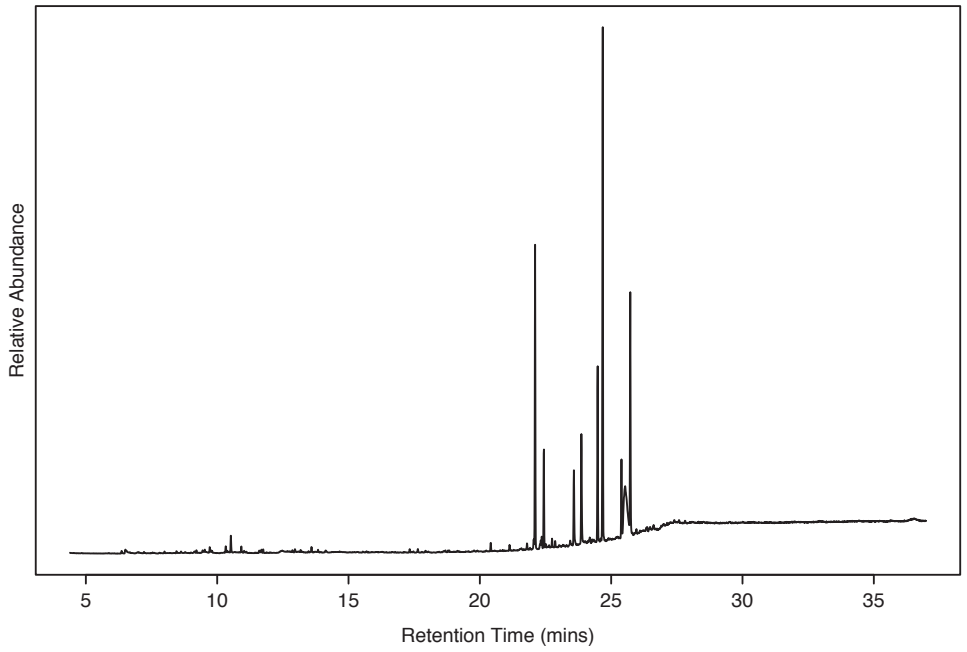
PBH023 | 07-30-70/72470





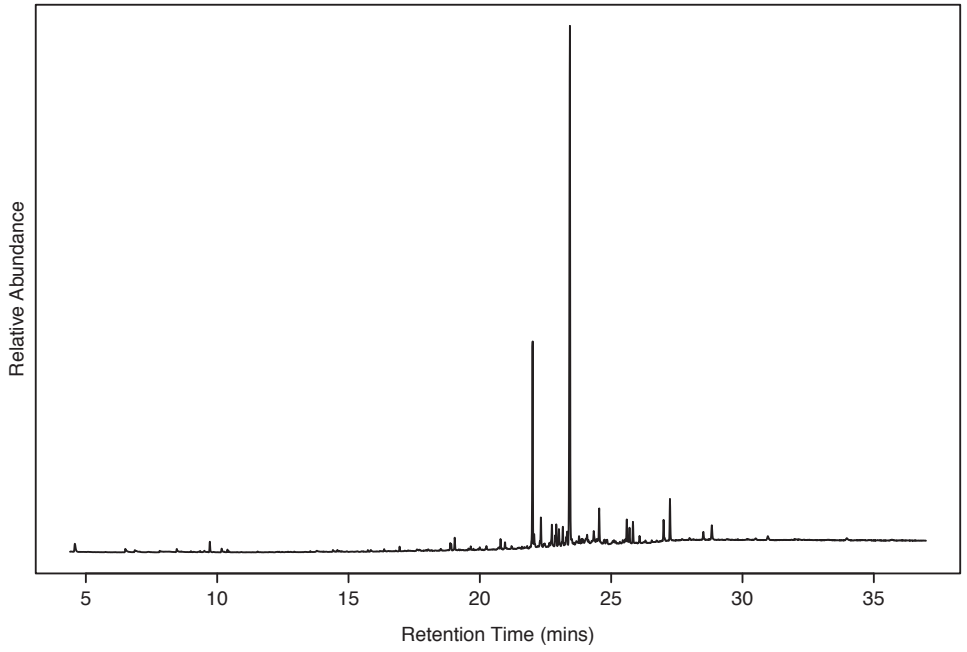
PBH024 | 64-18-70/4471





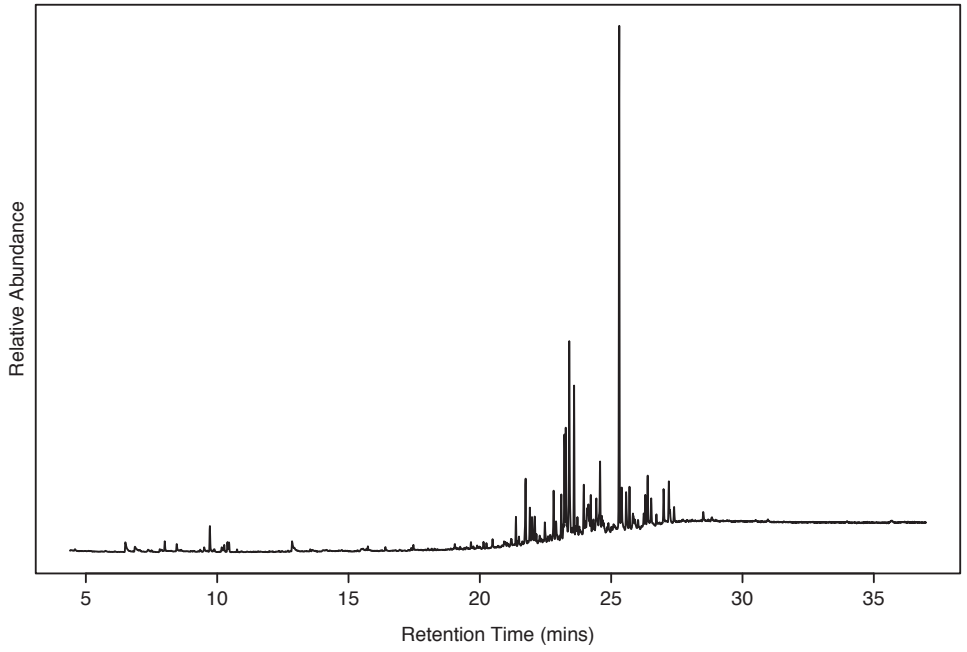
PBH025 |2004.1.620





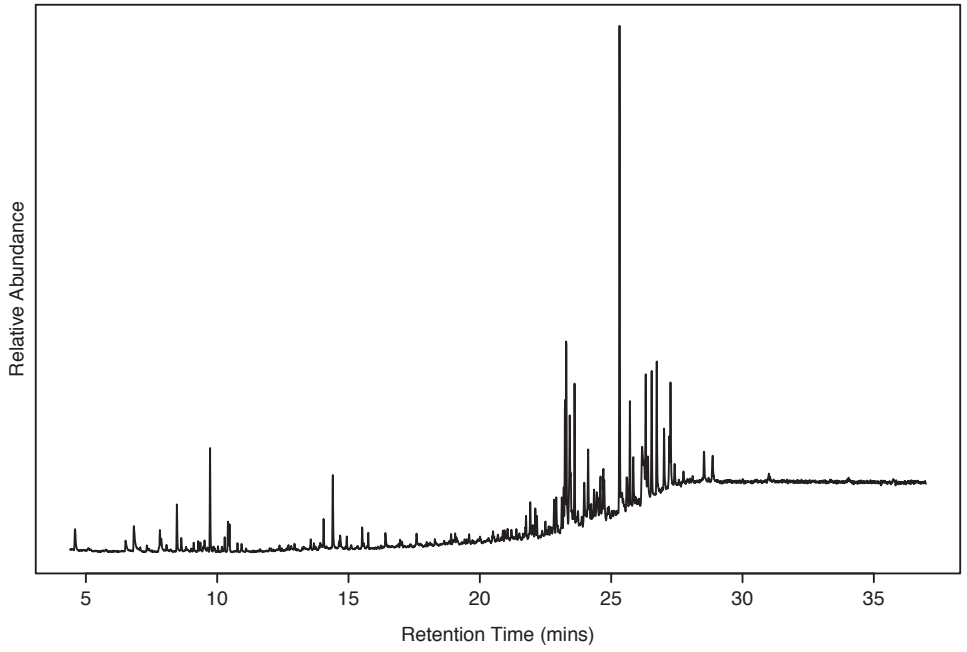
PBH026 |2004.1.631





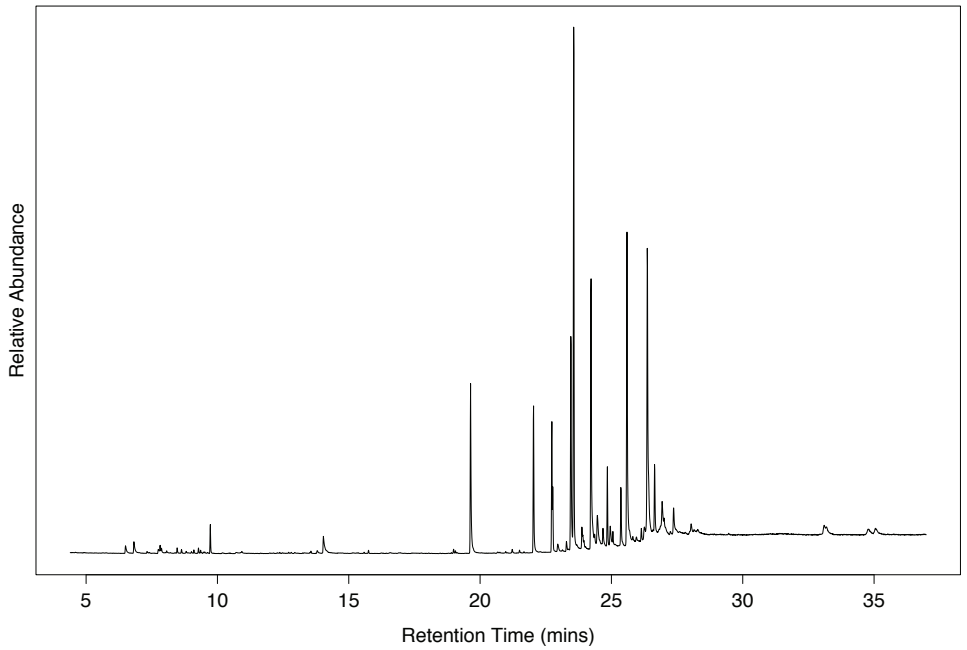
PBH027|2004.1.631





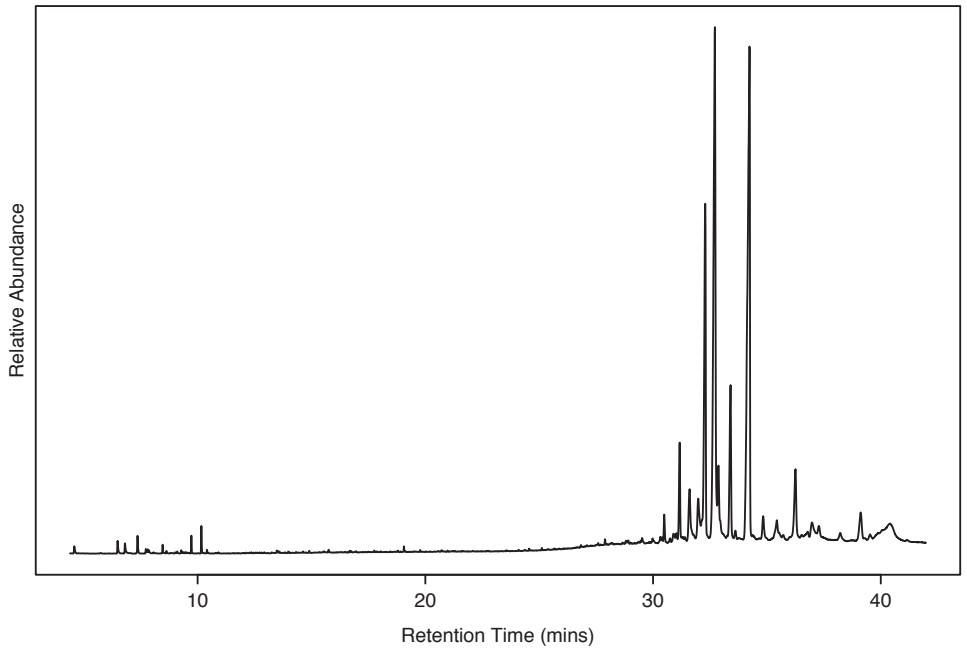
PBH028 | 2004.1.633





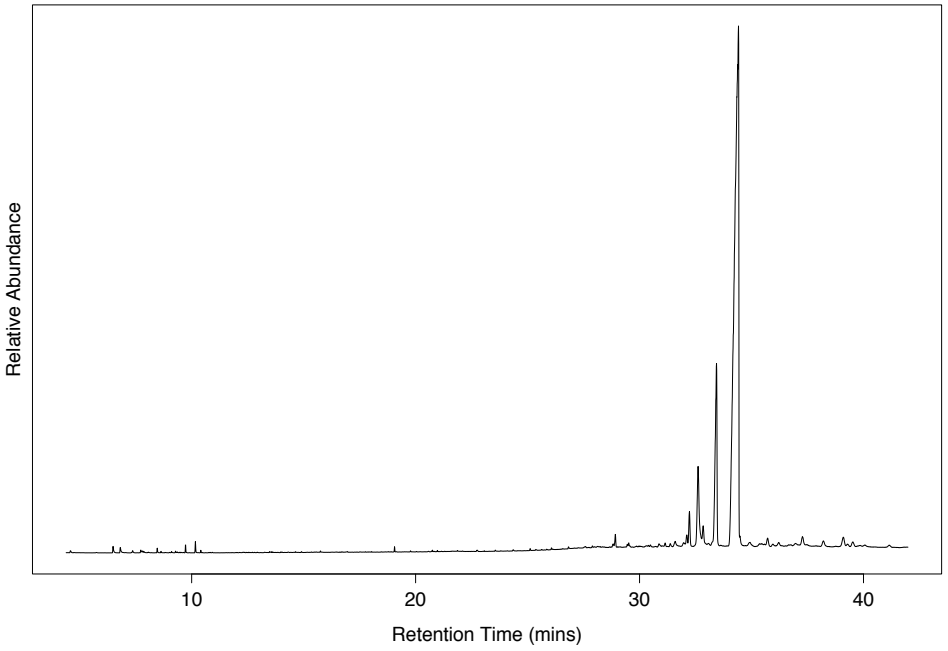
PBH029 | 2004.1.273





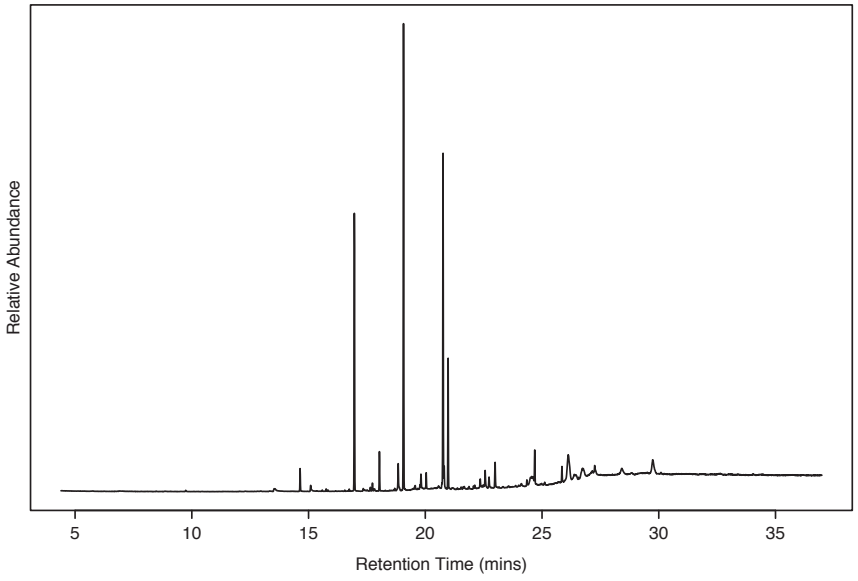
PBH030 | 2004.1.273





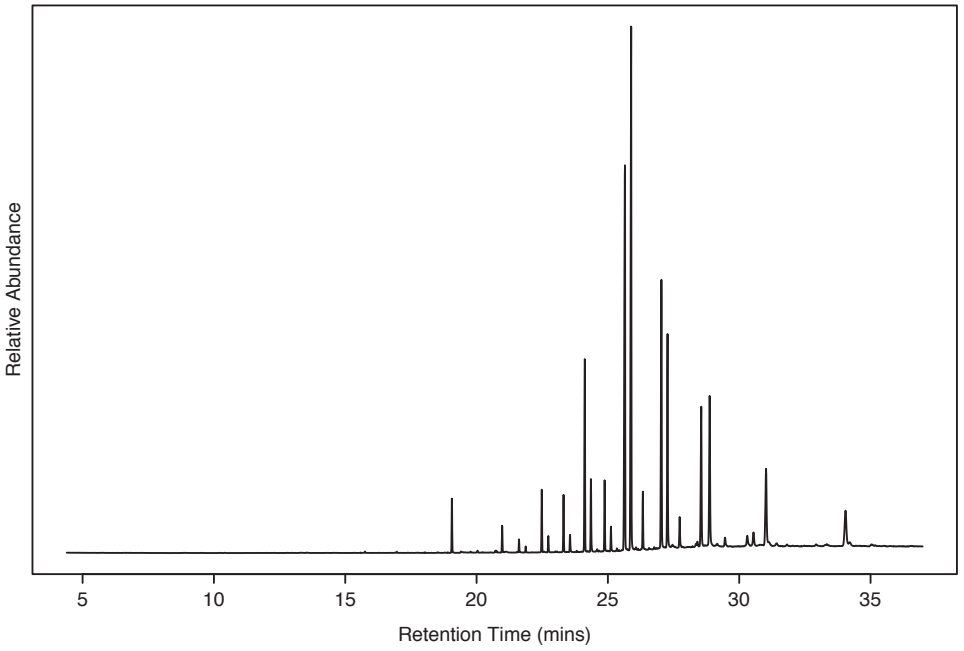
PBH031 | 99-29-70/56075





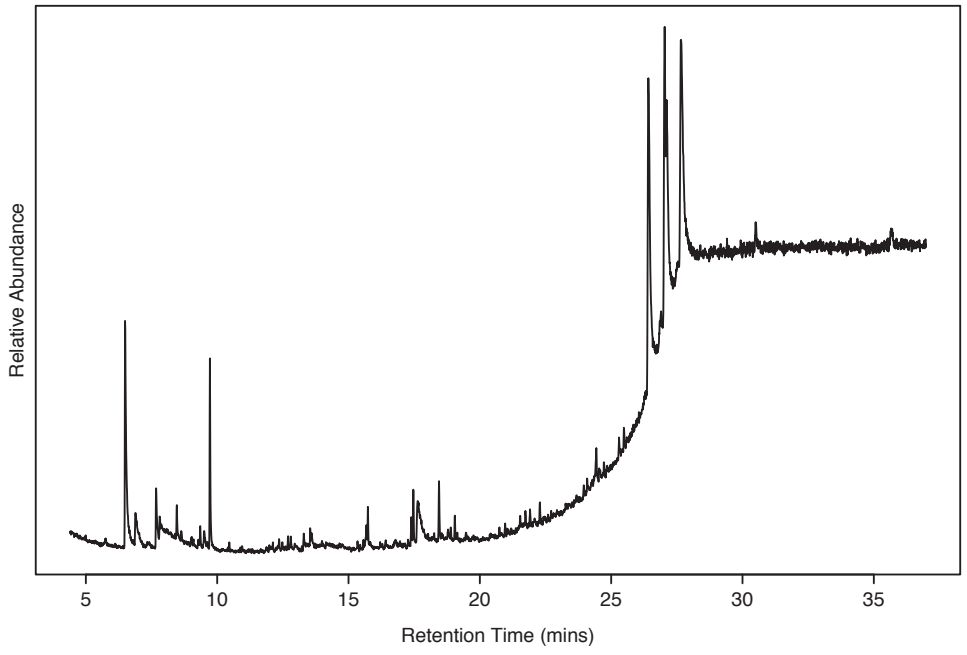
PBH032 | 2004.1.577





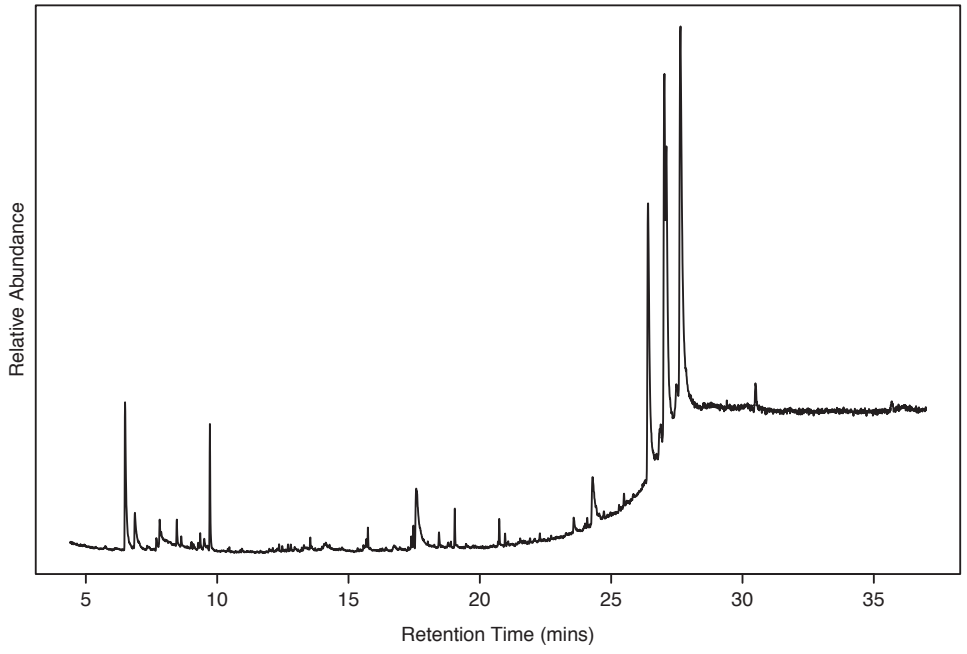
PBH033 | 32-68-70/D4027





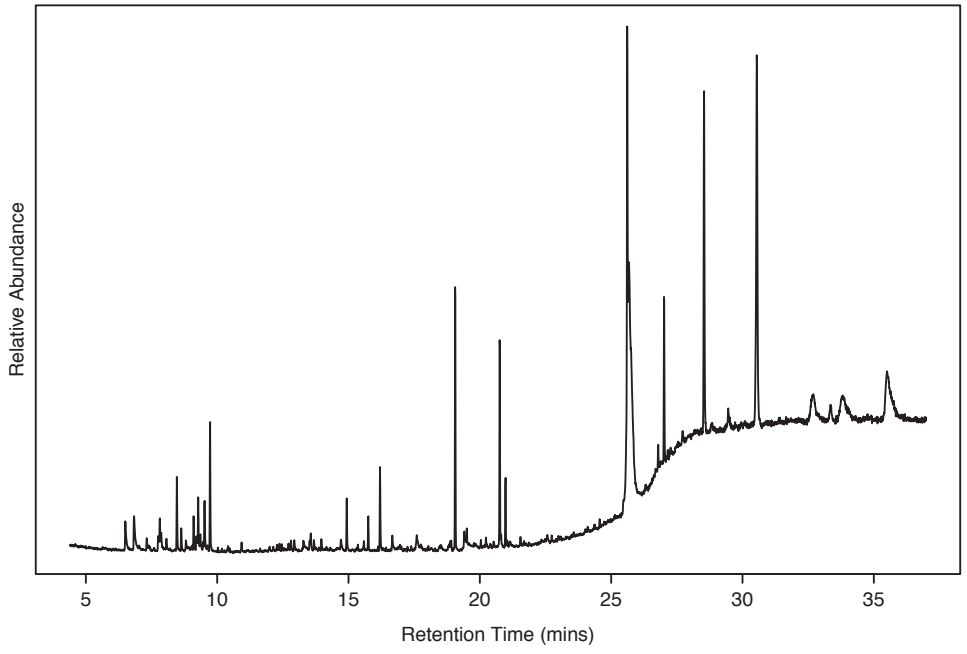
PBH034 | 32-68-70/D4027





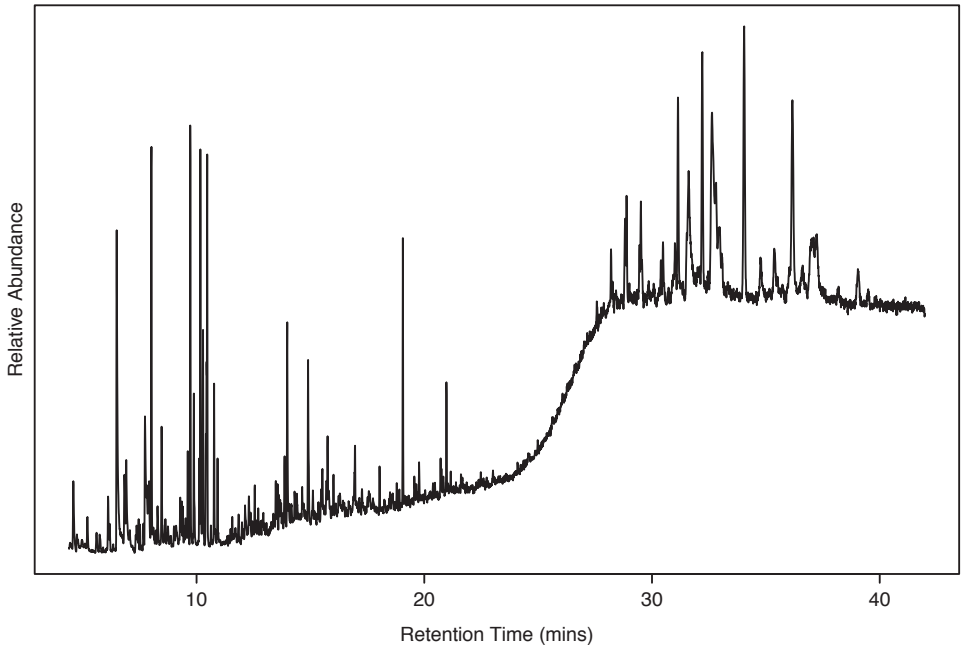
PBH035 | 32-68-70/D4027





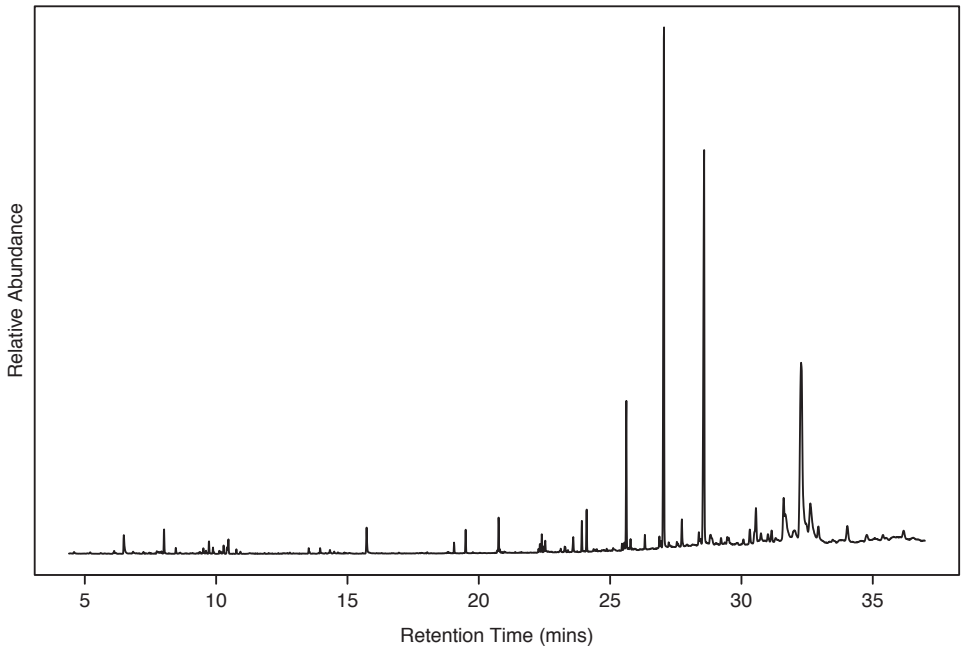
PBH036 | 12-4-70/84534



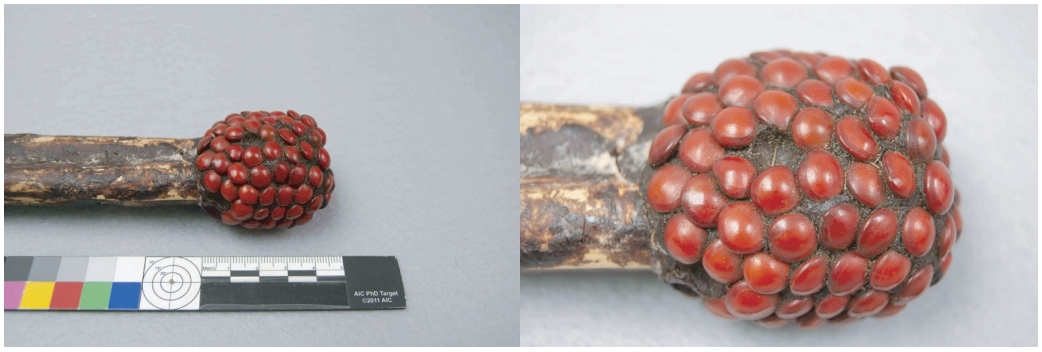


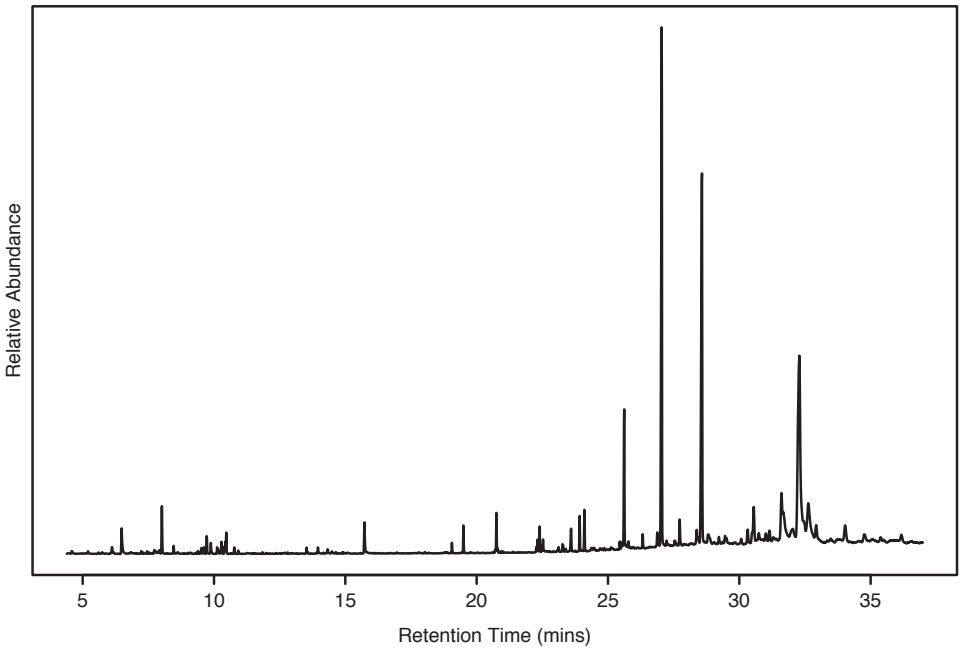
PBH037 | 51-32-70/3295





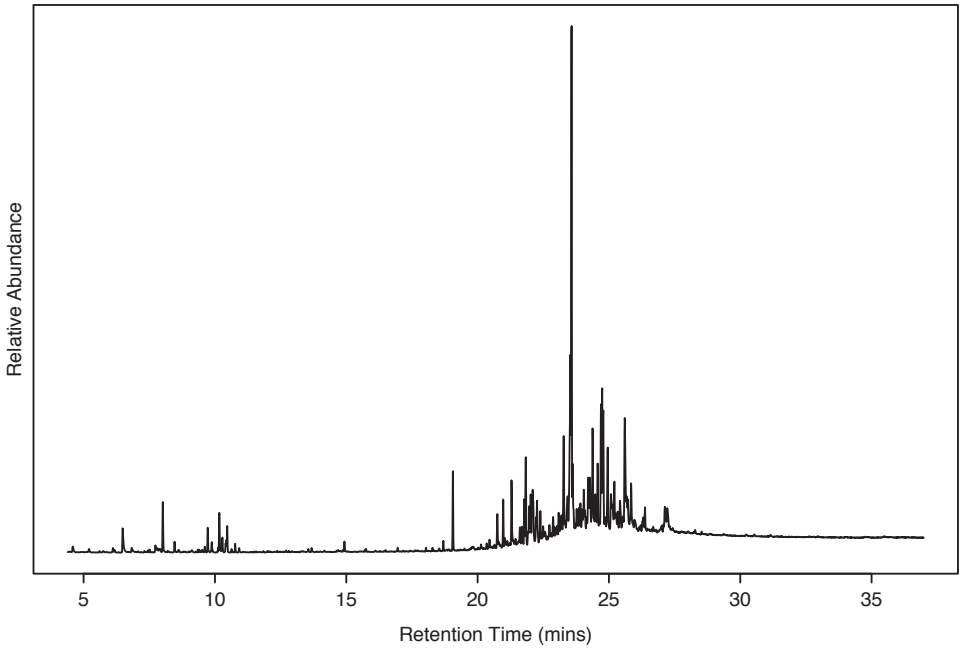
PBH038 | 51-32-70/3295





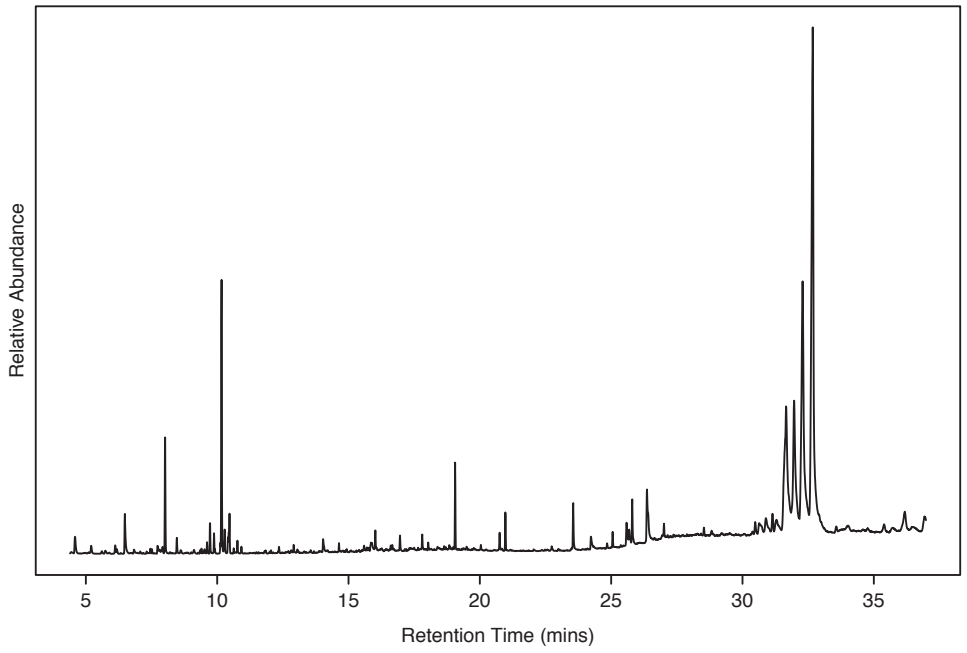
PBH039 | 51-32-70/3289





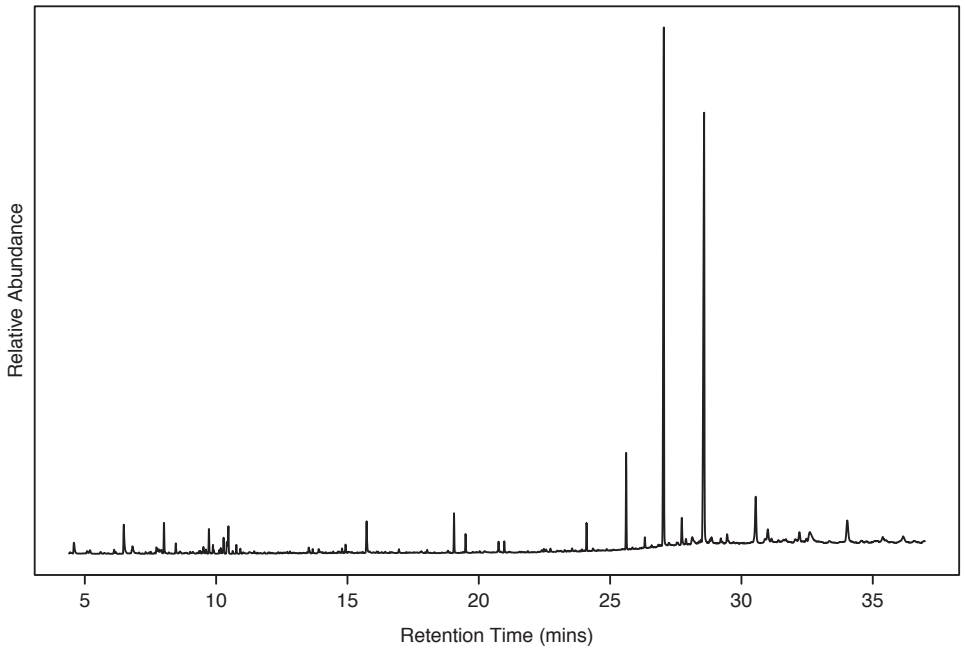
PBH040 | 51-32-70/3289





PBH041 | 51-32-70/3289



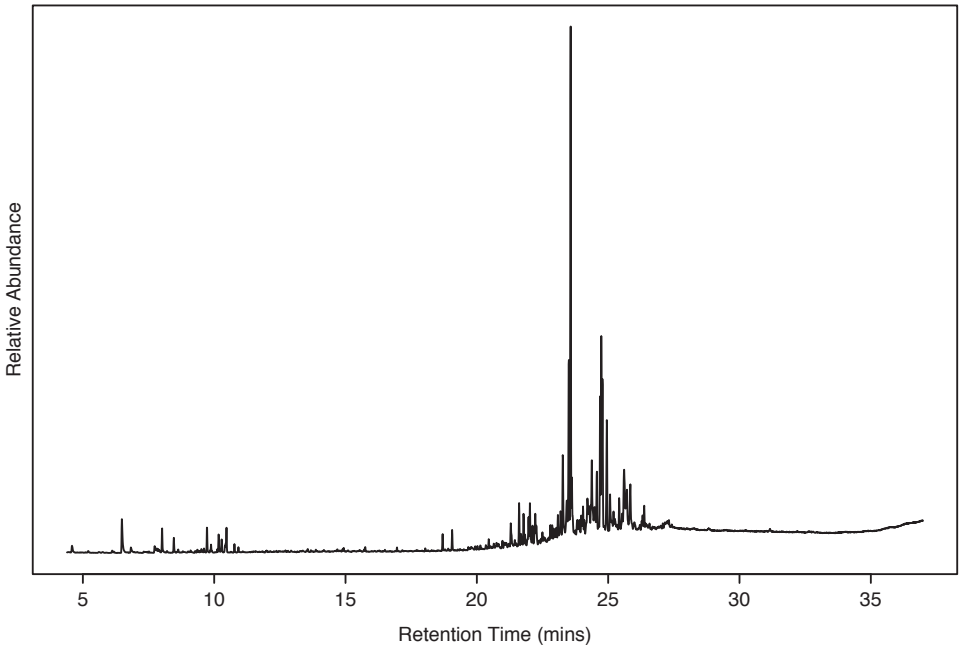


PBH042, PBH043 | 30-54-70/D3473



PBH042 | 30-54-70/D3473



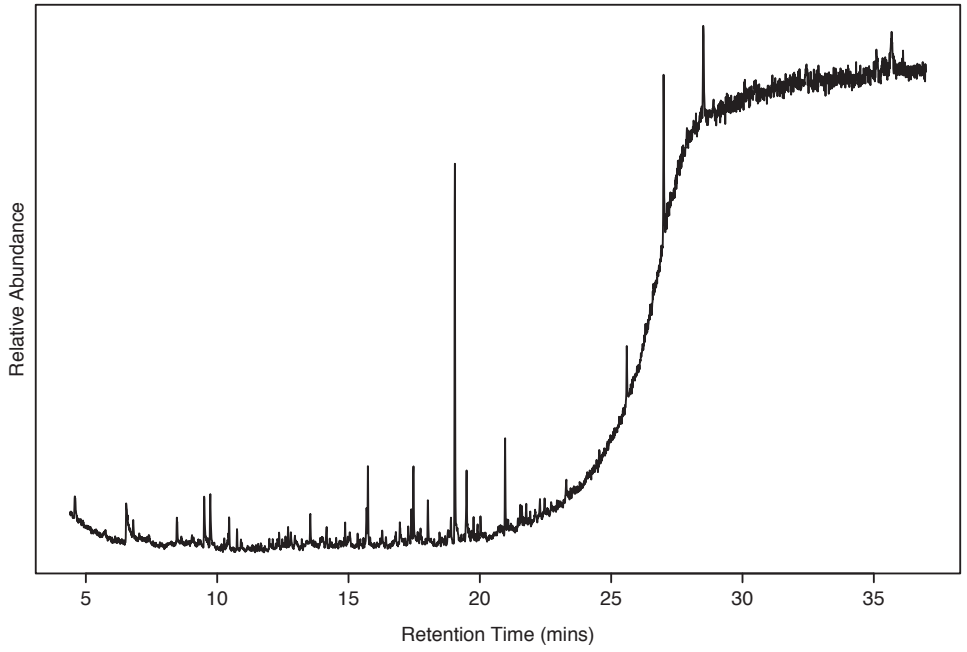


PBH042, PBH043 | 30-54-70/D3473



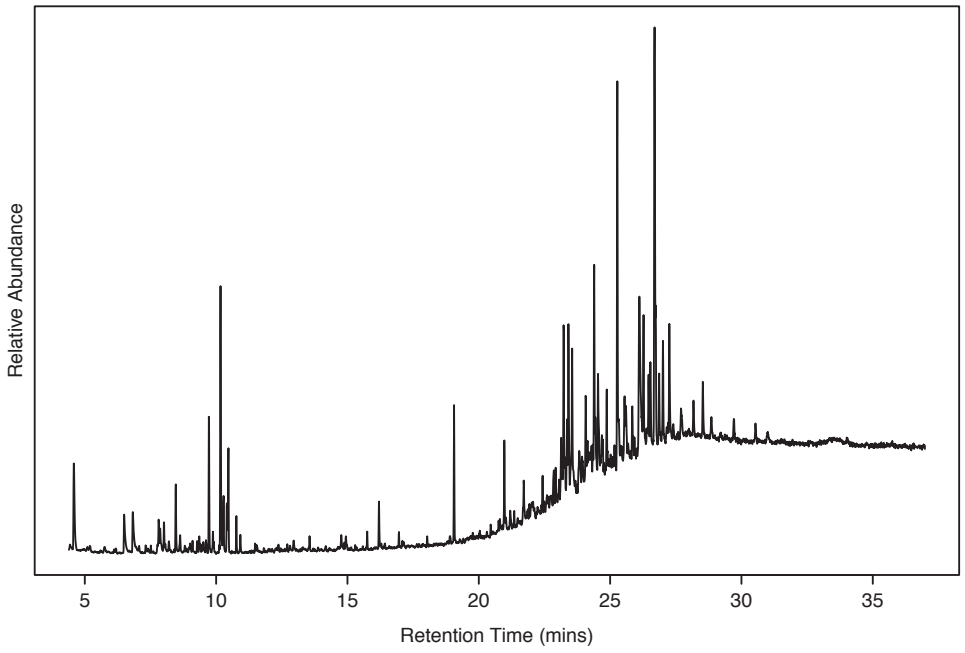
PBH043 | 30-54-70/D3473





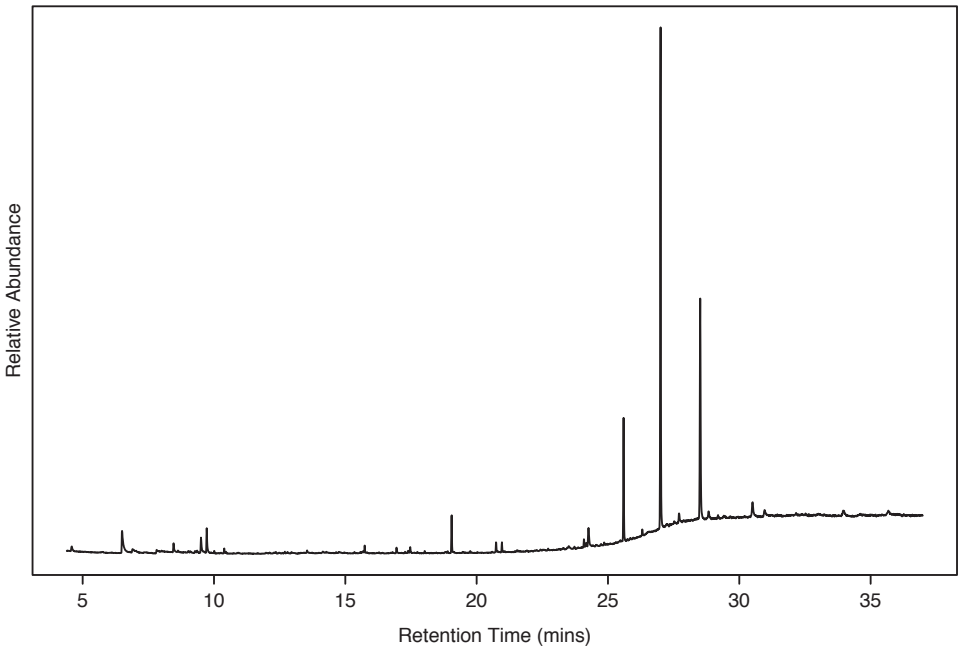
PBH044 | D3473





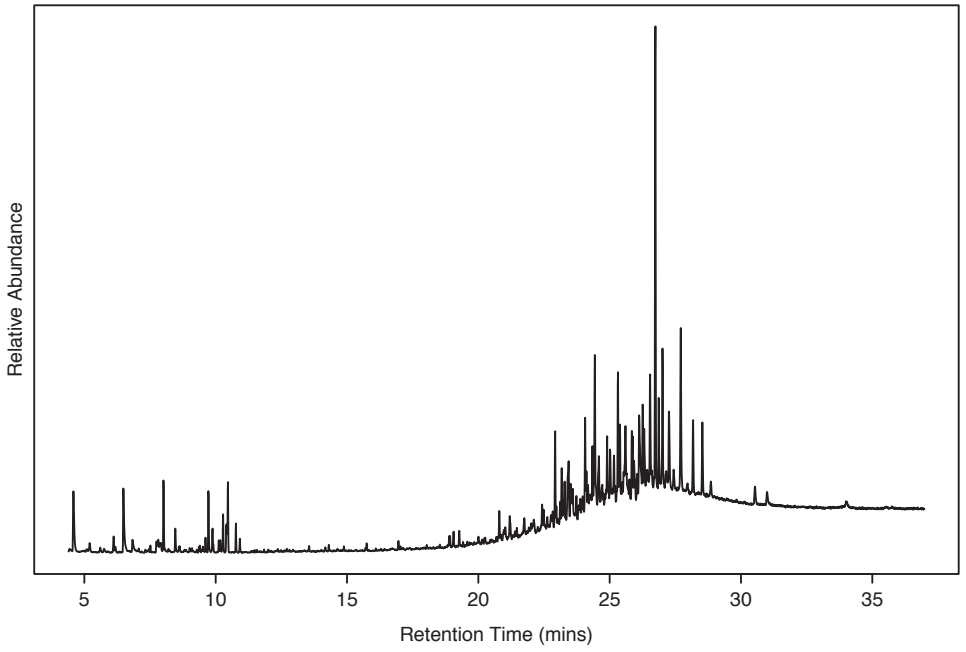
PBH045 | 30-54-70/D3449.1





PBH046 | 43-5-70/2247



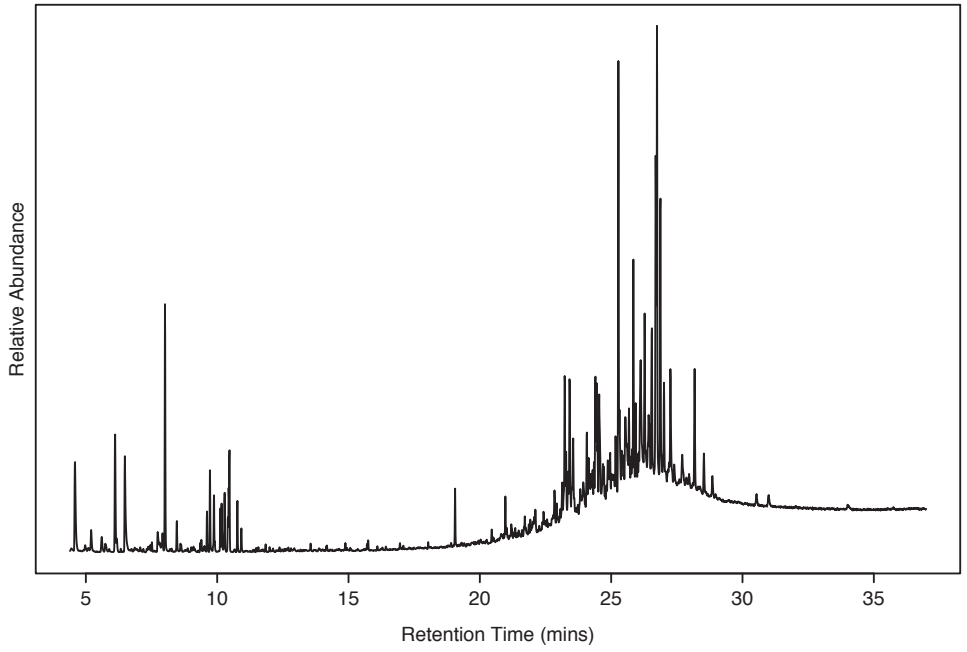


PBH047, PBH048 | 36-122-70/568



PBH047 | 36-122-70/568



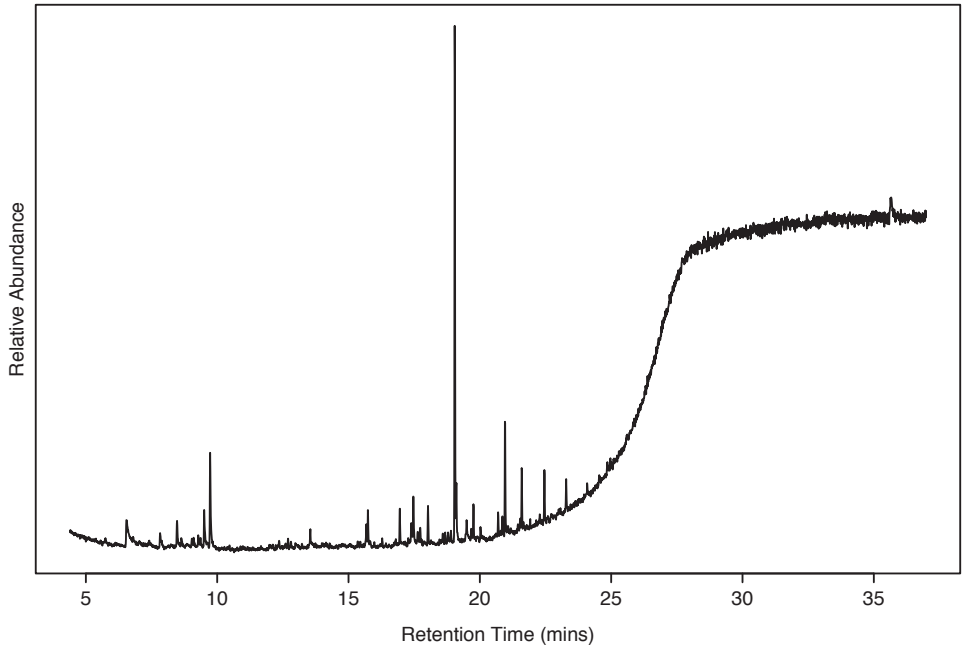


PBH047, PBH048 | 36-122-70/568



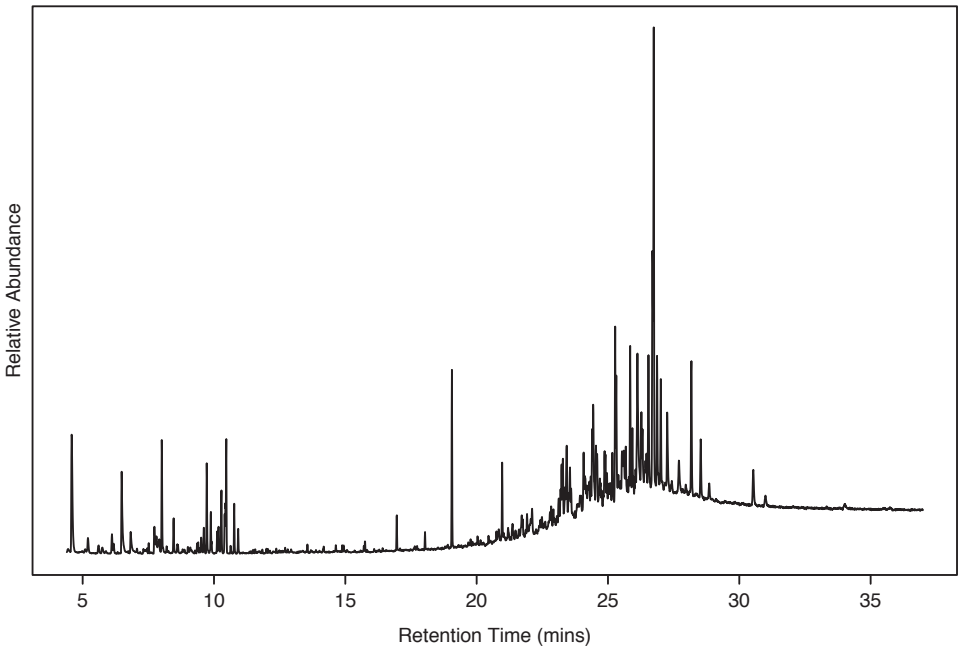
PBH048 | 36-122-70/568





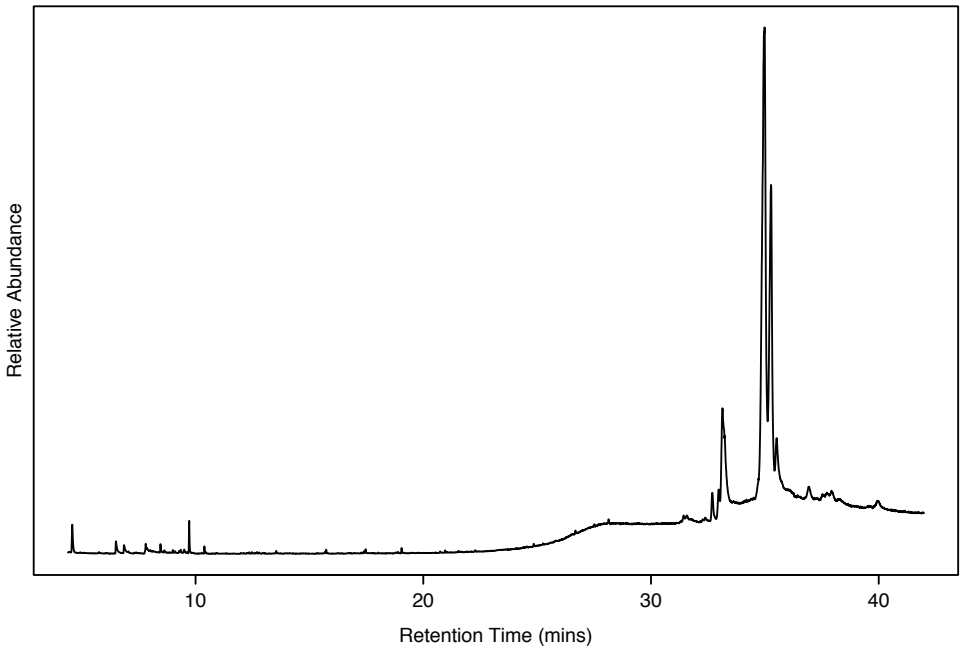
PBH049 | 36-122-70/572





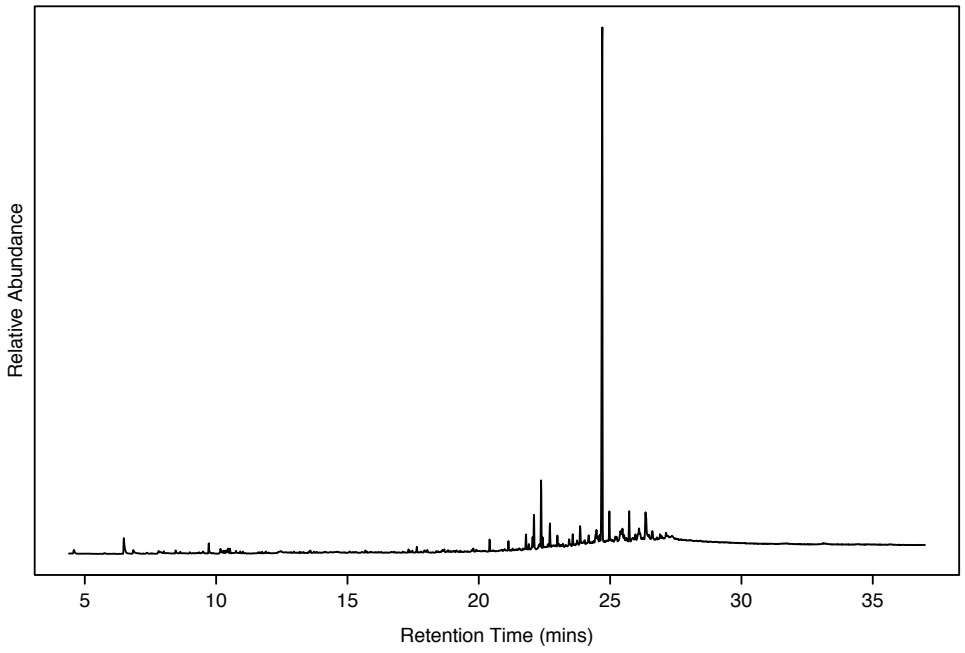
PBH050 | 967-71-70/4658



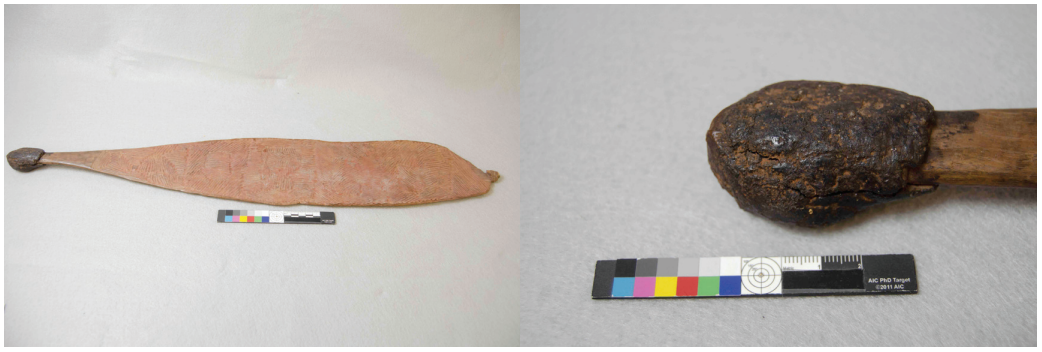


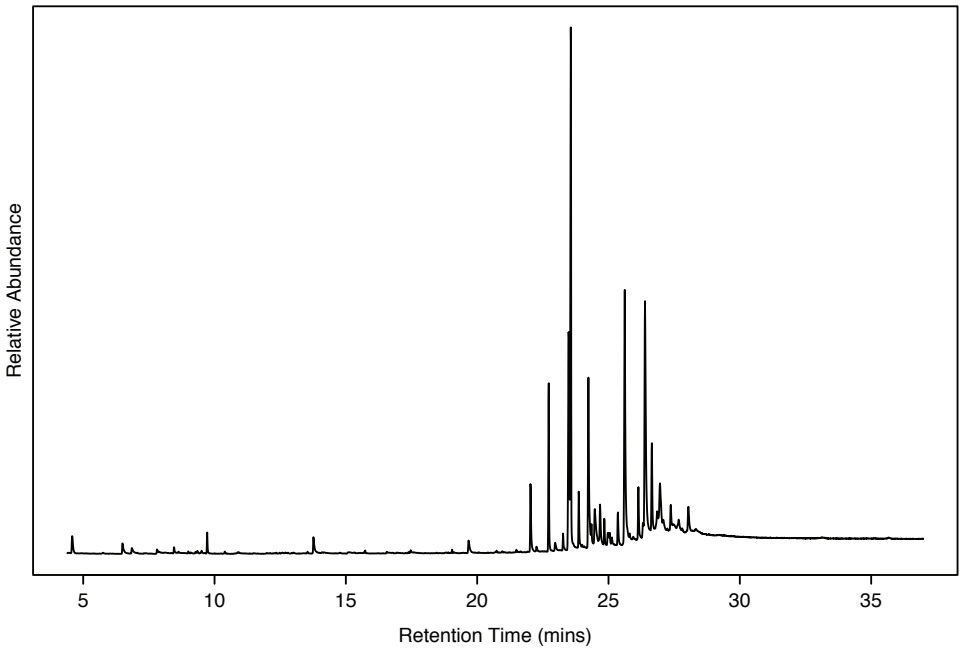
PBH051 | 08-36-70/74411





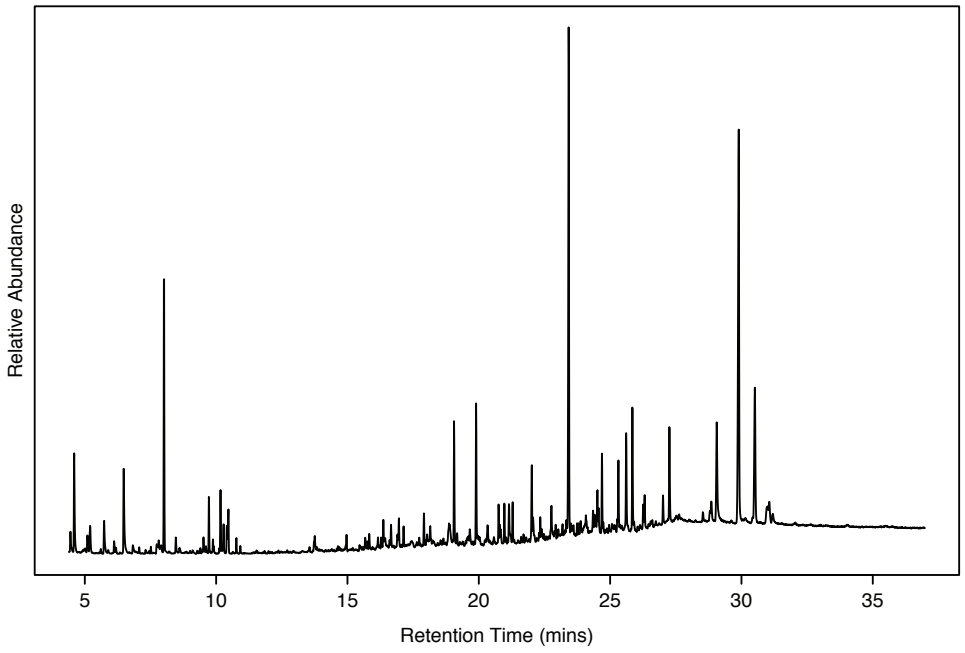
PBH052 | 25-46-70/D2441





PBH053 | 25-46-70/D2425



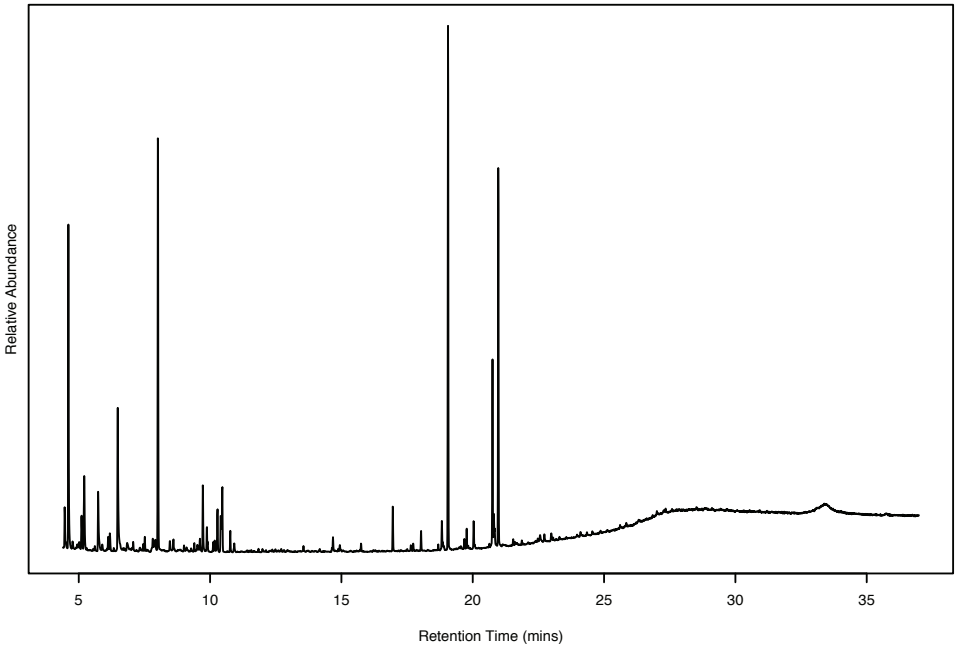


PBH054, PBH055 | 32-68-70/D3961



PBH054 | 32-68-70/D3961



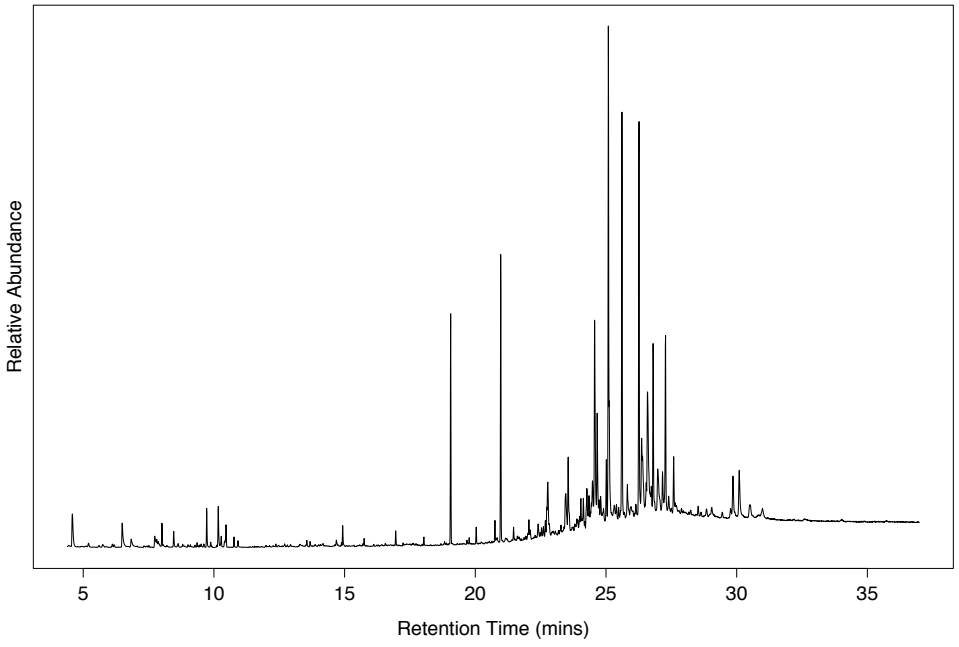


PBH054, PBH055 | 32-68-70/D3961



PBH055 | 32-68-70/D3961



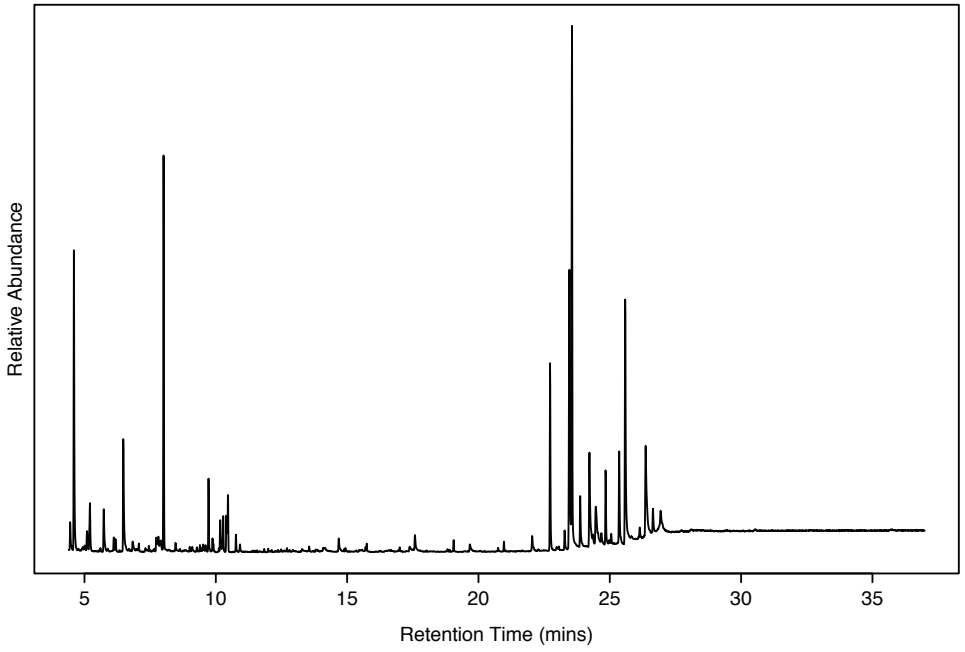


PBH056, PBH057 | 32-68-70/D3962.1



PBH056 | 32-68-70/D3962.1



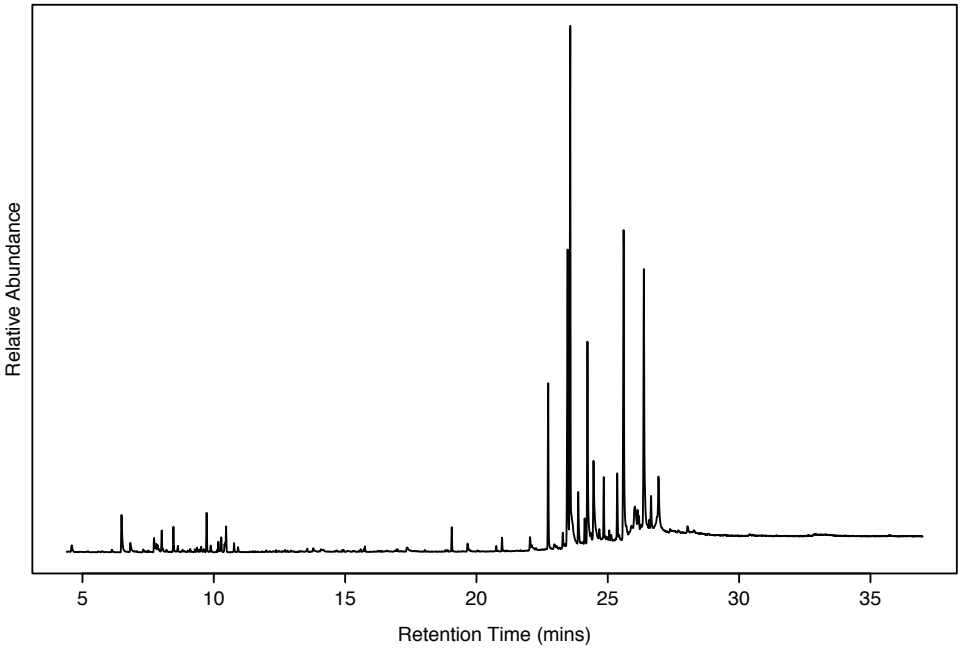


PBH056, PBH057 | 32-68-70/D3962.1



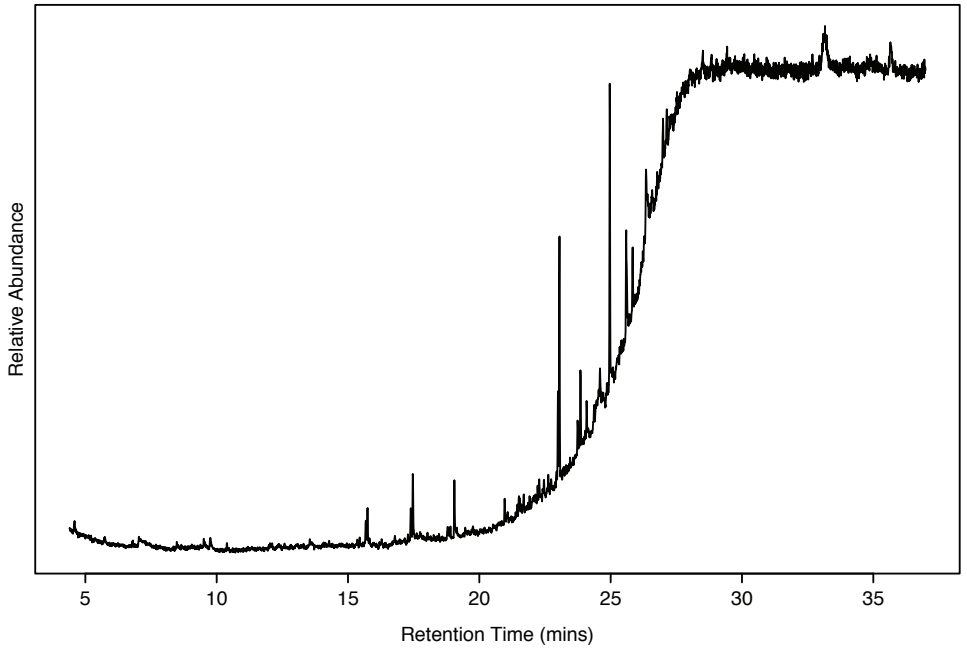
PBH057 | 32-68-70/D3962.1





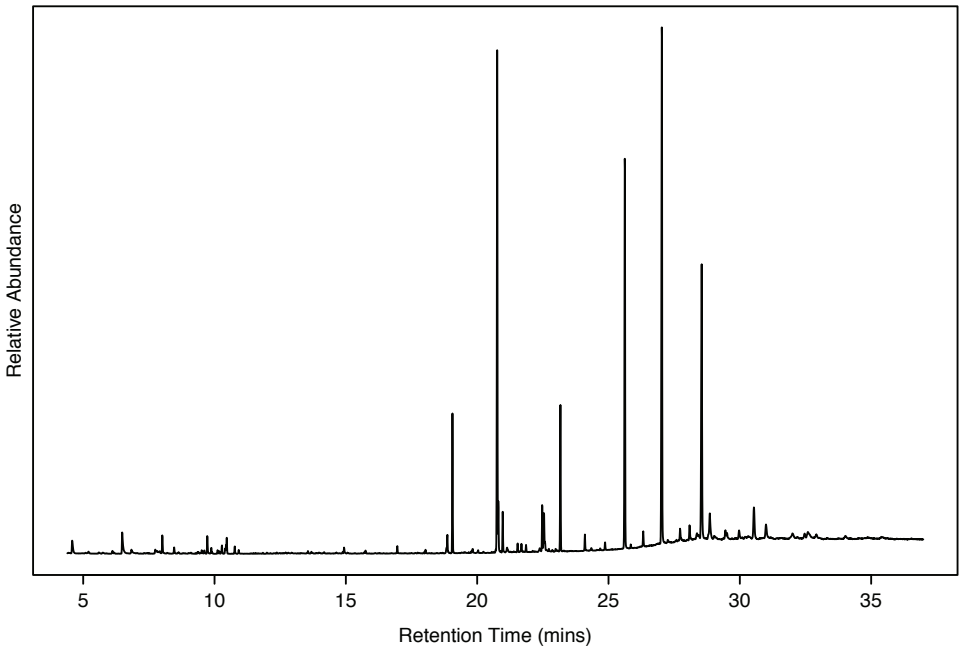
PBH058 | 15-14-70/86042





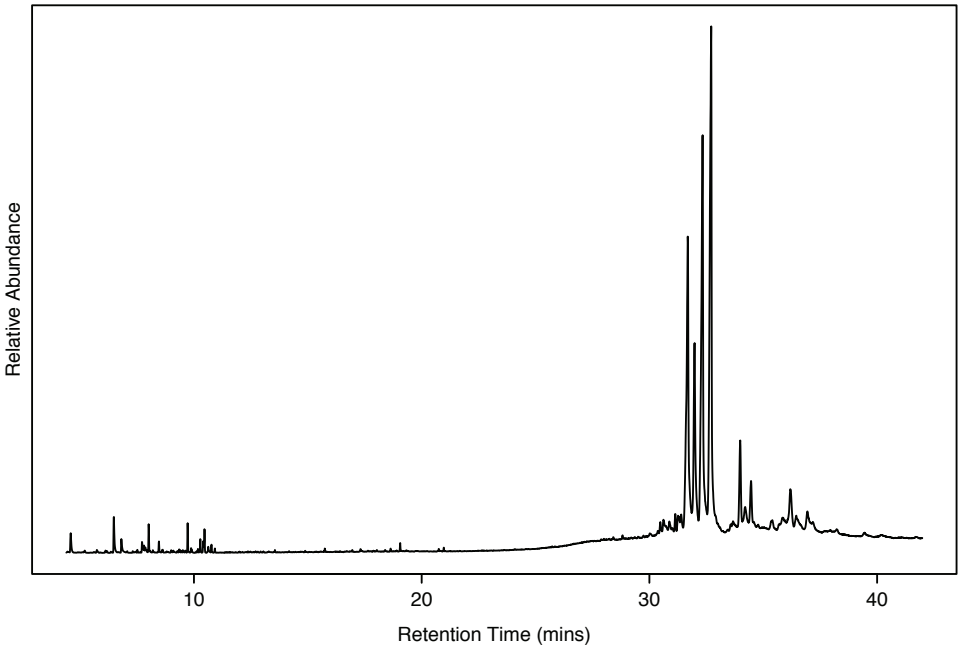
PBH059 | 52-4-70/3575



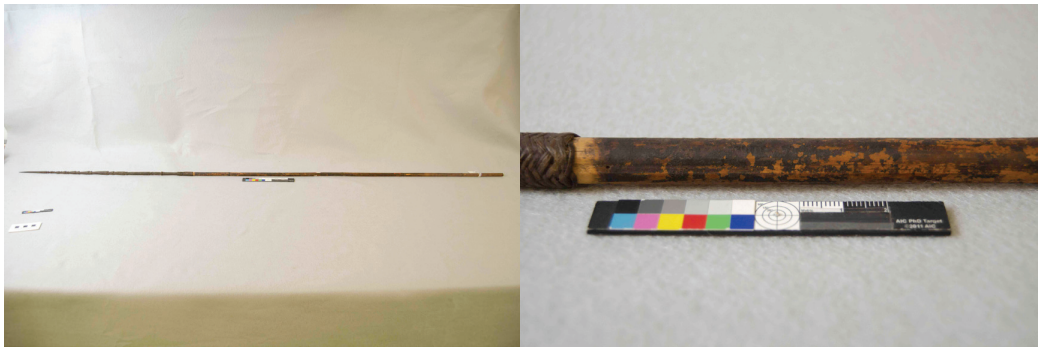


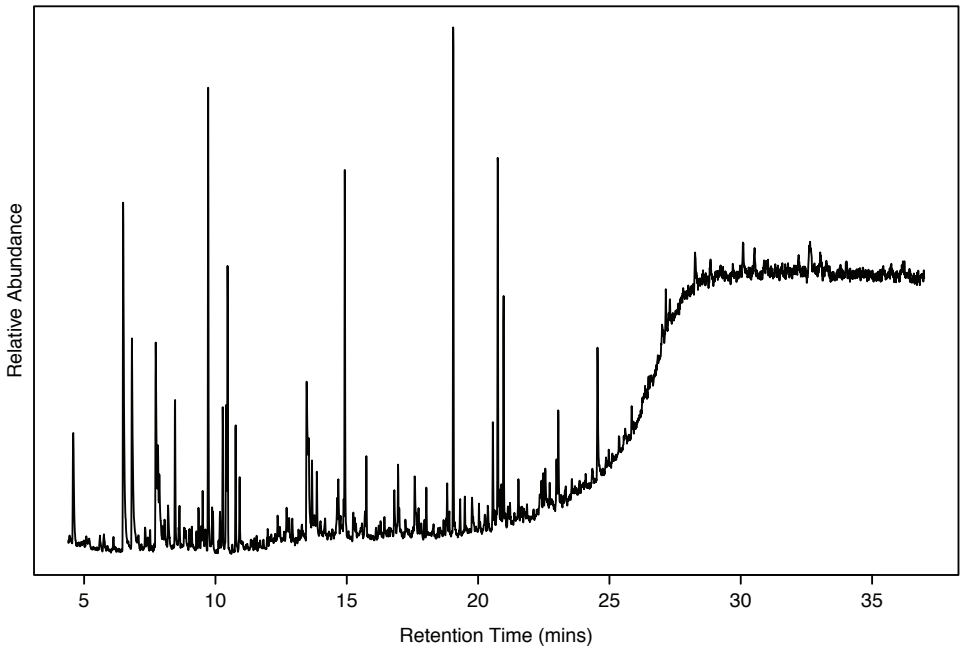
PBH060 | 64-18-70/4556.6





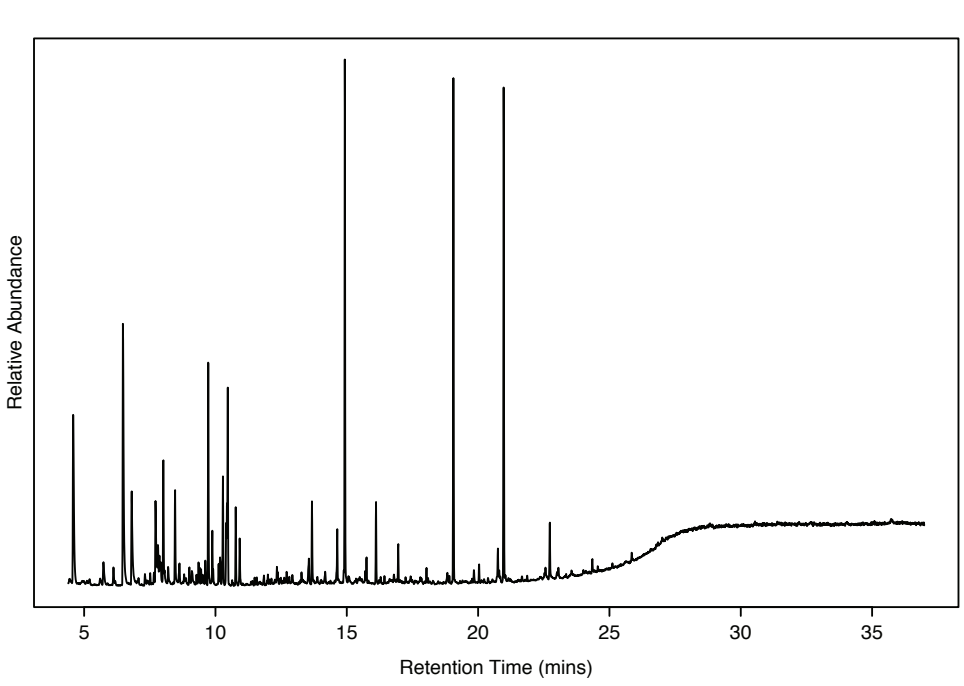
PBH061 | 47-73-70/2801.1





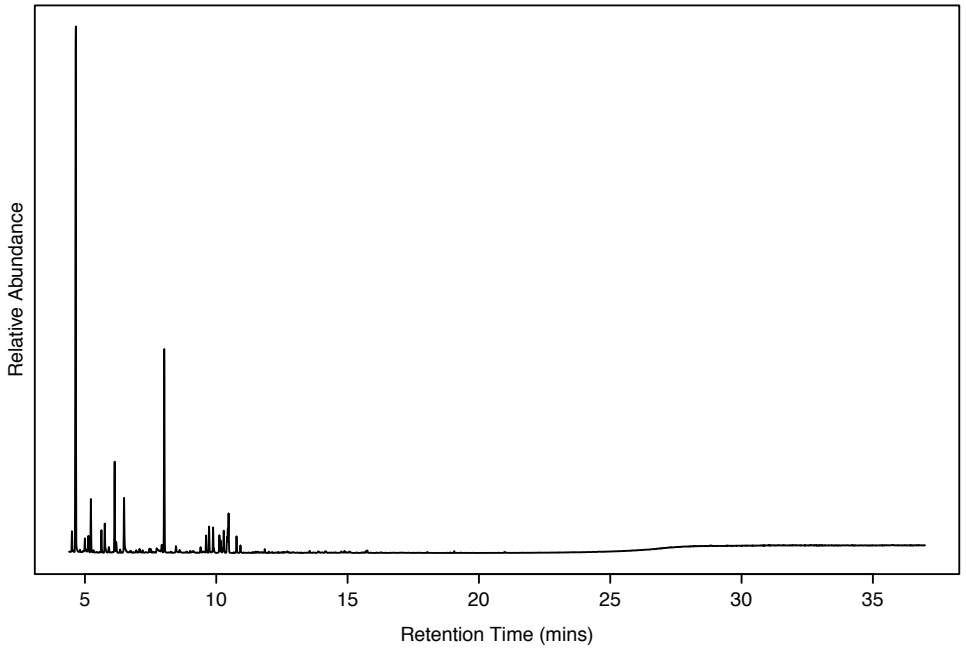
PBH062 | 40-63-70/1974





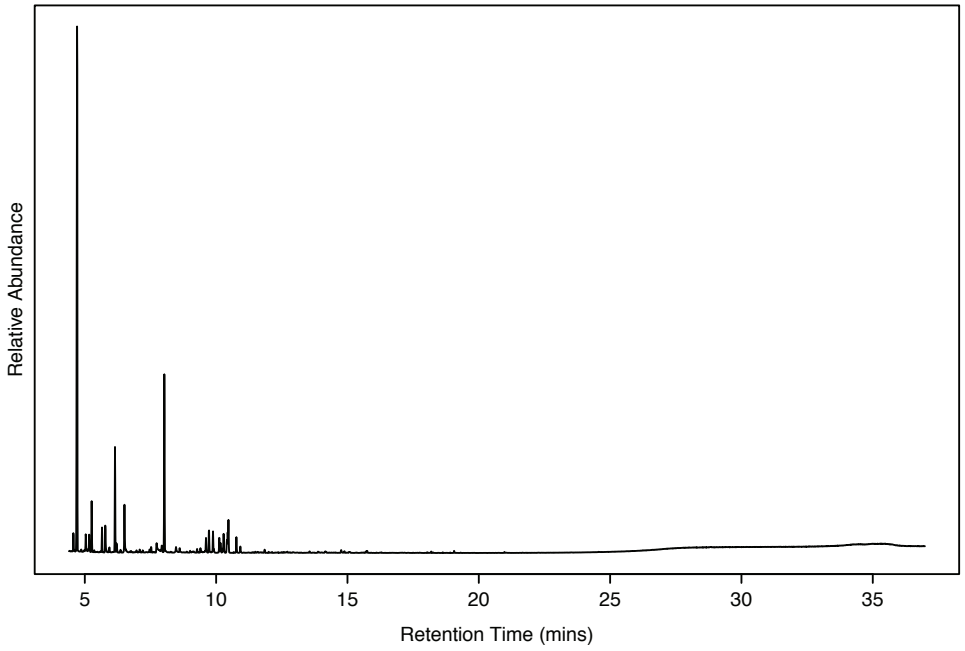
PBH063 | 39-17-70/1292





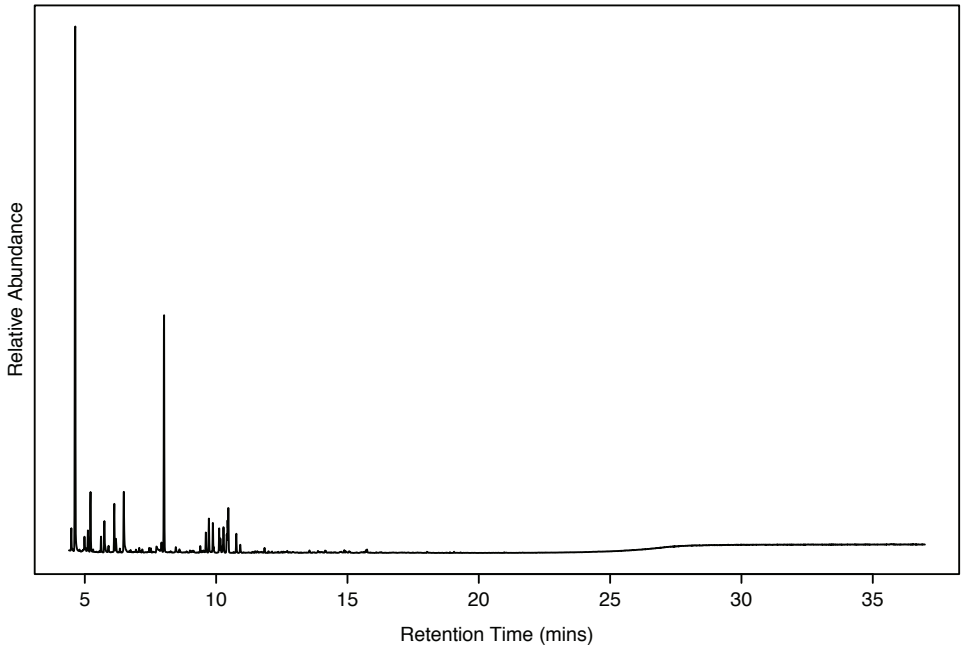
PBH064 | 39-17-70/1278





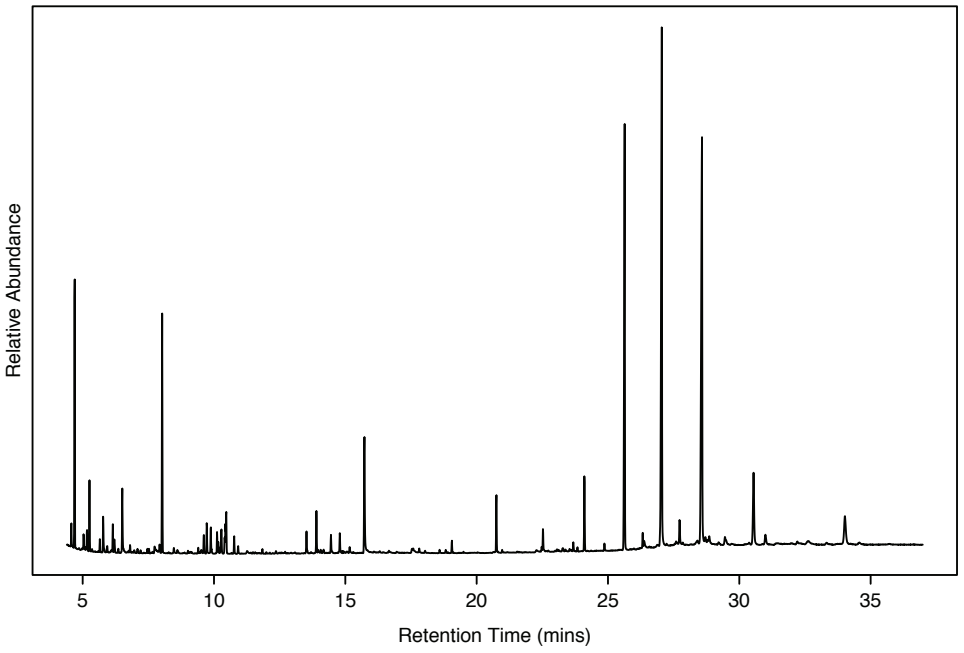
PBH065 | 39-17-70/1283





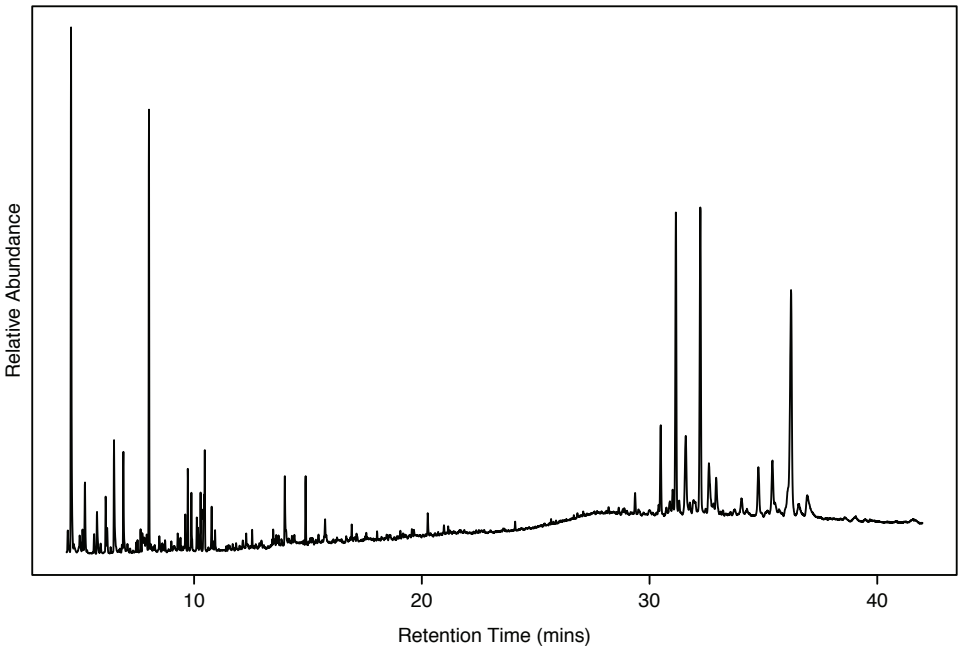
PBH066 | 58-55-70/3875





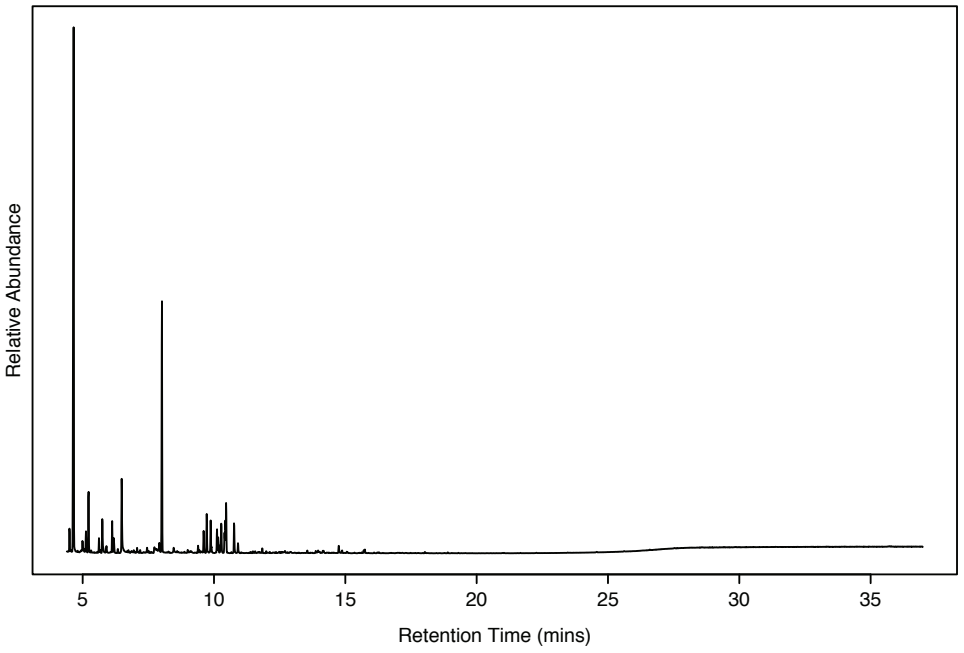
PBH067 | 35-92-70/323



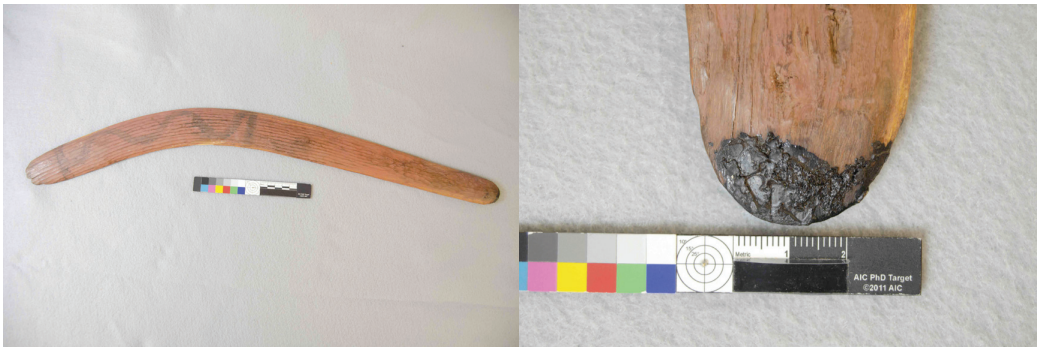


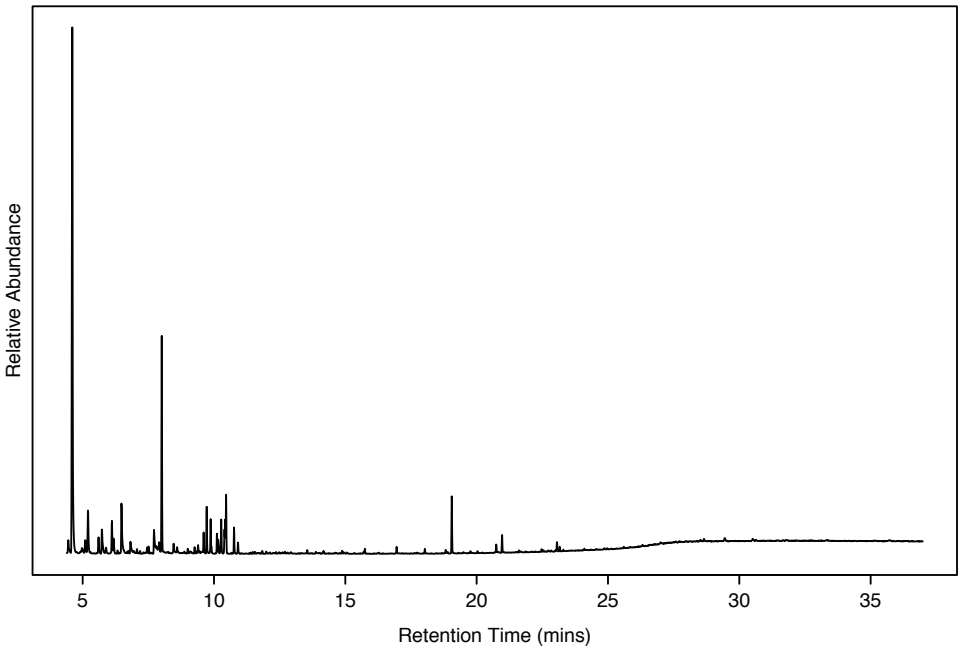
PBH068 | 51-32-70/3260





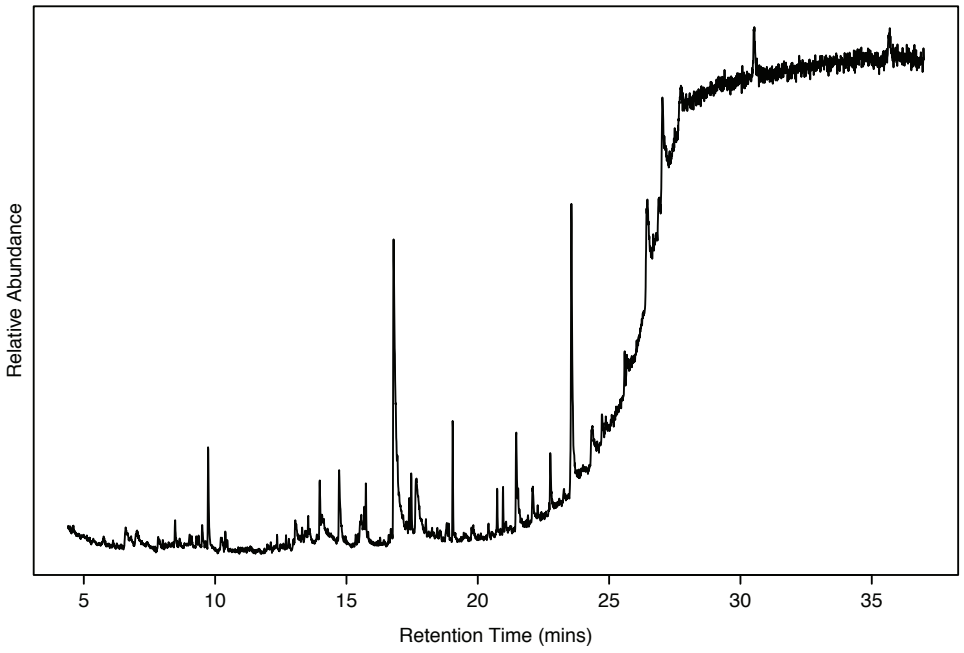
PBH069 | 51-32-70/3259





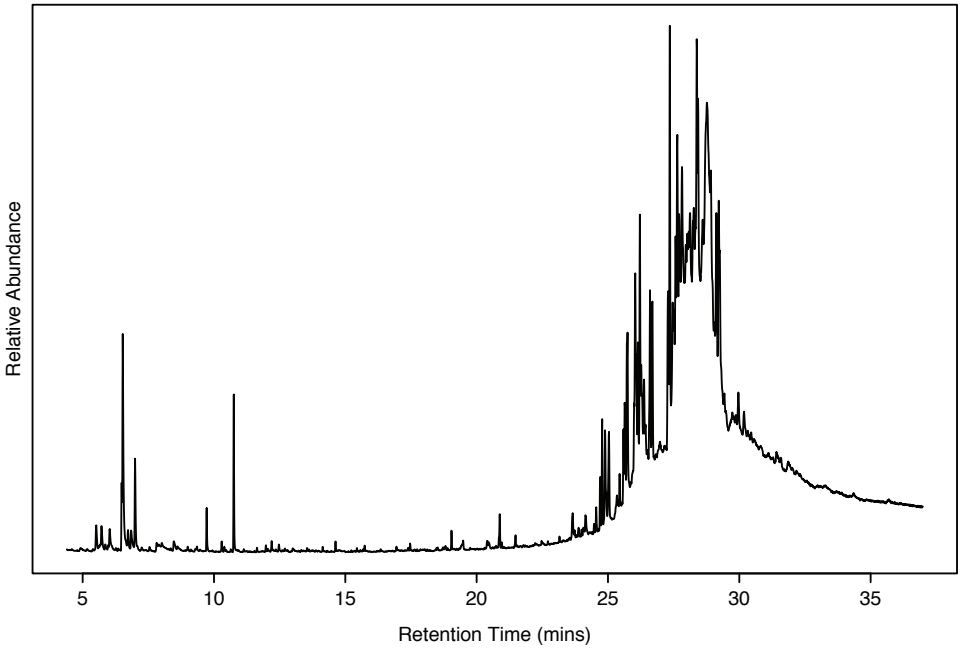
PBH070 | 25-46-70/D2419



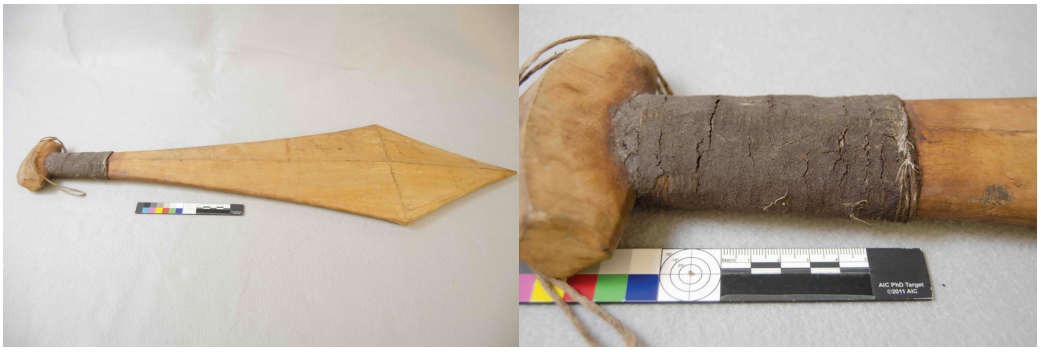


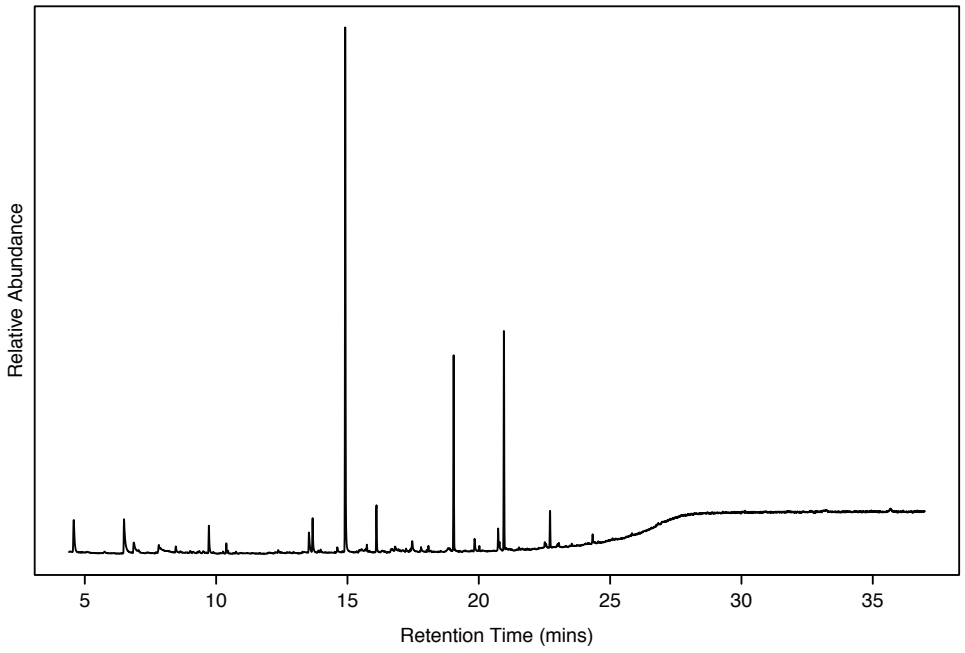
PBH071 | 974-52-70/5536





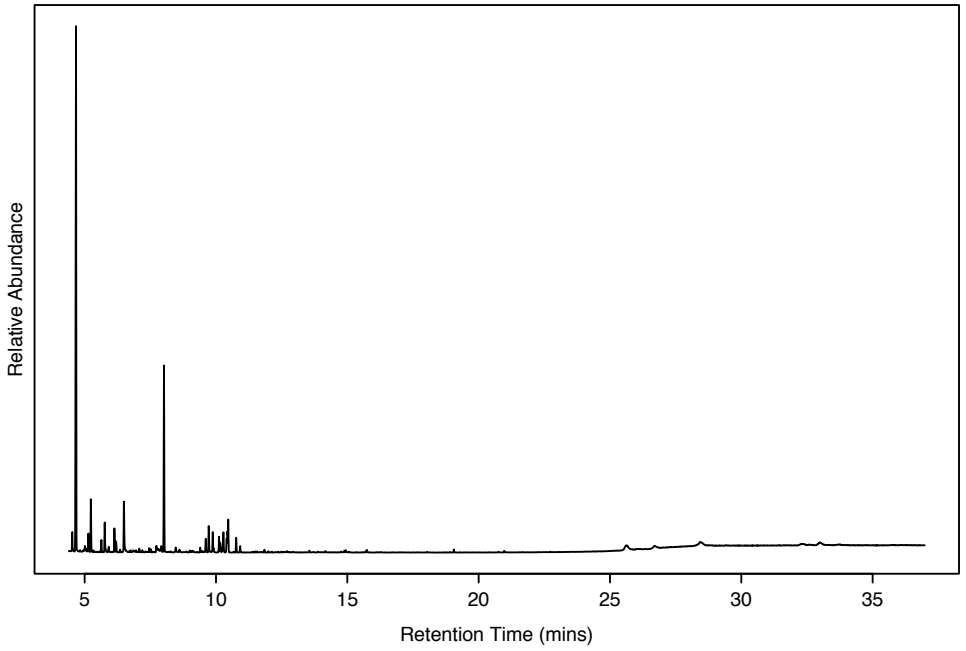
PBH072 | 970-29-70/4762





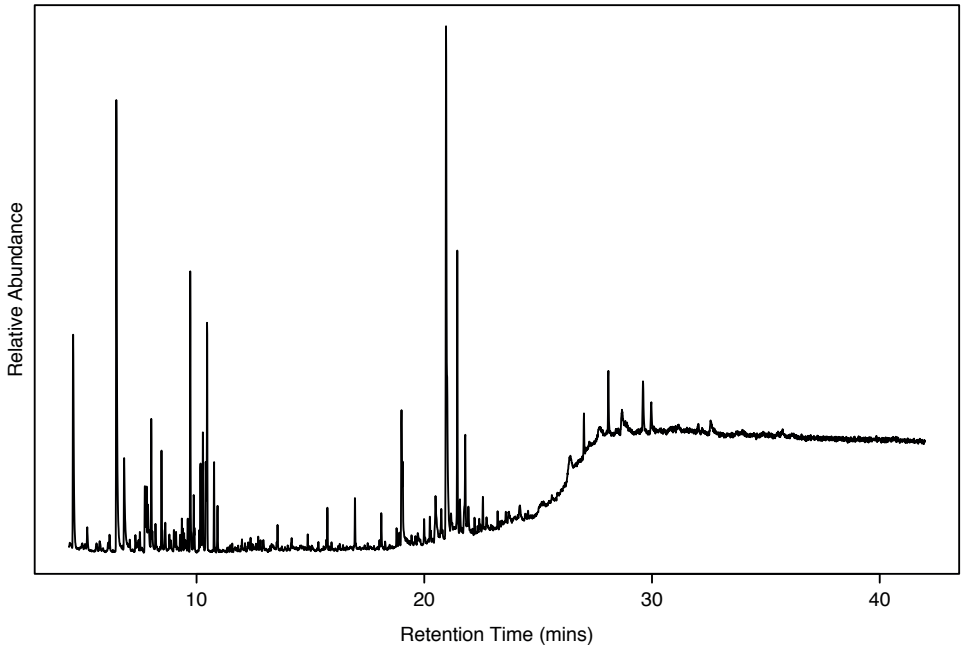
PBH073 | 2004.1.276





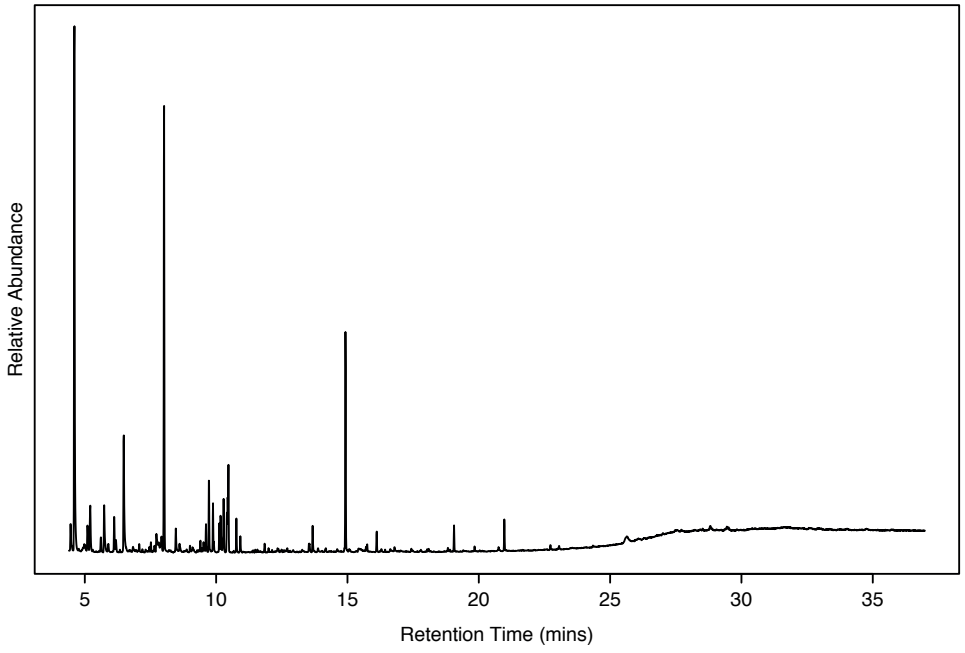
PBH074 | 04-19-70/63130





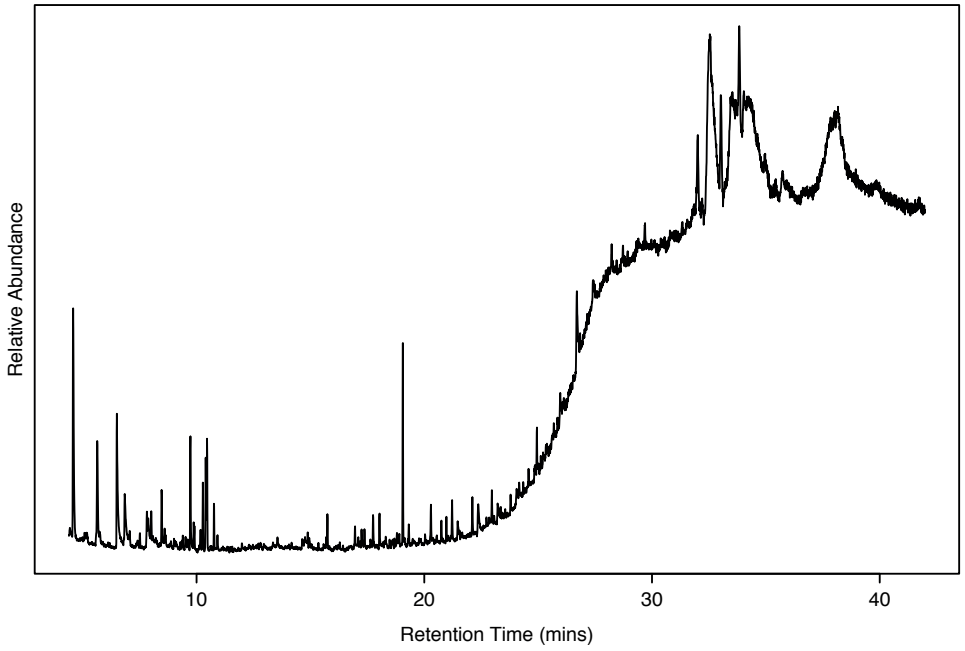
PBH075 | 47-72-70/2754





PBH076 | 970-29-70/4760

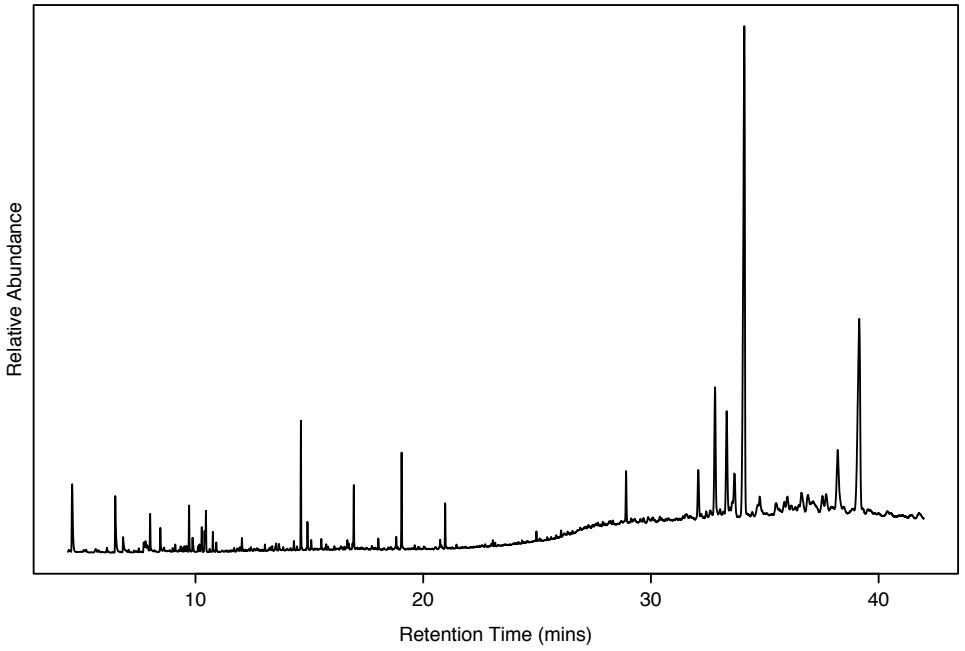




PBH077 | 47-54-70/2520

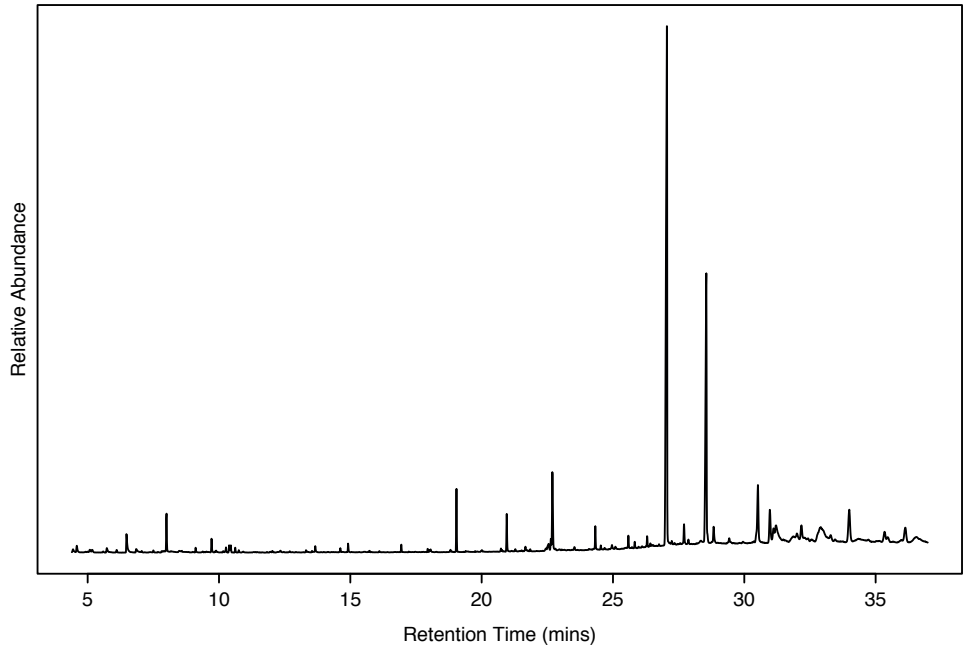






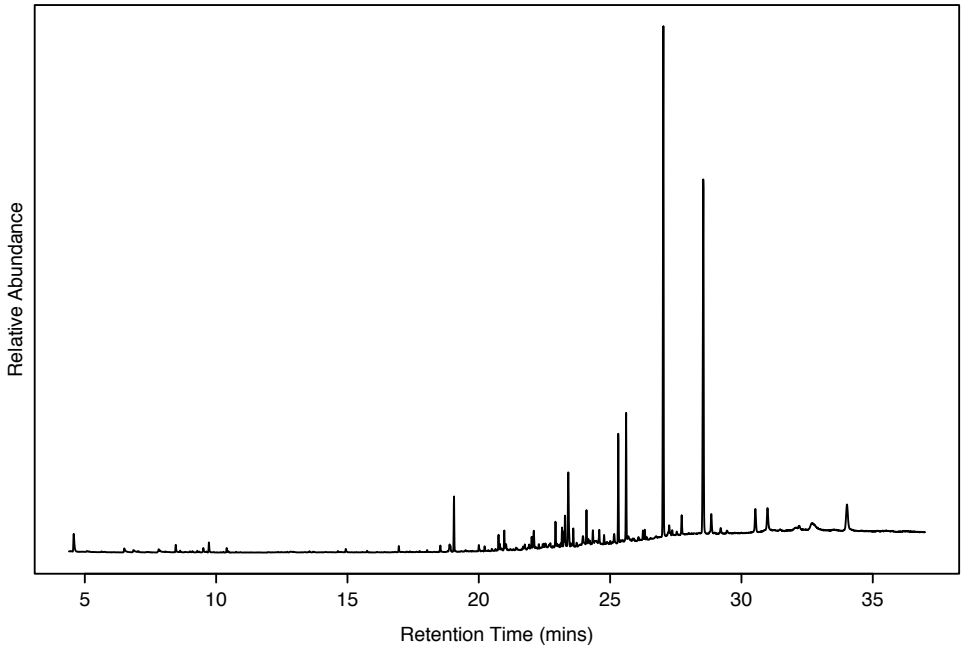
PBH078 | 48-56-70/3077





PBH079 | 996-22-70/5726



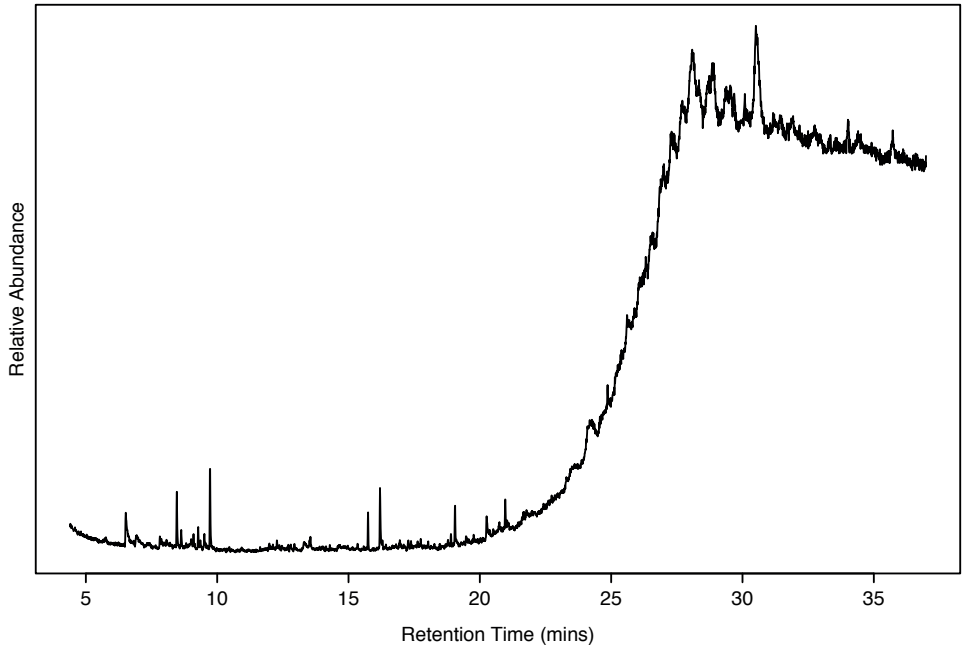


PBH080, PBH081 | 47-54-70/2524



PBH080 | 47-54-70/2524



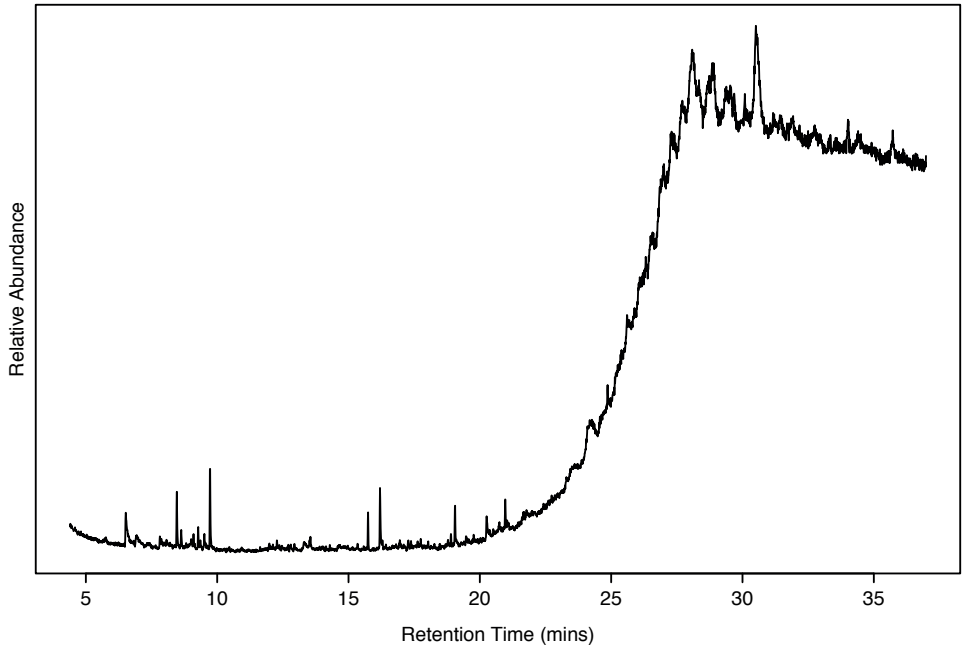


PBH080, PBH081 | 47-54-70/2524



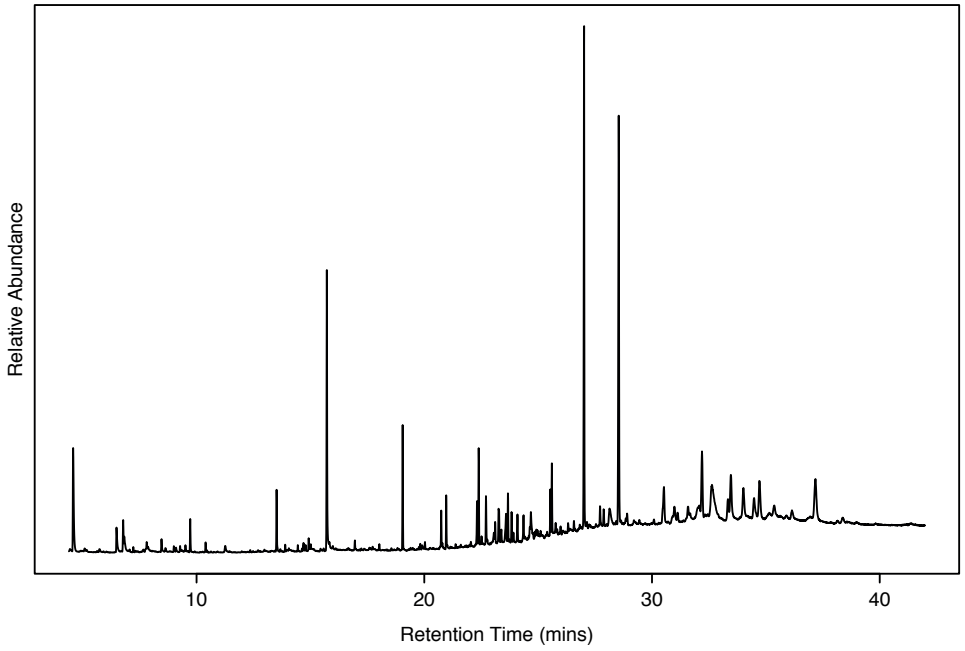
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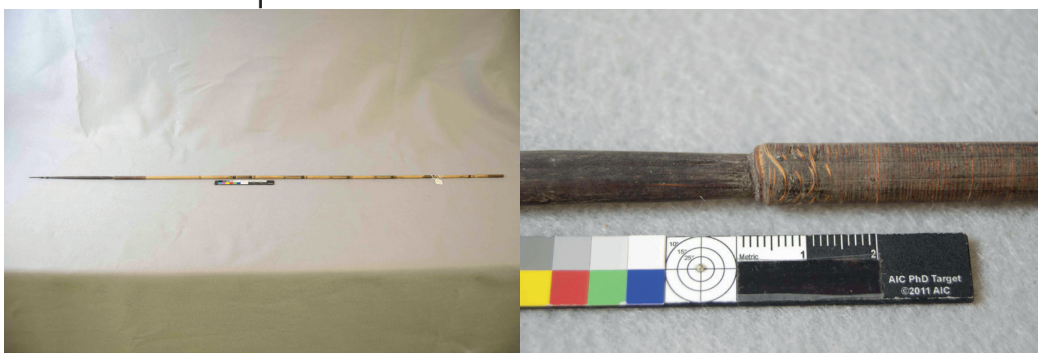


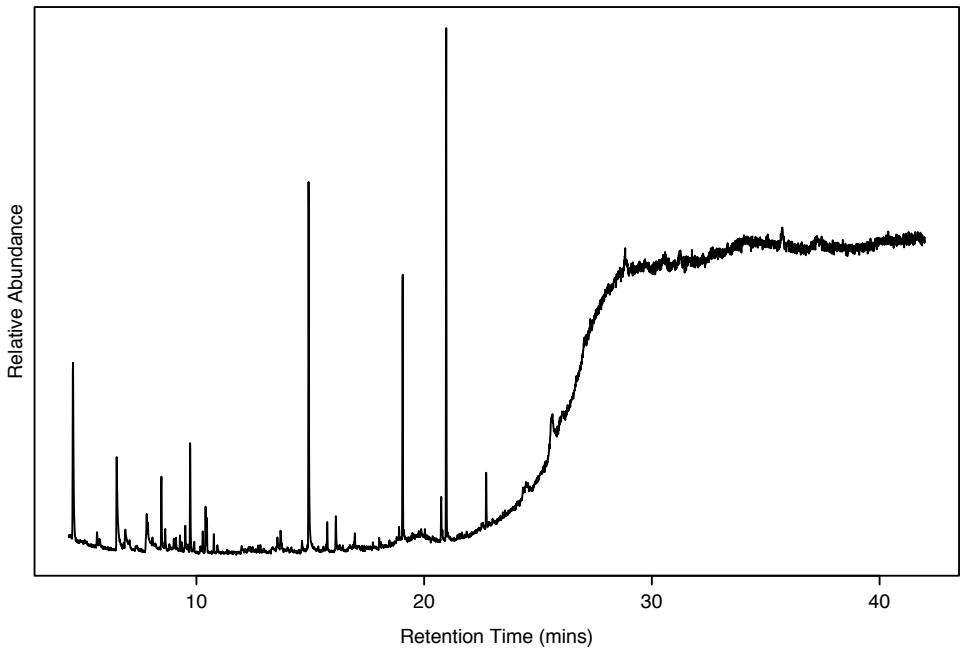
PBH082 | 01-7-70/566761





PBH083 | 40-12-70/1812.1



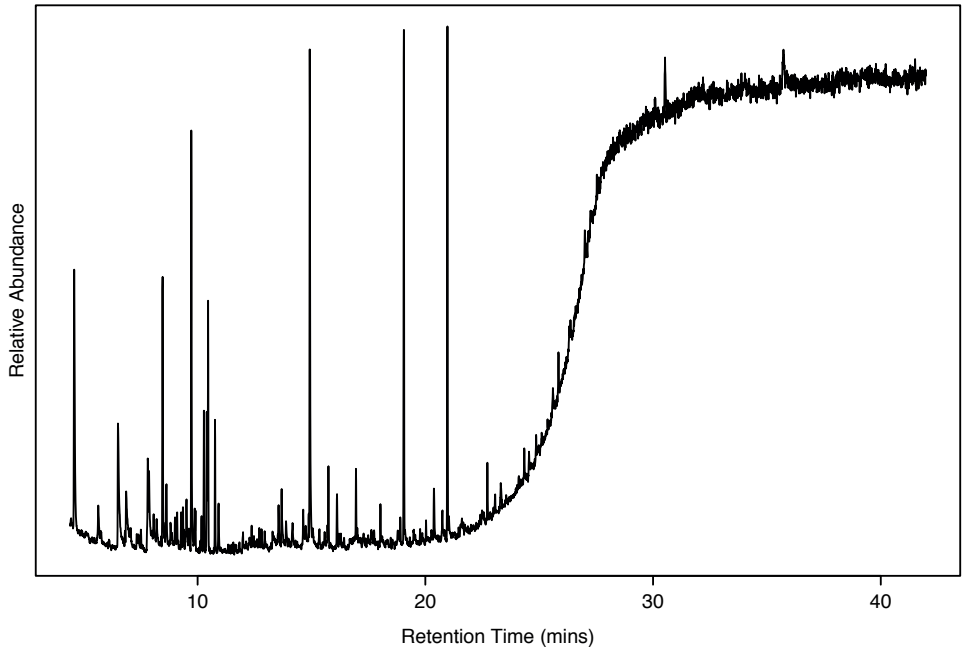


PBH084, PBH085 | 46-78-70/2387



PBH084 | 46-78-70/2387



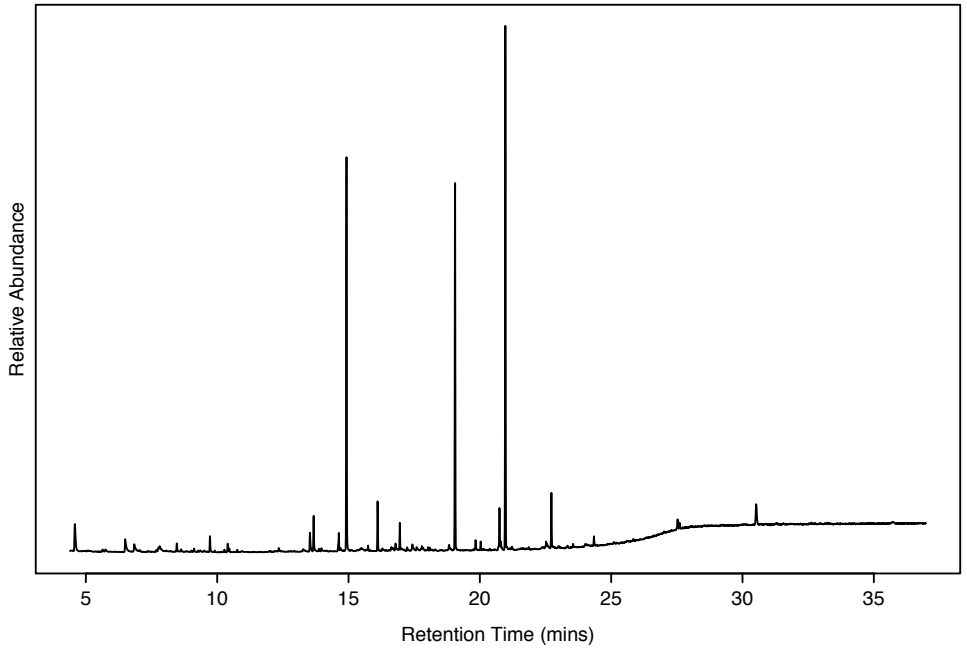


PBH084, PBH085 | 46-78-70/2387



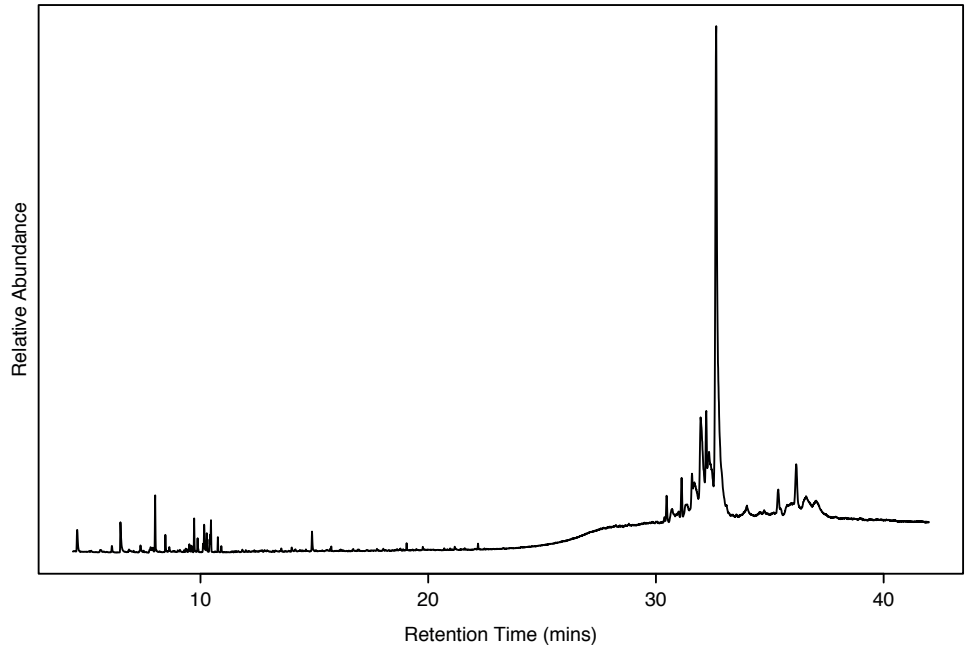
PBH085 | 46-78-70/2387





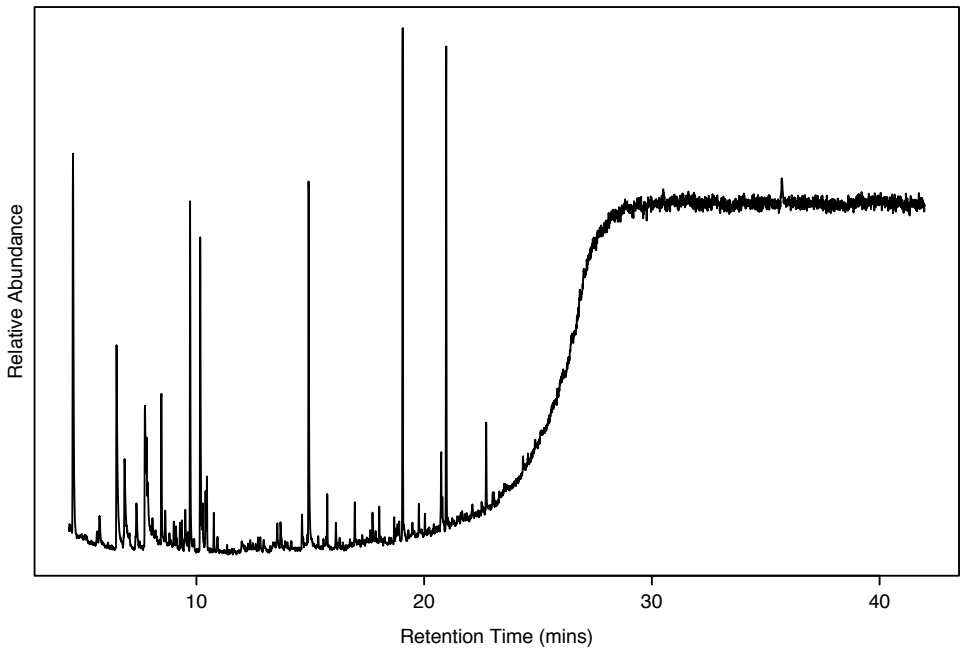
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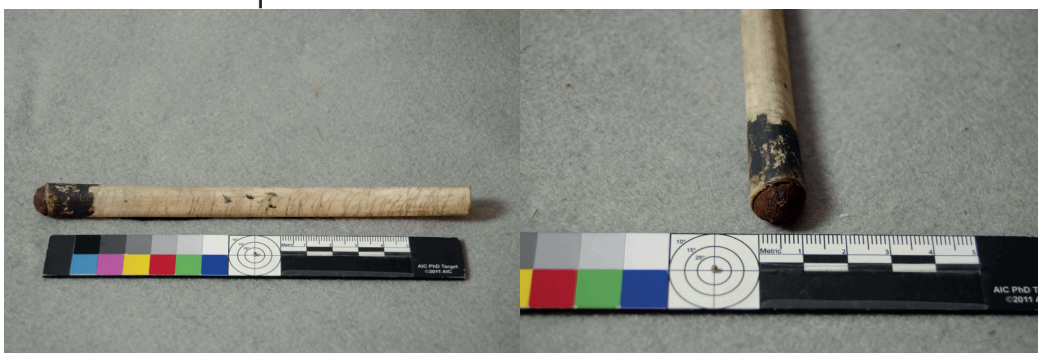


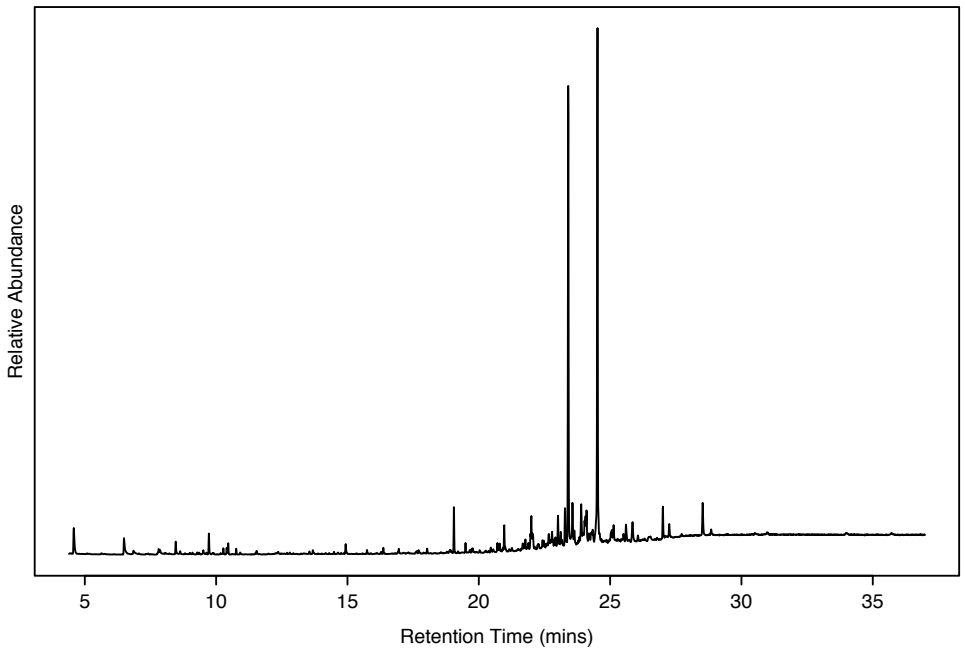
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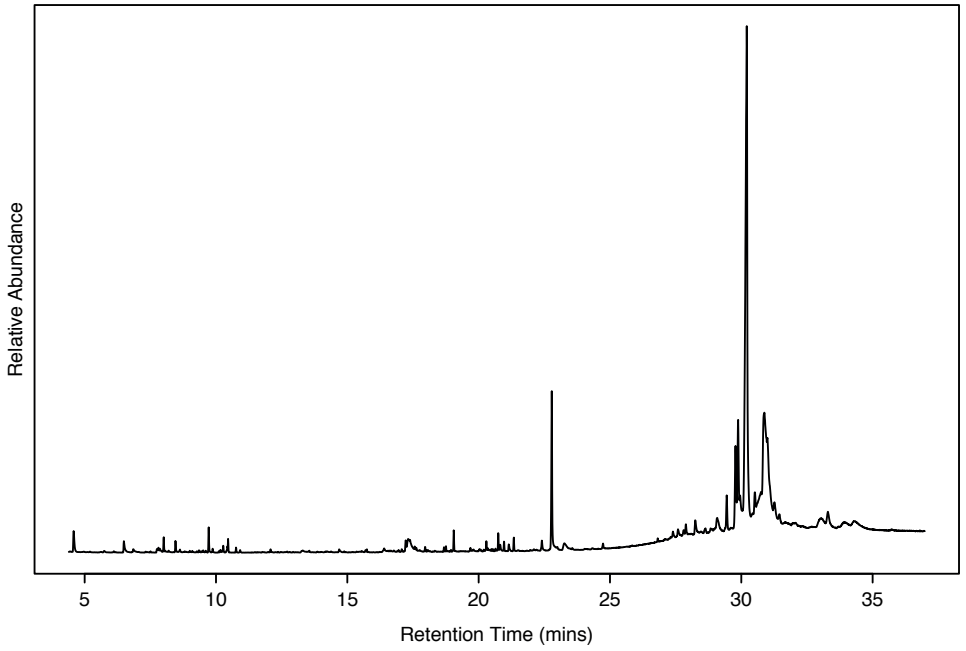
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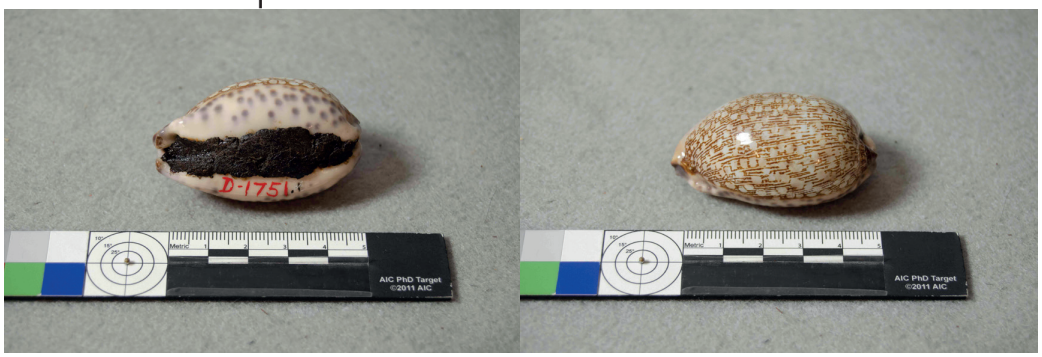


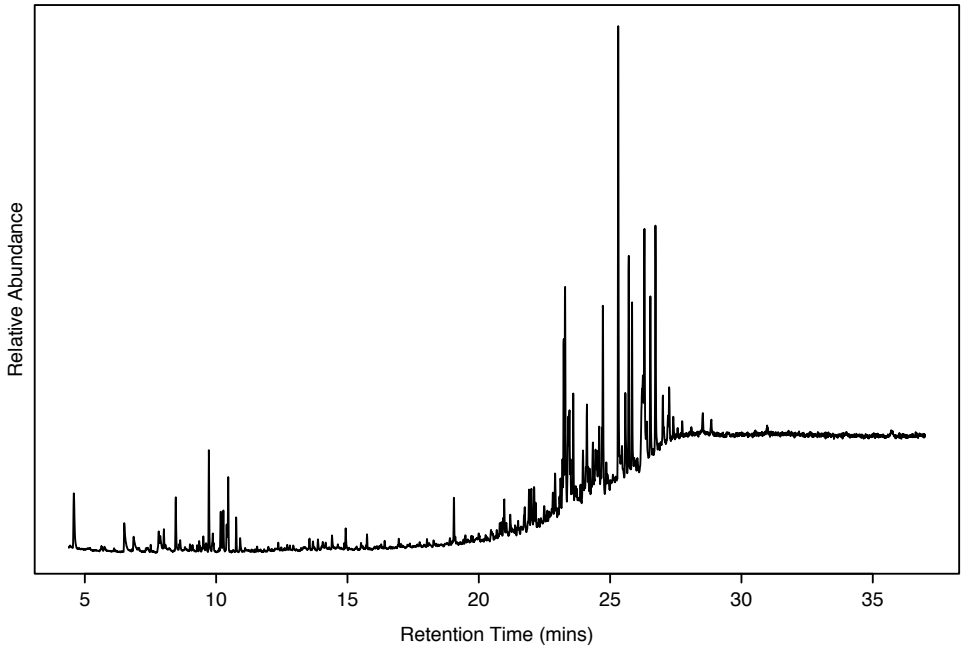
PBH089 | 23-68-70/D4006



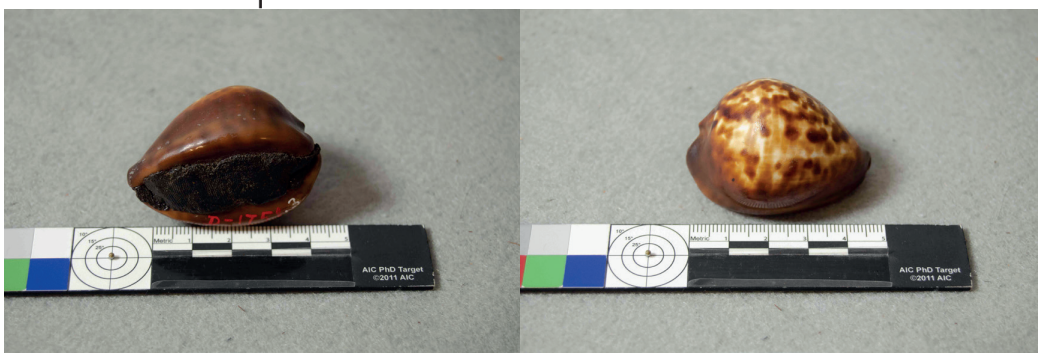


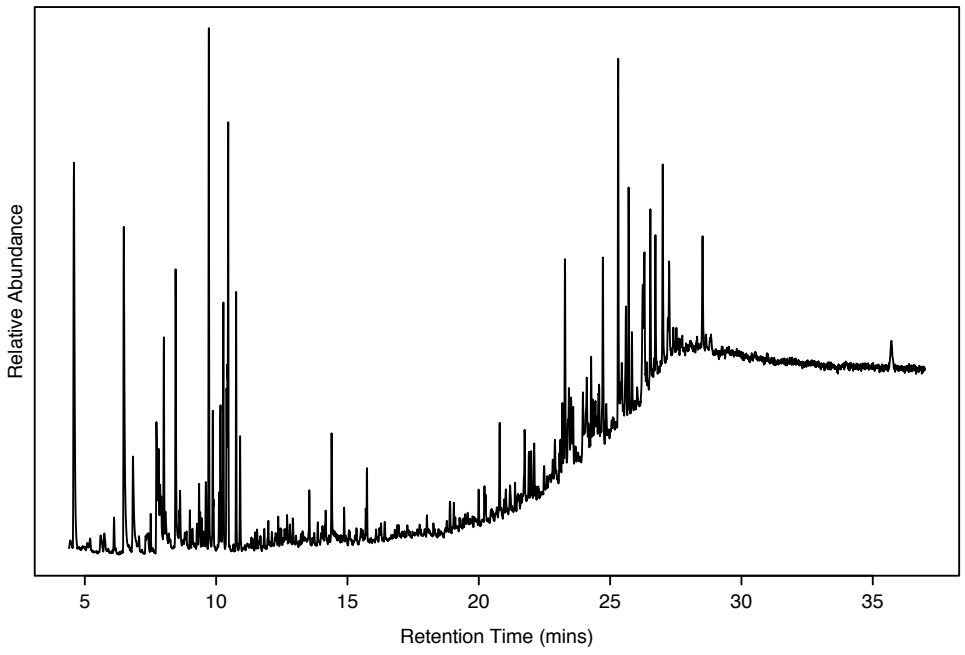
PBH090 | 23-46-70/D1751.1



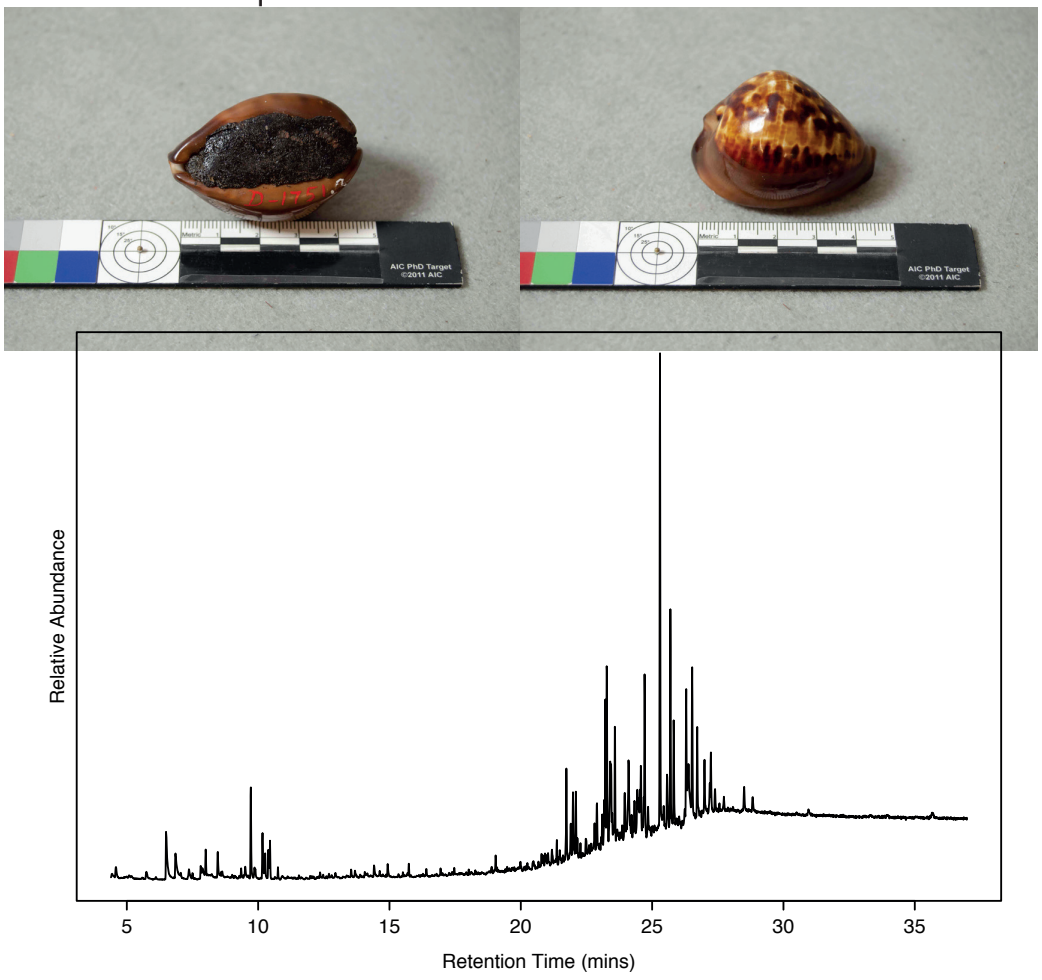


PBH091 | 23-46-70/D1751.2

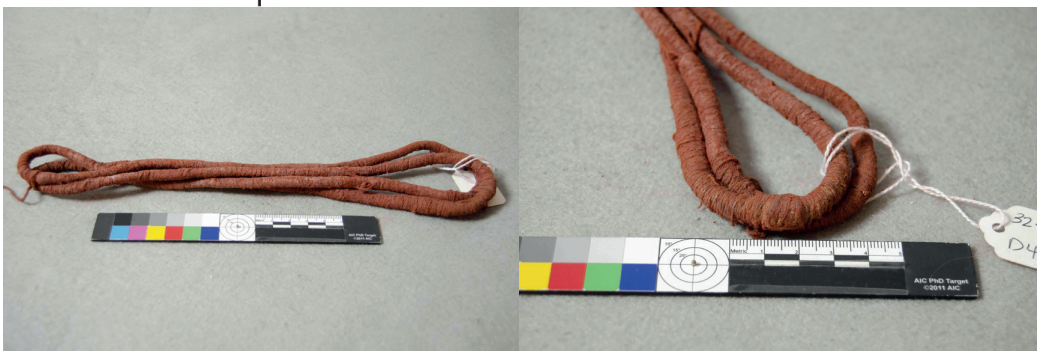


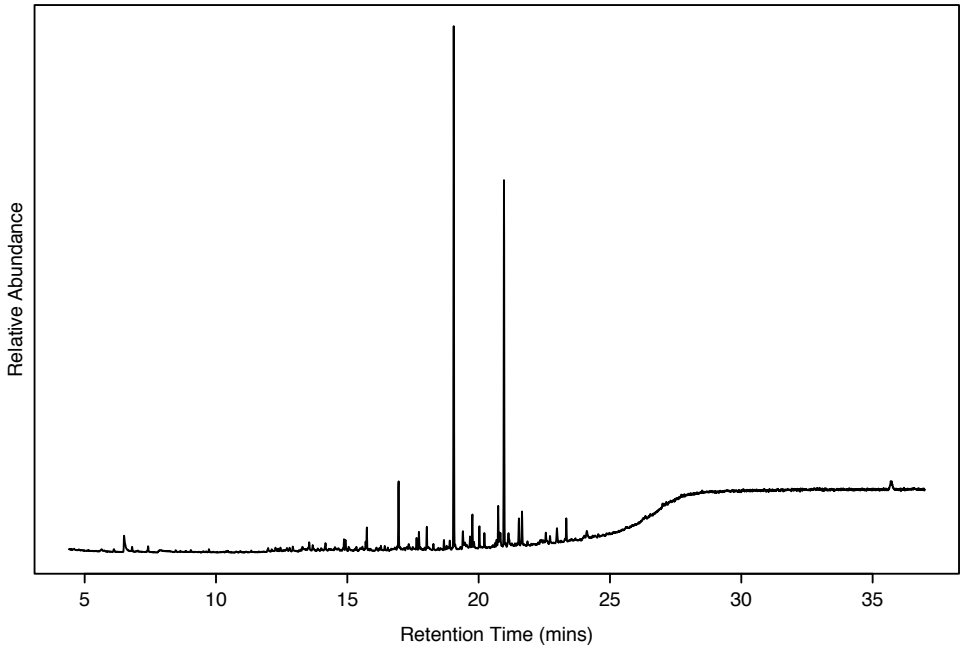


PBH092 | 23-46-70/D1751.3



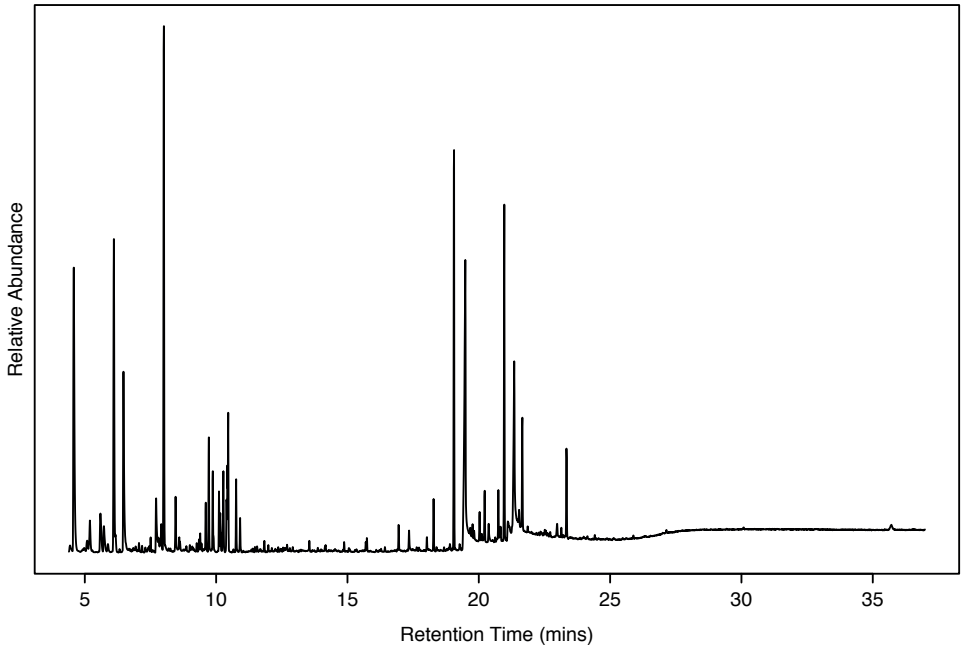
PBH093 | 32-68-70/D4049.2





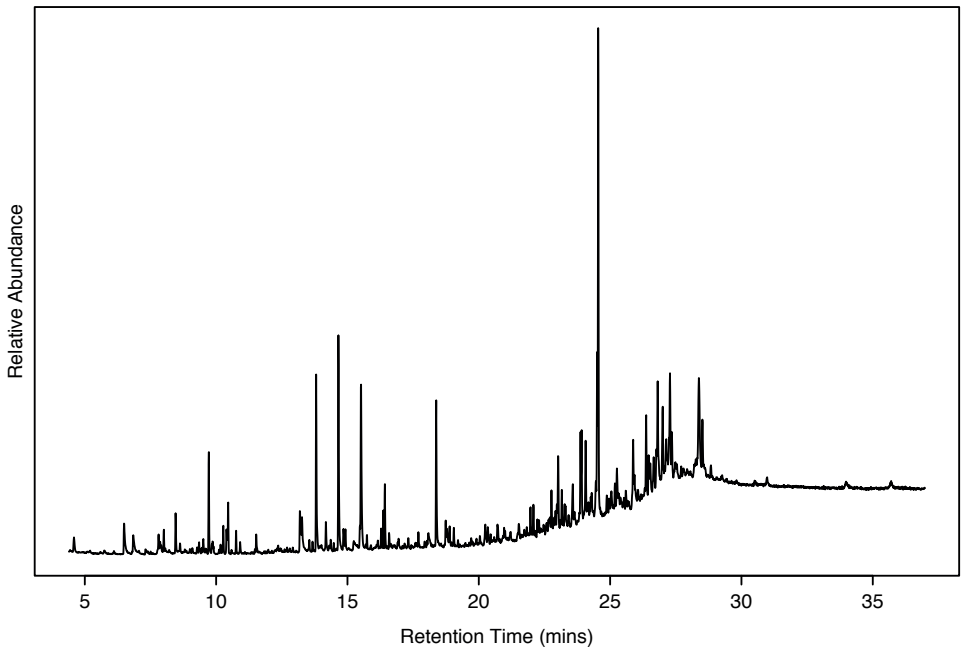
PBH094 | 32-68-70/D4049.6





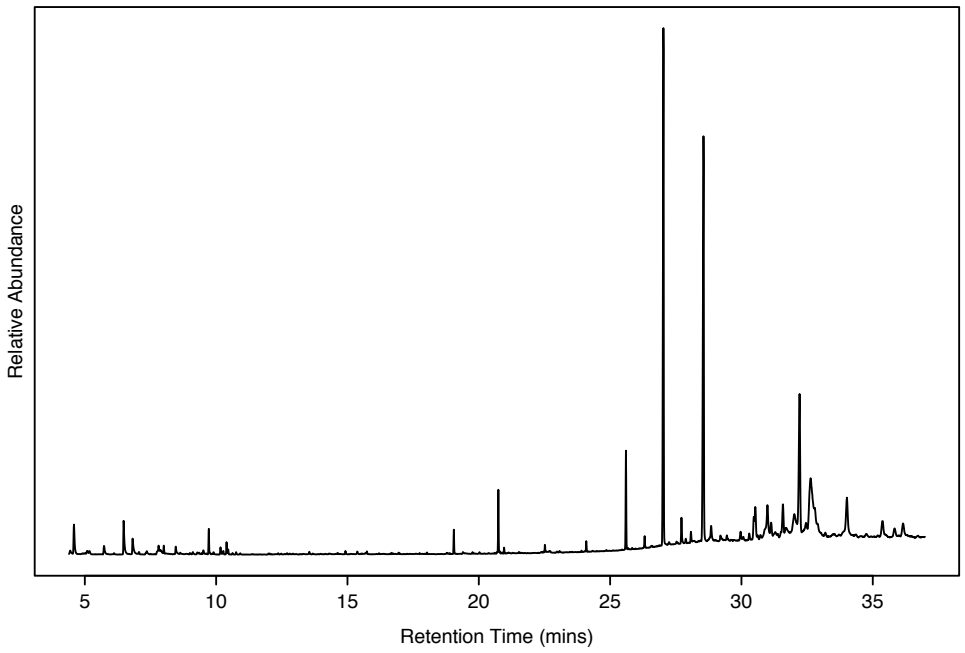
PBH095 | 26-53-70/D2692





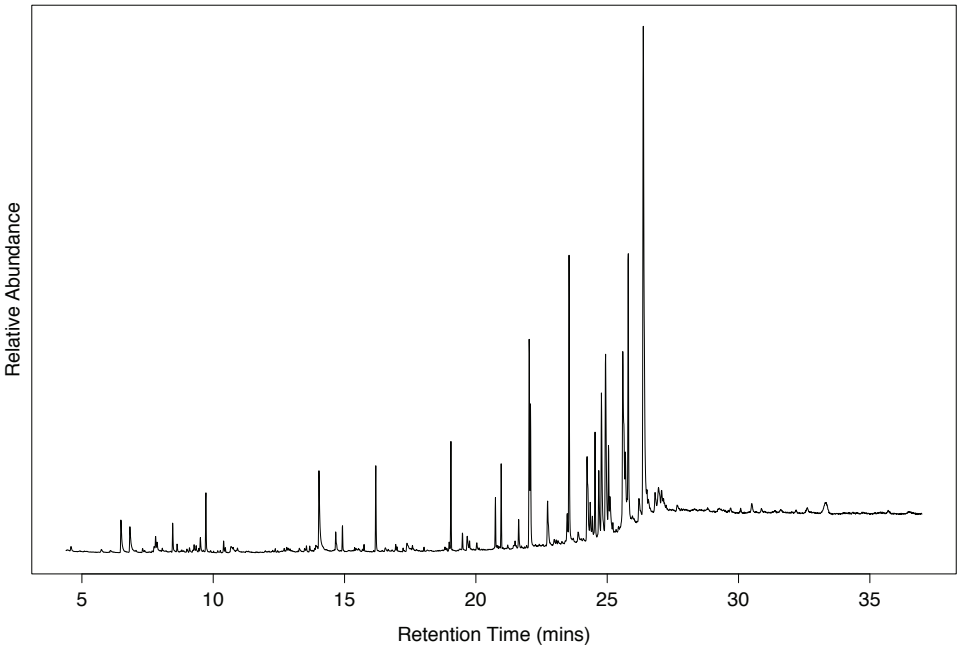
PBH096 | 36-122-70/588





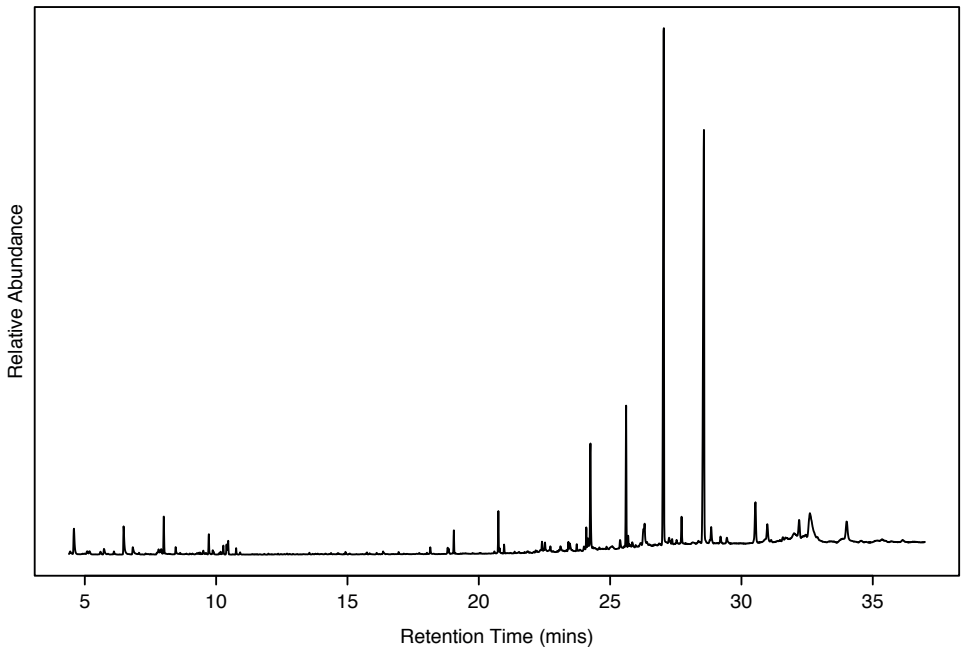
PBH097 | 46-78-70/2312





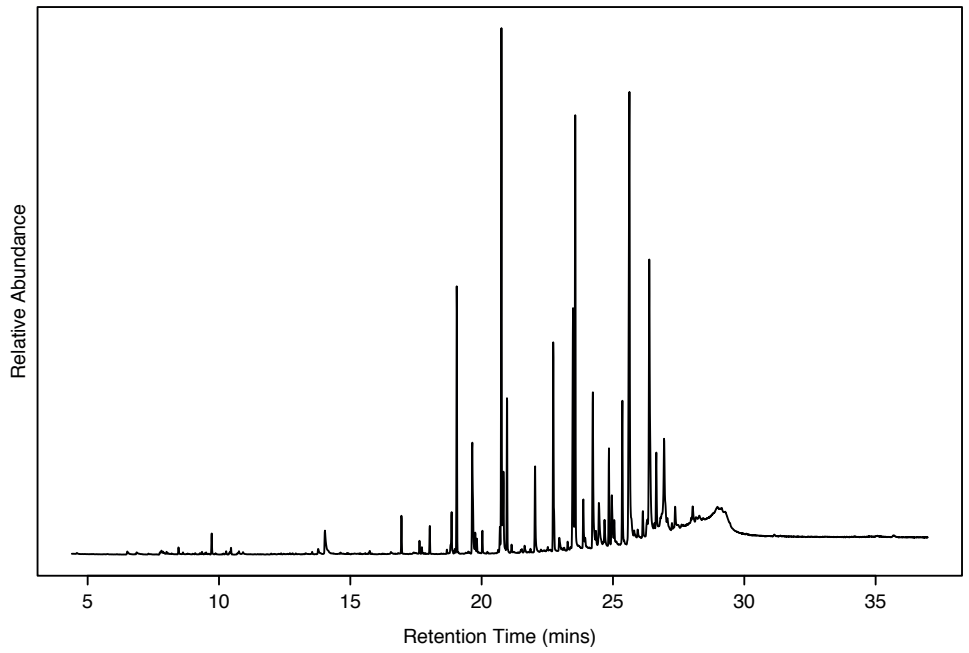
PBH098 | 51-32-70/3277





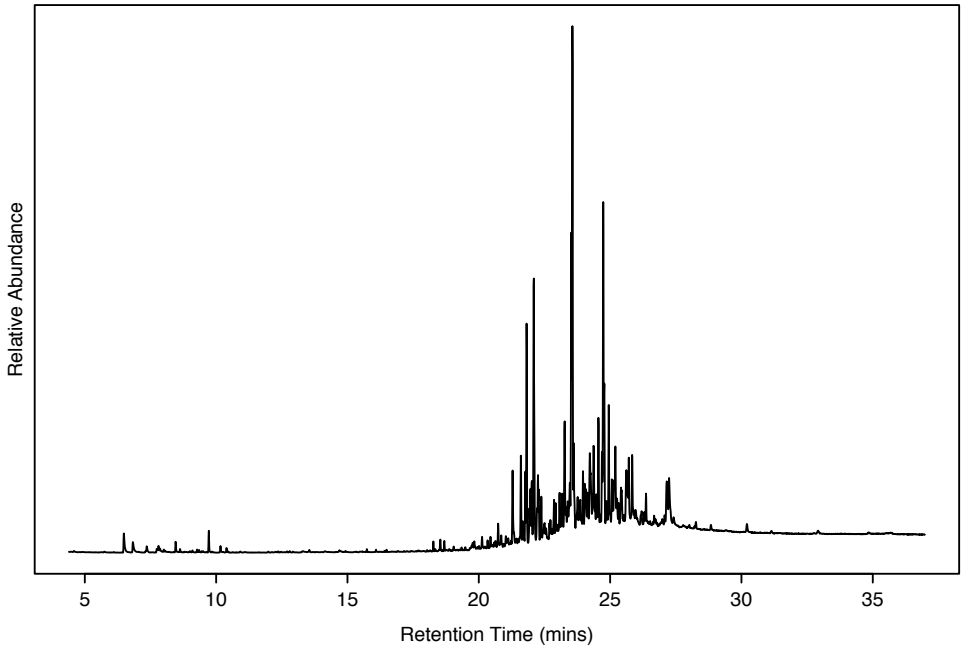
PBH099 | 967-71-70/4676





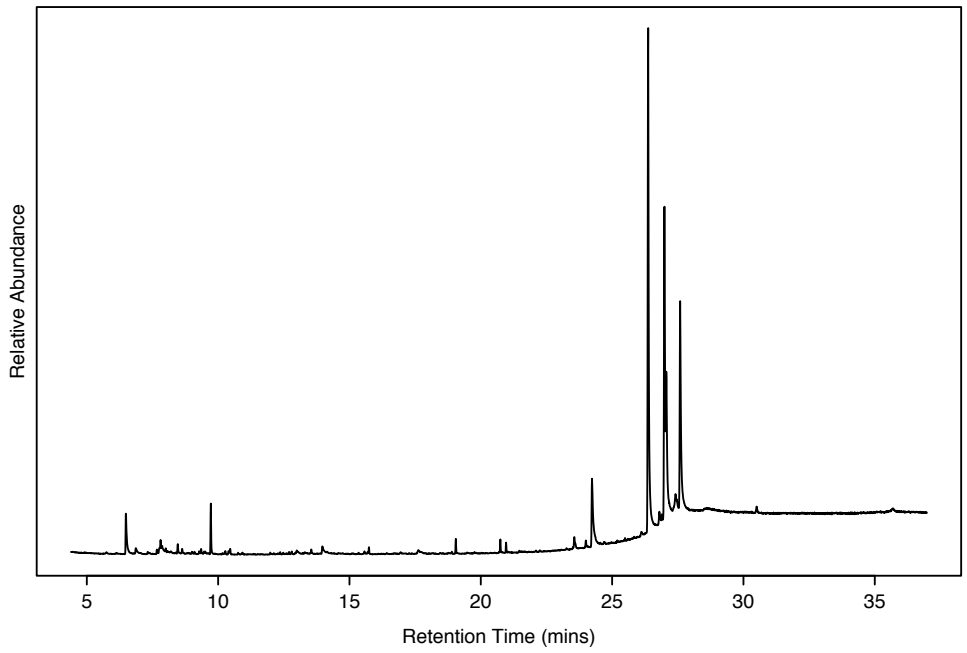
PBH100 | 30-54-70/D3444





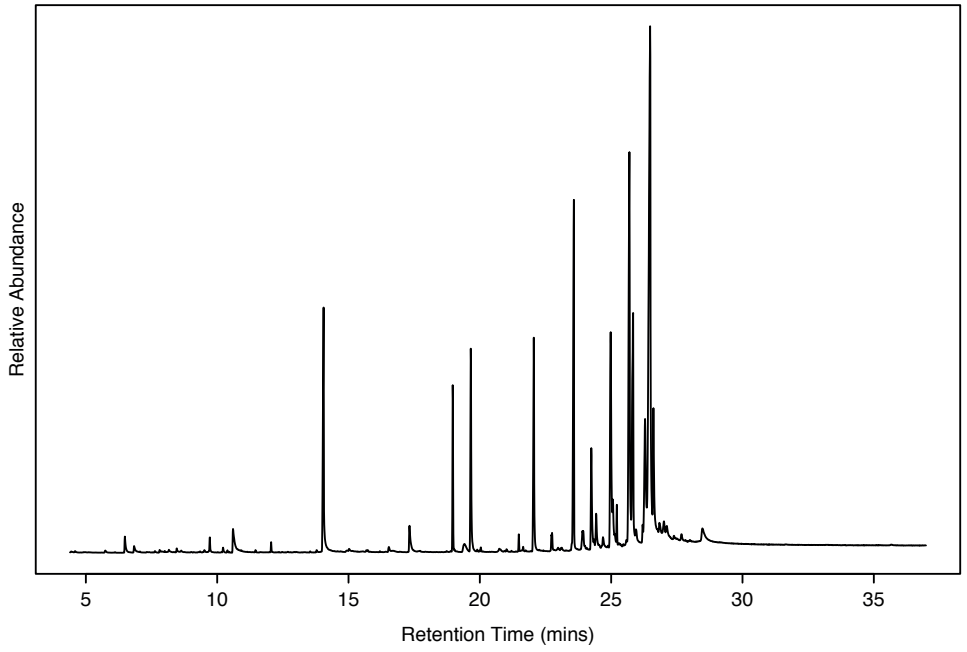
PBH101 | 20-42-70/D1310





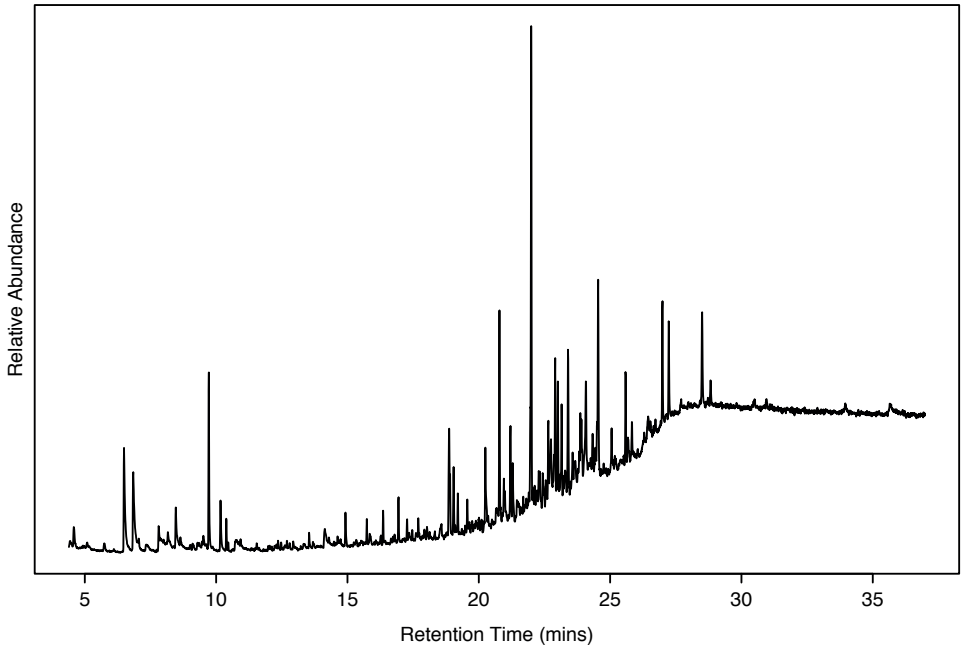
PBH102 | 32-68-70/D4028





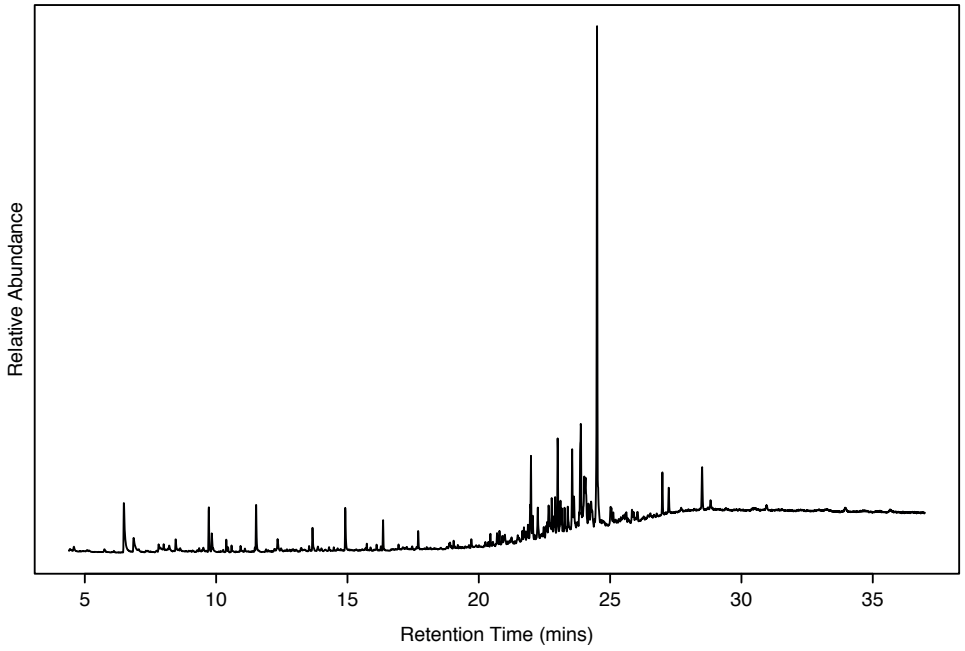
PBH103 | 25-46-70/D2420





PBH104 | 23-46-70/D1734



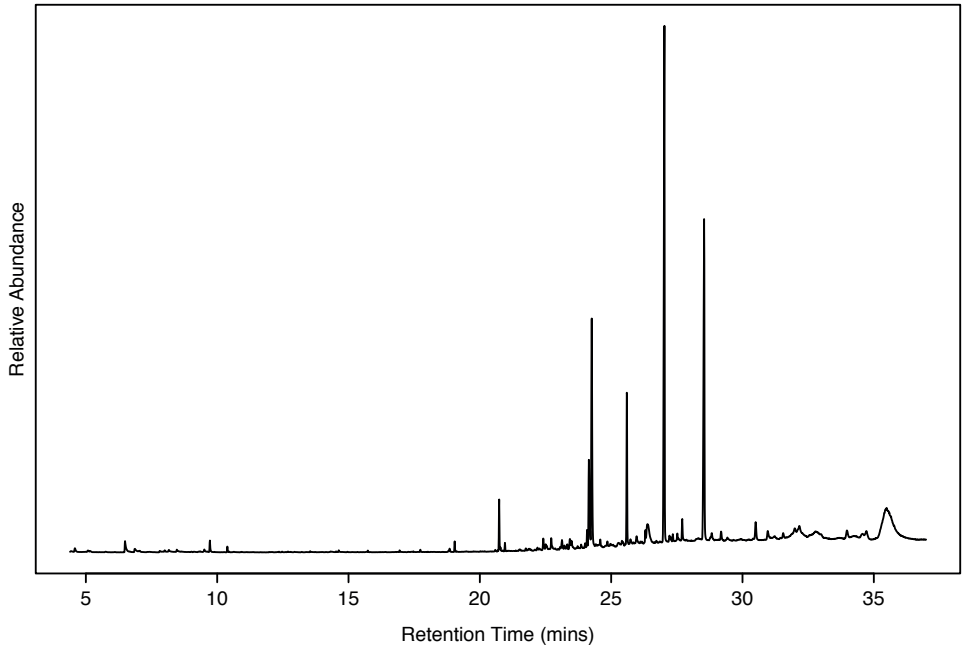


PBH105, PBH106 | 30-54-70/D3455.3



PBH105 | 30-54-70/D3455.3



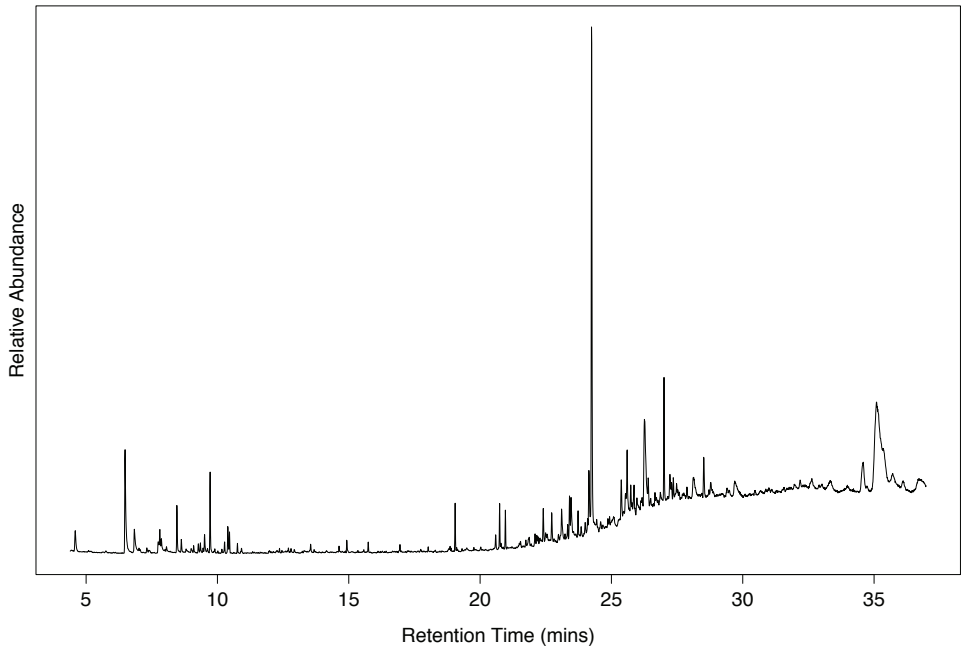


PBH105, PBH106 | 30-54-70/D3455.3



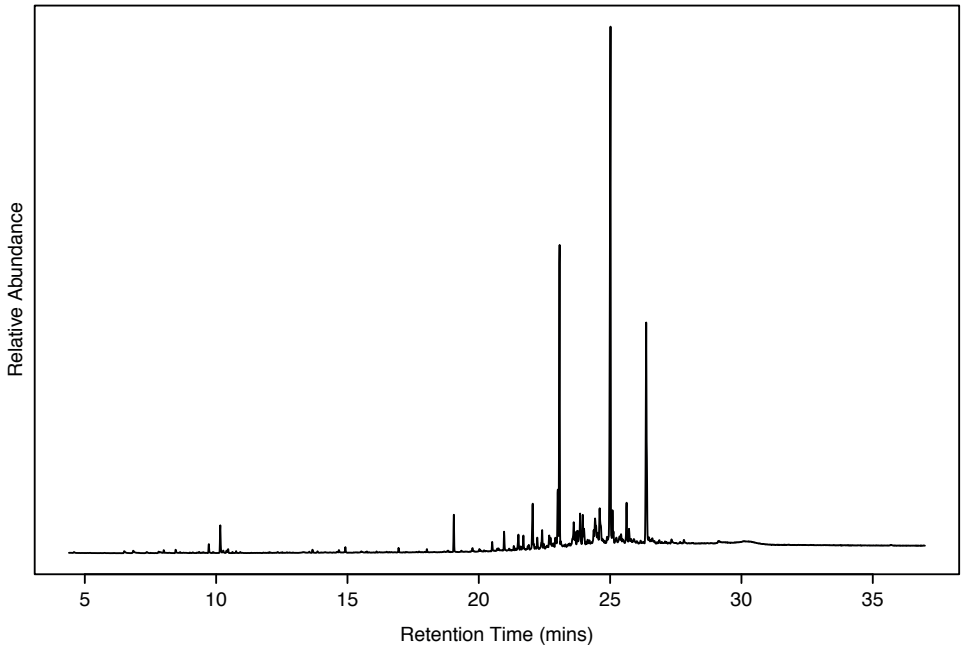
PBH106 | 30-54-70/D3455.3





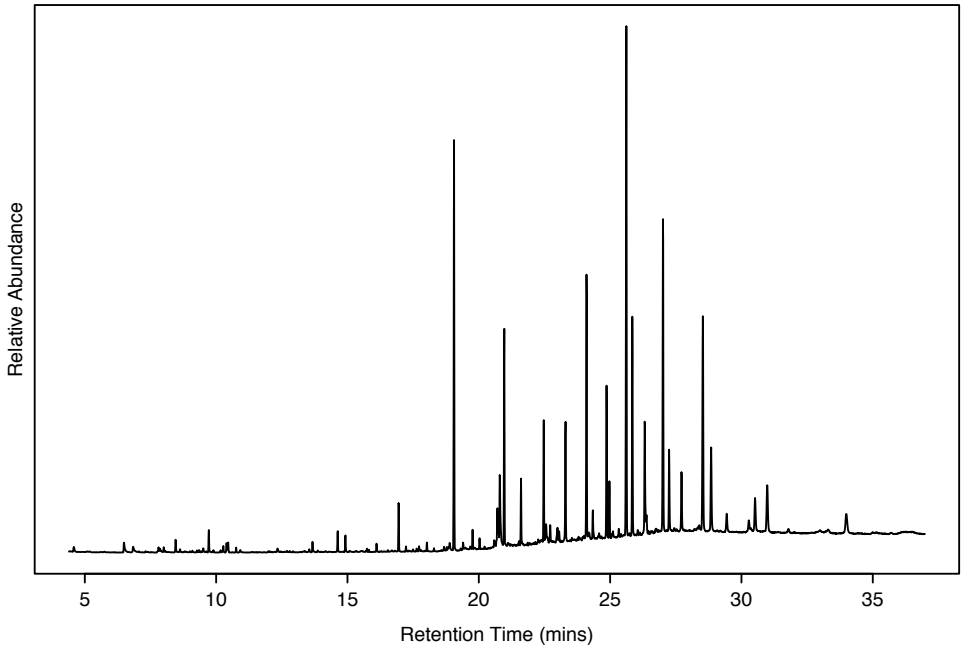
PBH107 | 96-25-70/49482.1





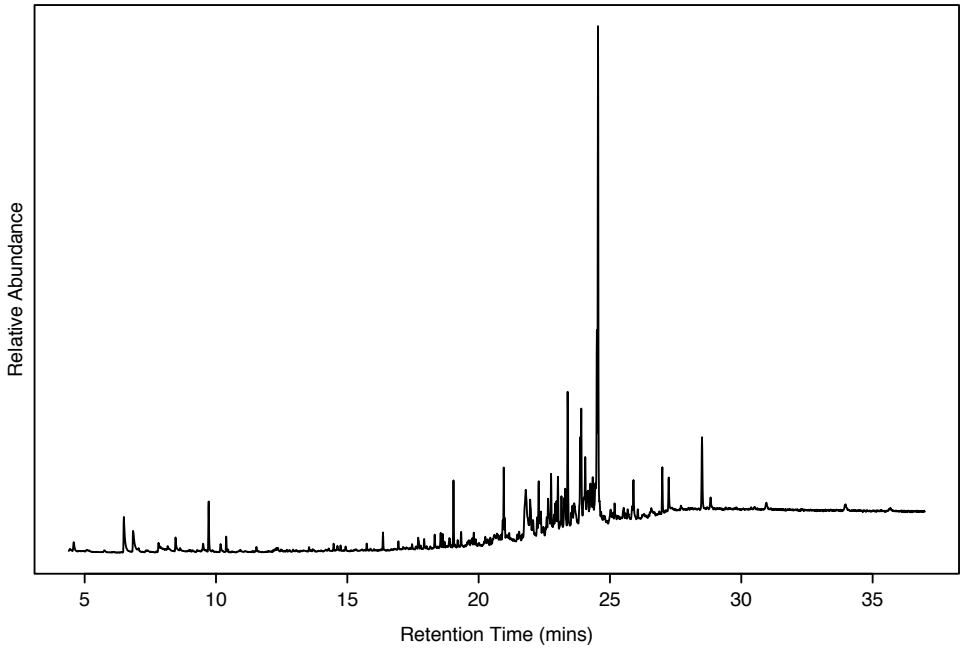
PBH108 | 30-54-70/D3438.1





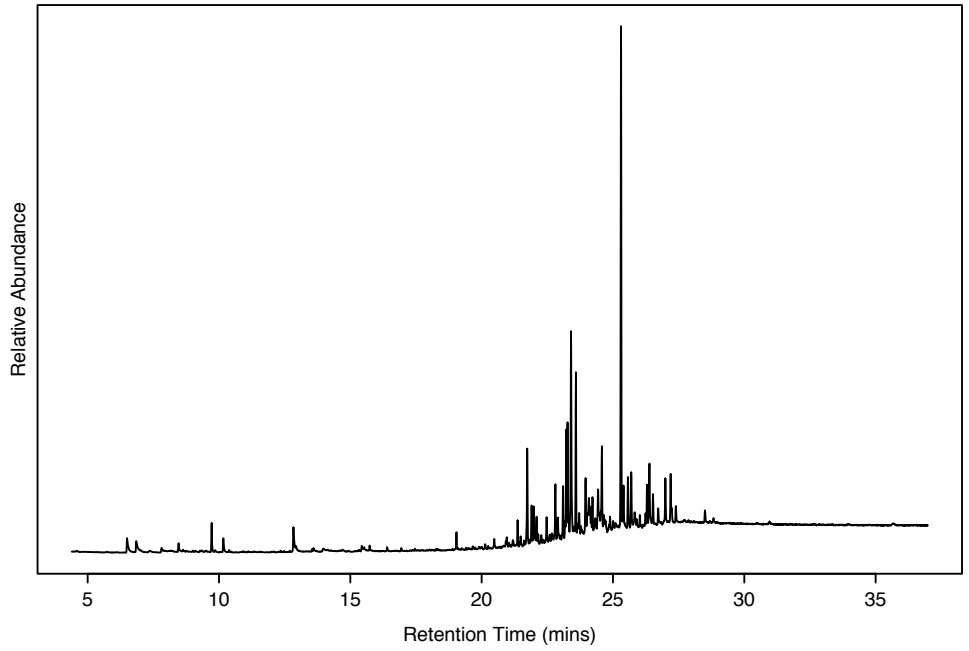
PBH109 | 23-46-70/D1748.3





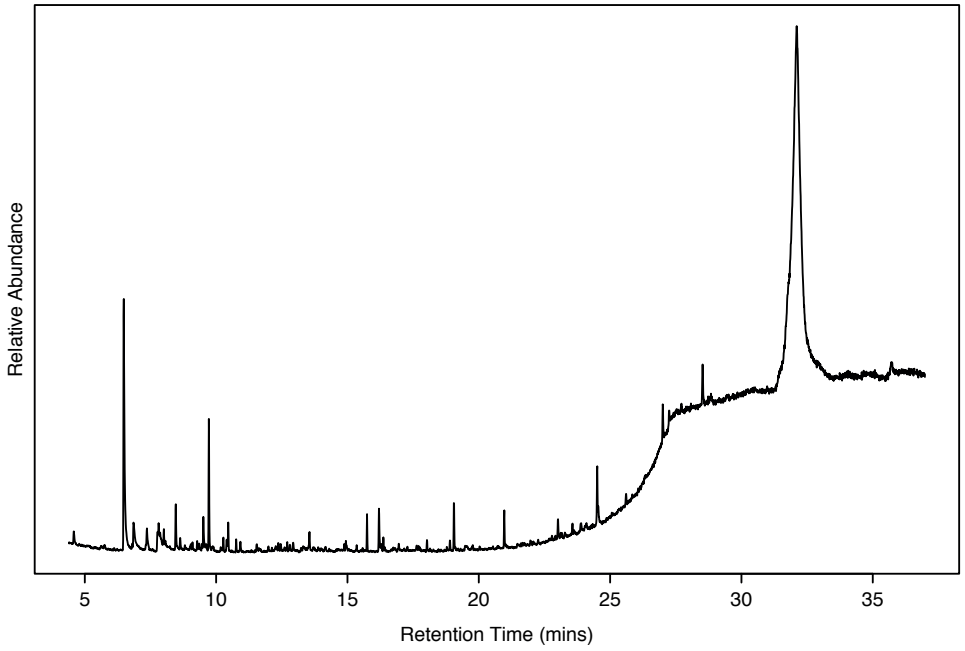
PBH110 | 23-46-70/D1748.4





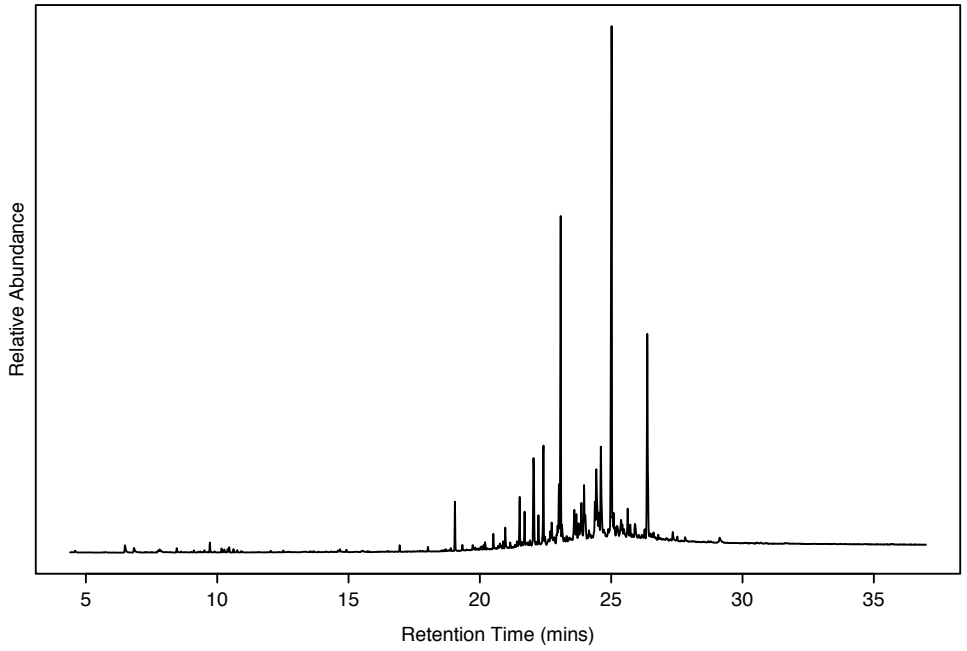
PBH111 | 32-68-70/D3944





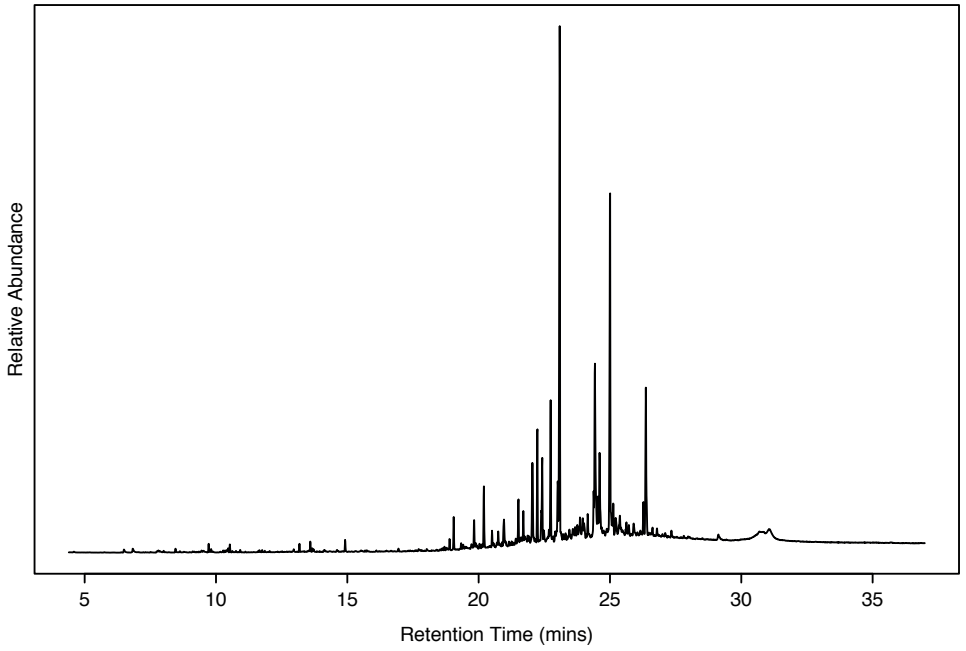
PBH112 | 96-25-70/49474.1





PBH113 | 967-91-70/4651



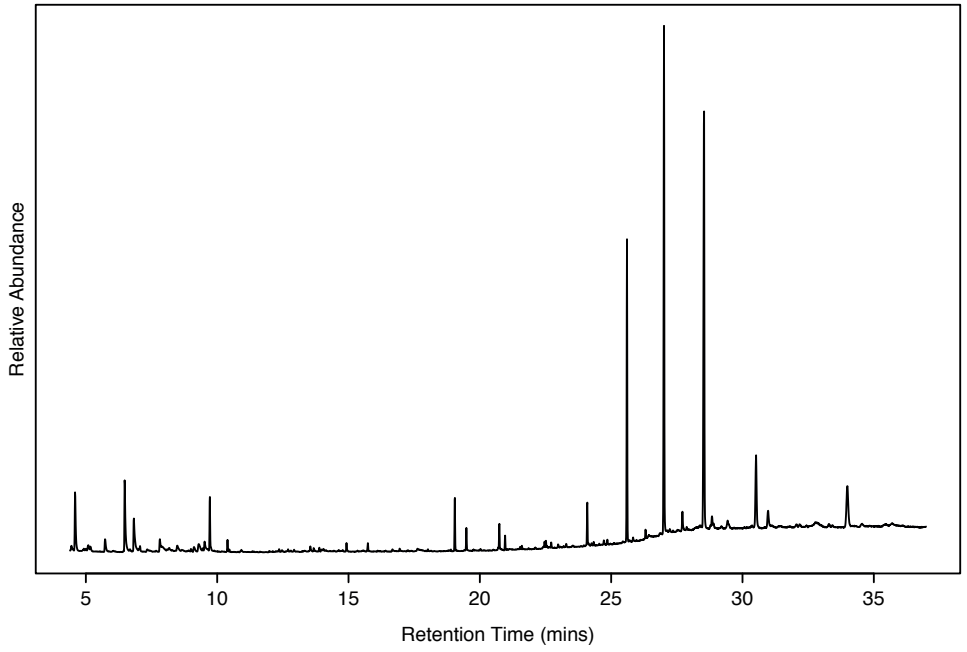


PBH114, PBH115 | 30-54-70/D3421



PBH114 | 30-54-70/D3421



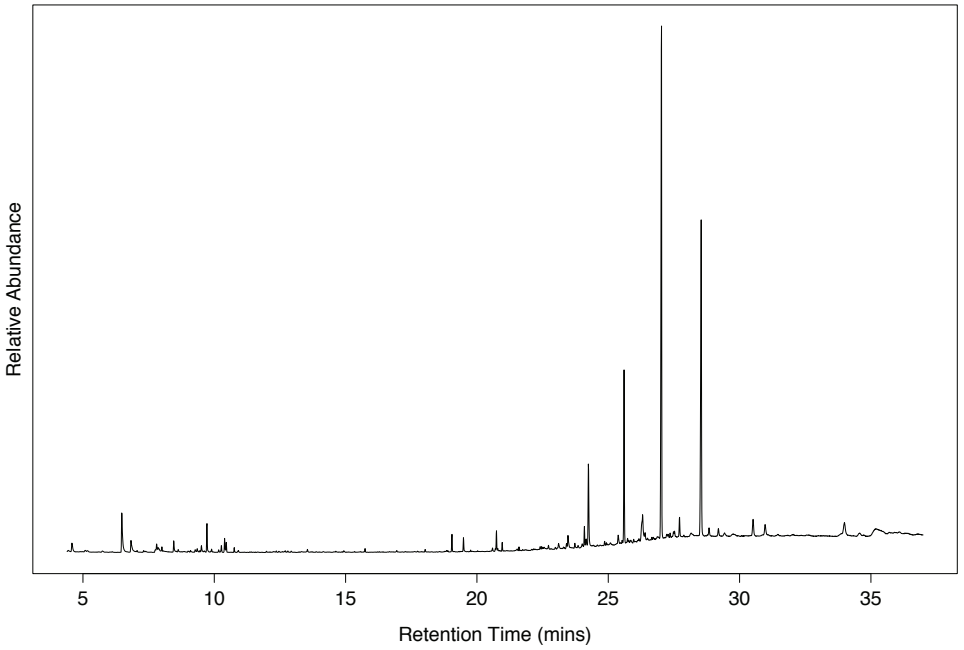


PBH114, PBH115 | 30-54-70/D3421



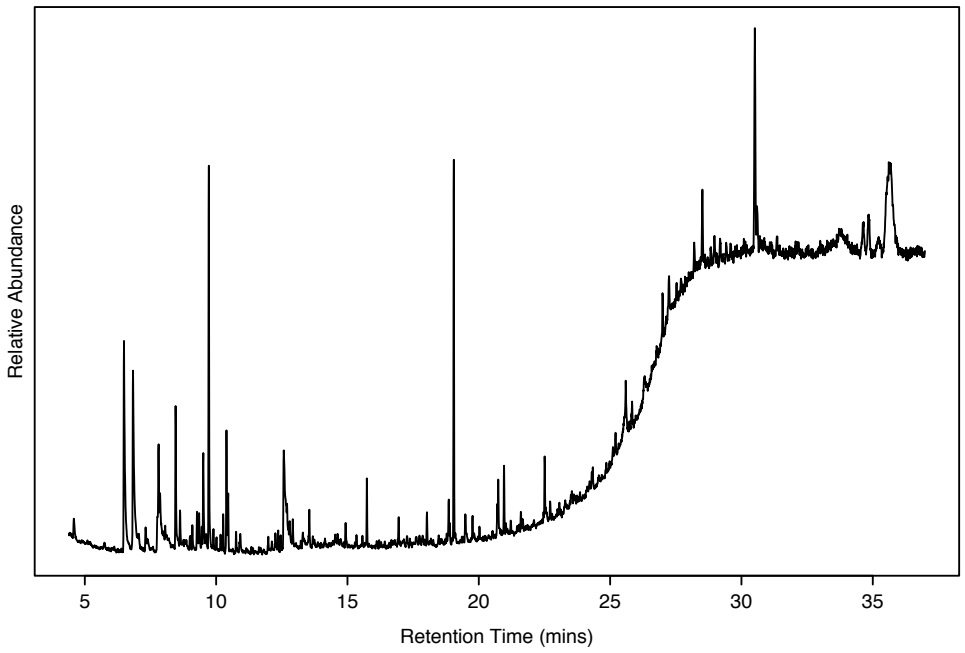
PBH115 | 30-54-70/D3421





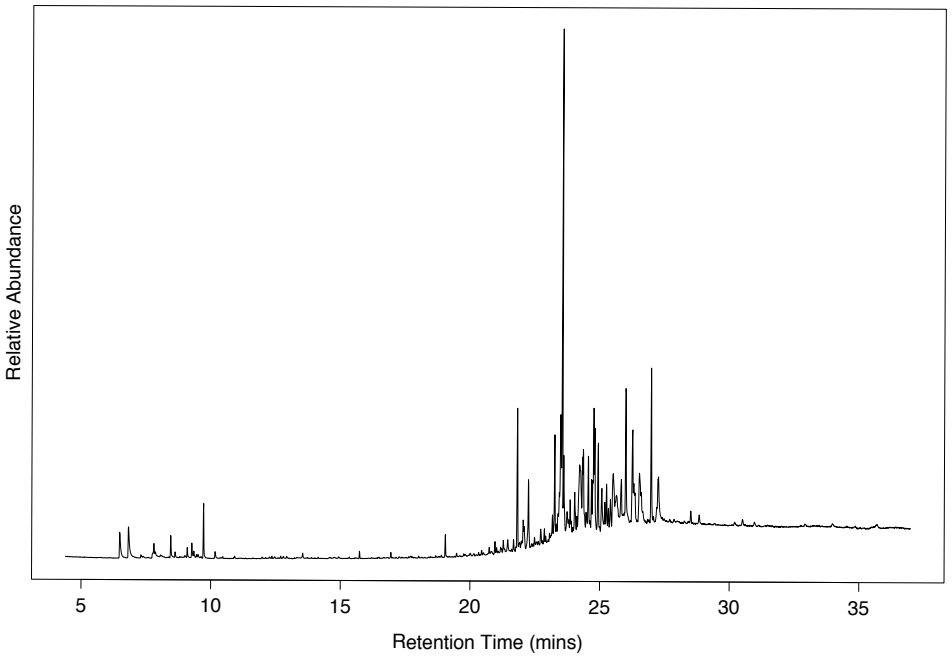
PBH116 | 30-54-70/D3421.1





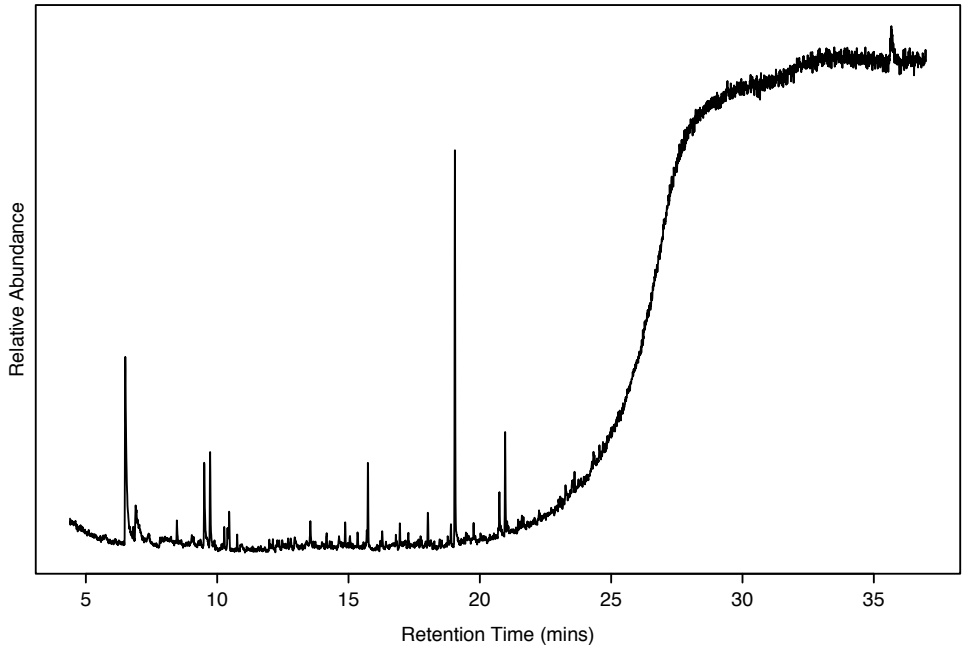
PBH117 | 20-42-70/D1309.1





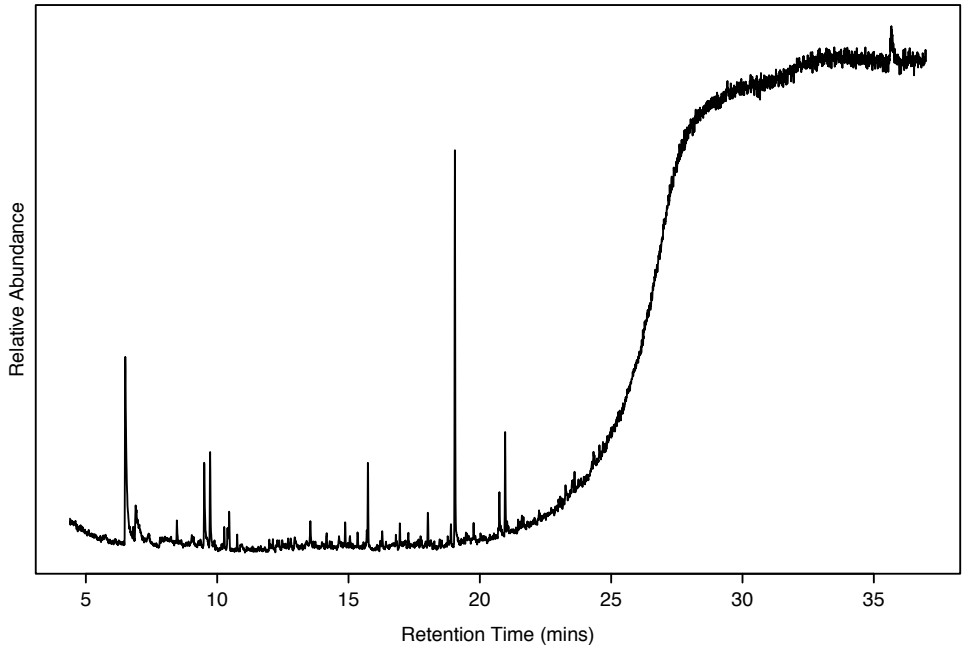
PBH118 | 20-42-70/D1309.2





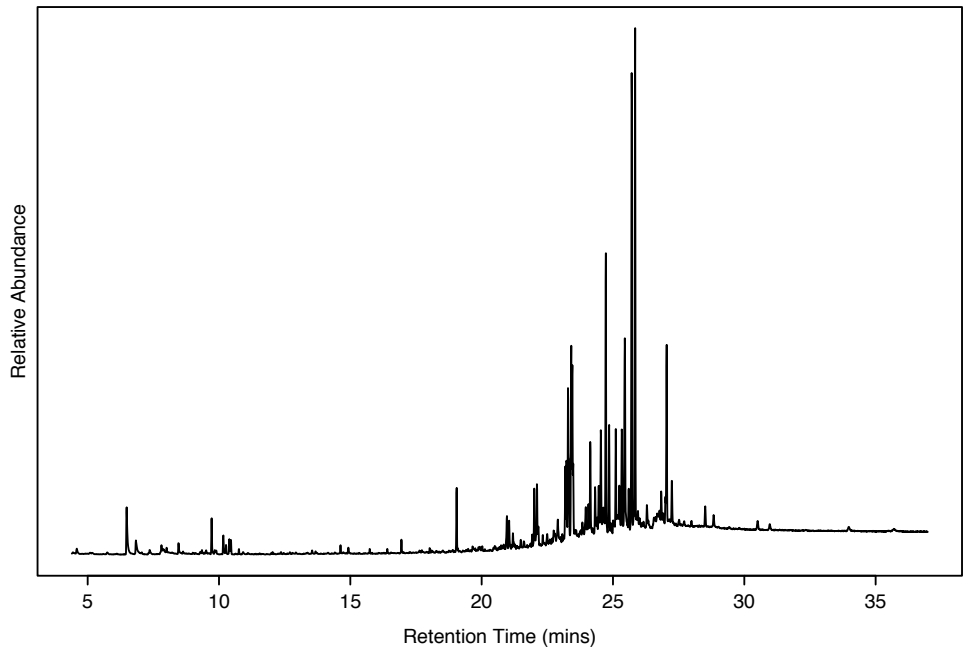
PBH119 | 20-42-70/D1309.3





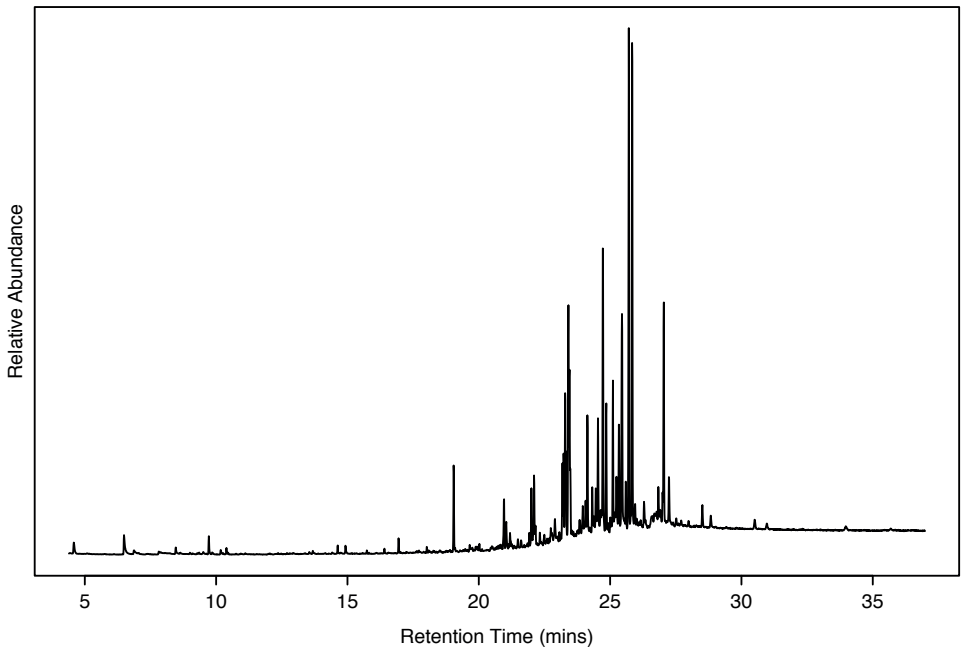
PBH120 | 22-29-70/D1694.1





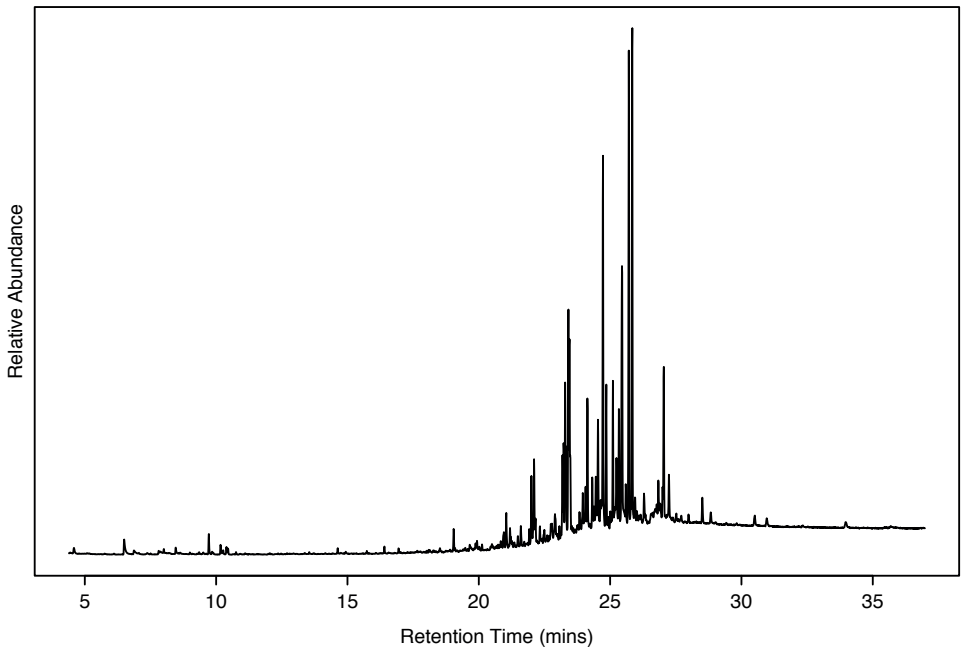
PBH121 | 22-29-70/D1694.2





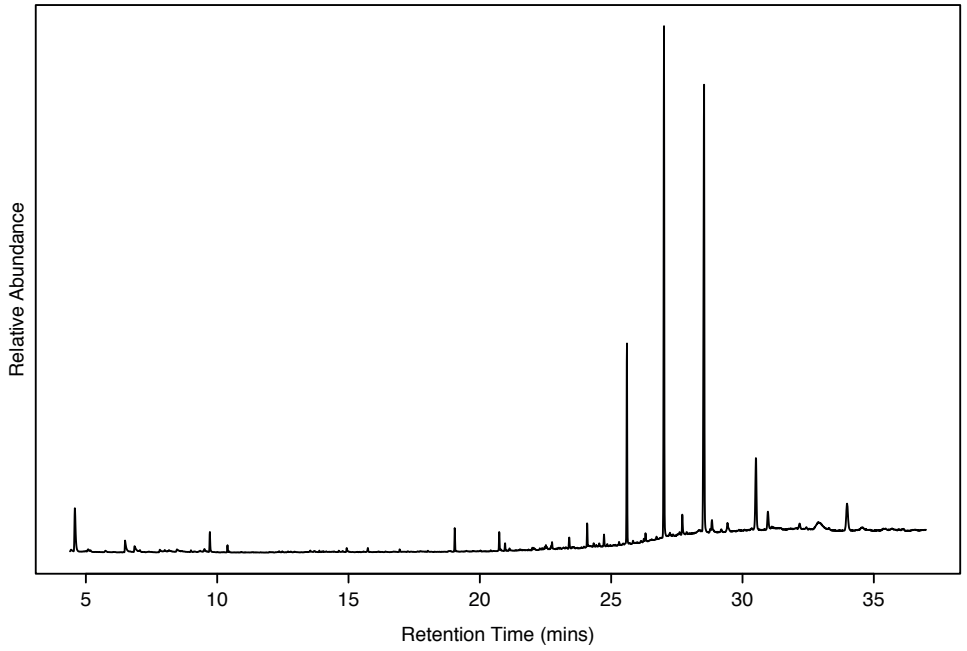
PBH122 | 22-29-70/D1694.3





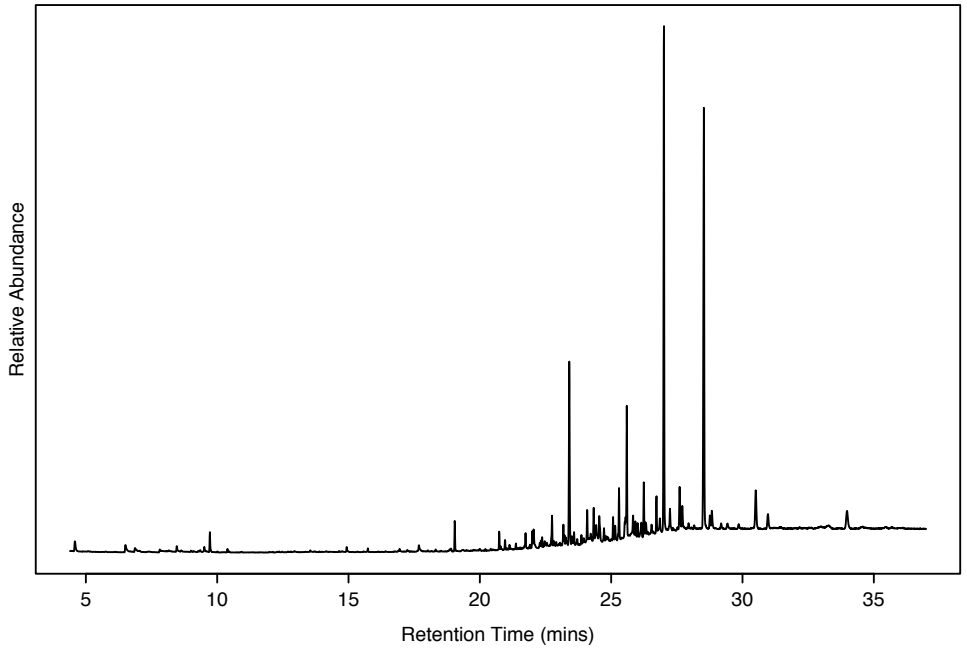
PBH123 | 30-54-70/D3482.1





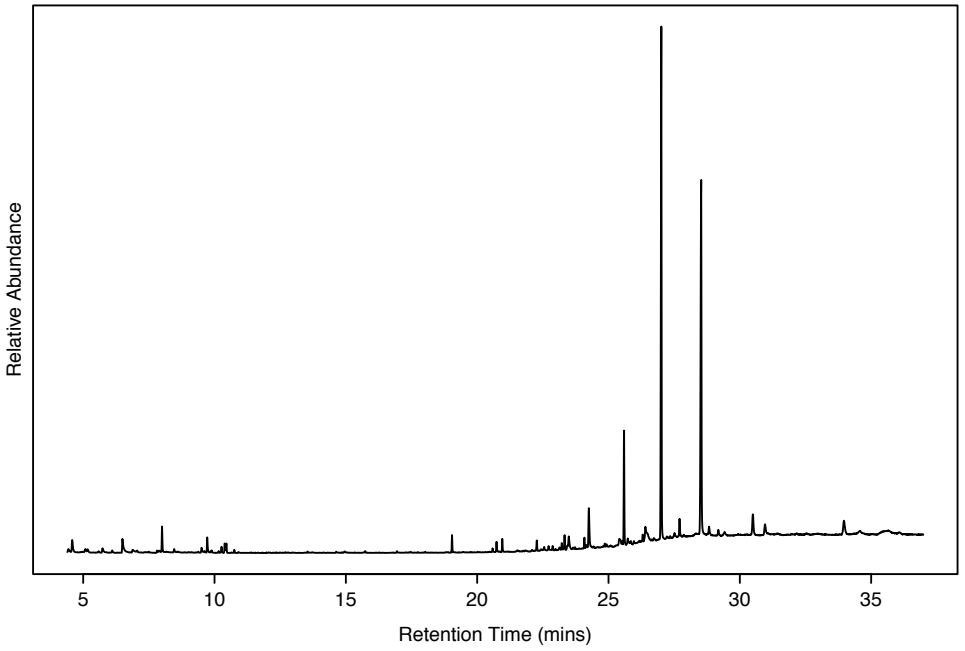
PBH124 | 30-54-70/D3482.1





PBH125 | 30-54-70/D3486

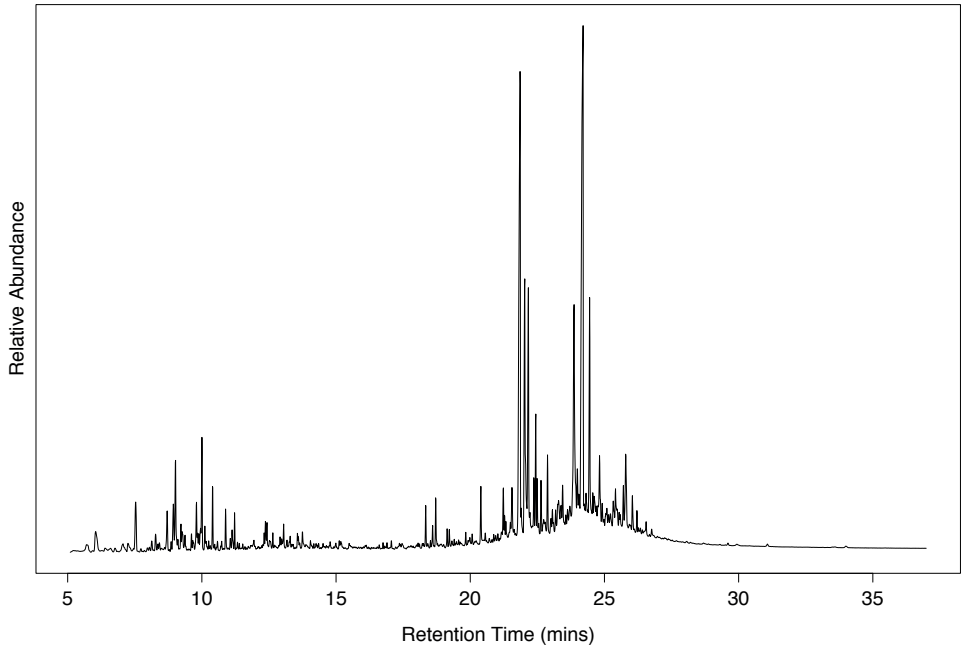




Pitt Rivers Museum

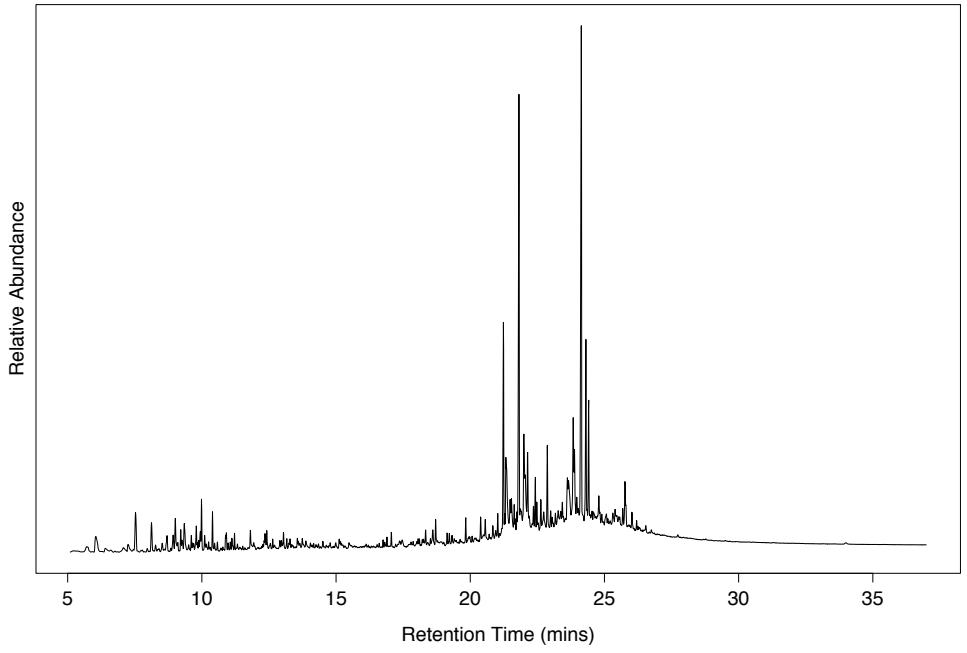
PRM01 | 1886.1.1168





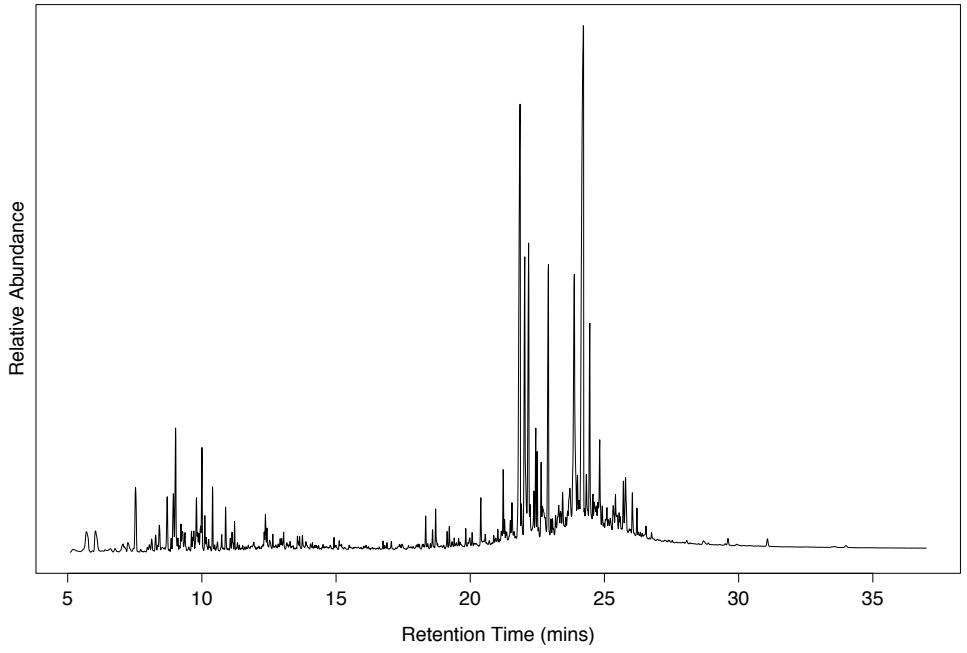
PRM02 | 1932.13.6





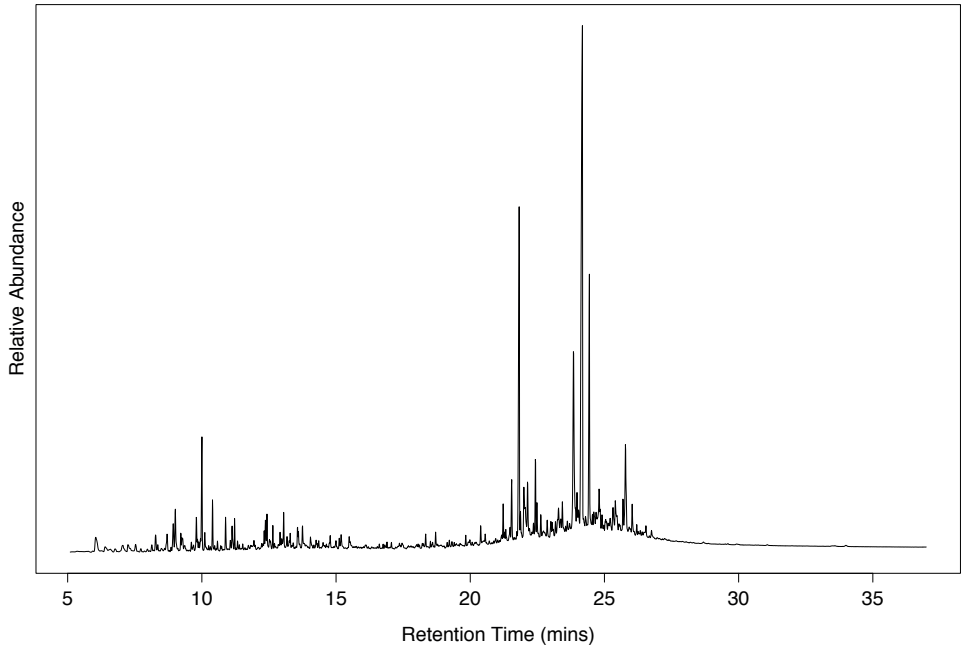
PRM03 | 1933.40.32





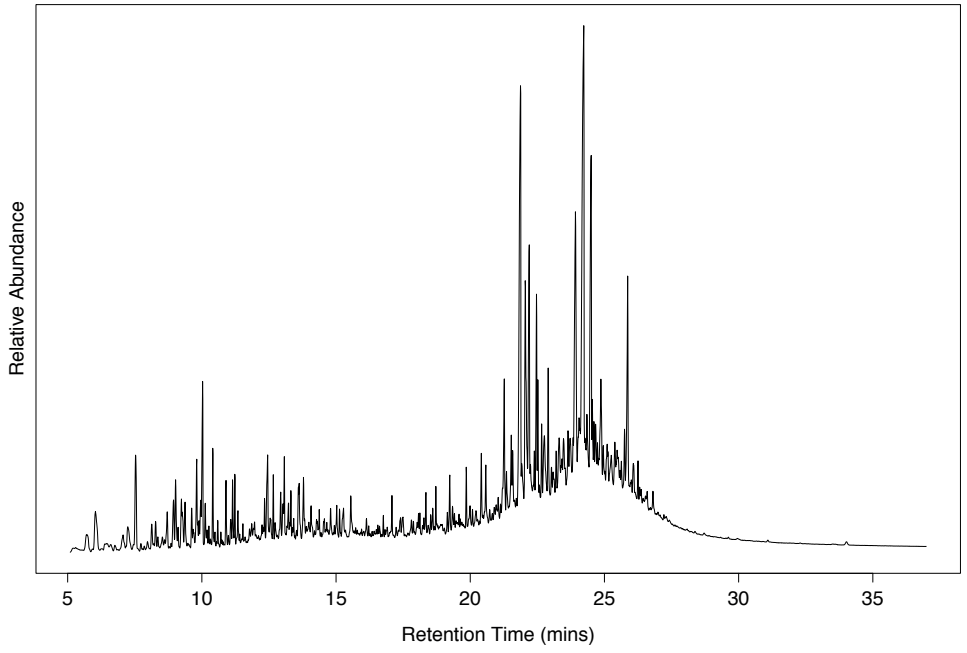
PRM04 | 1933.51.61





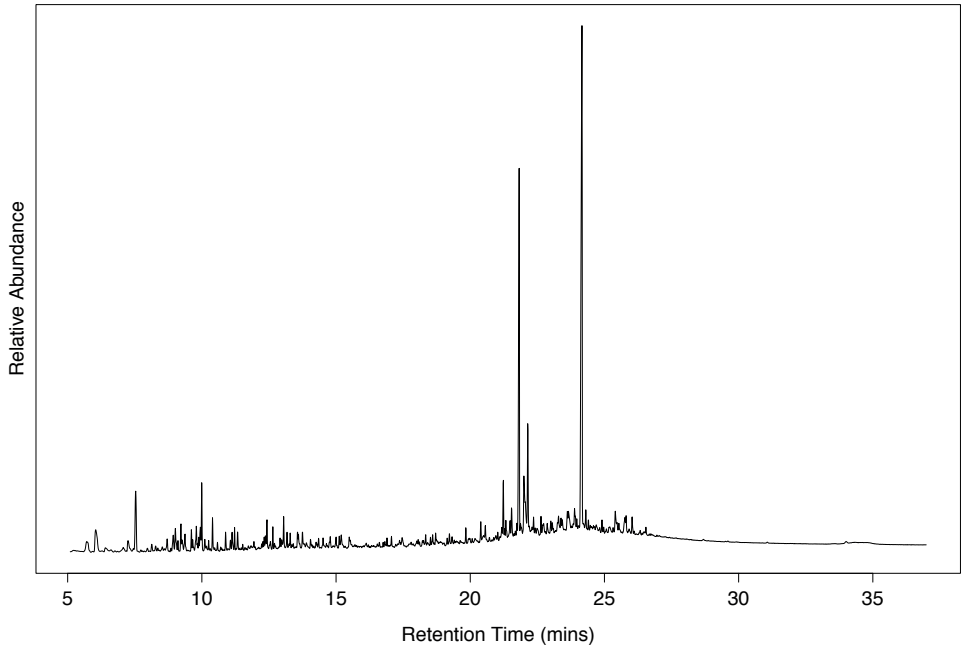
PRM05 | 1925.23.66



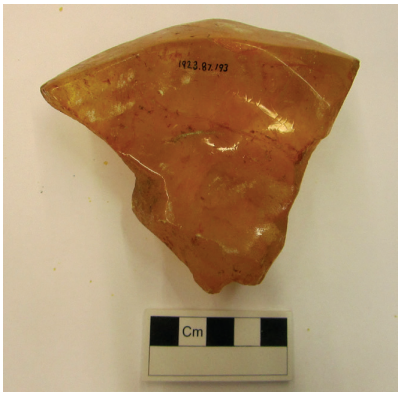


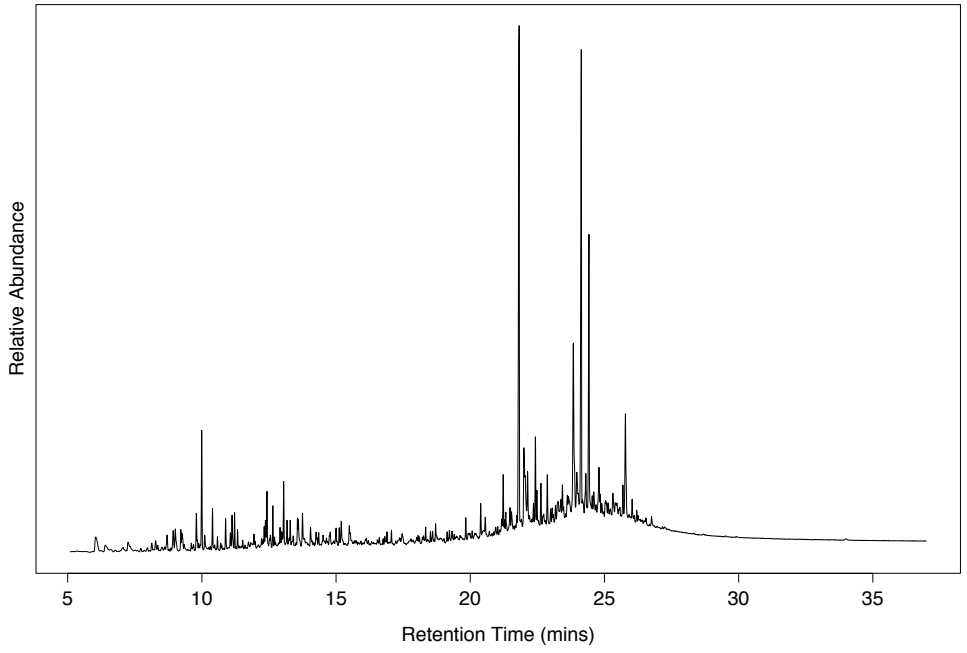
PRM06 | 1923.87.192.2





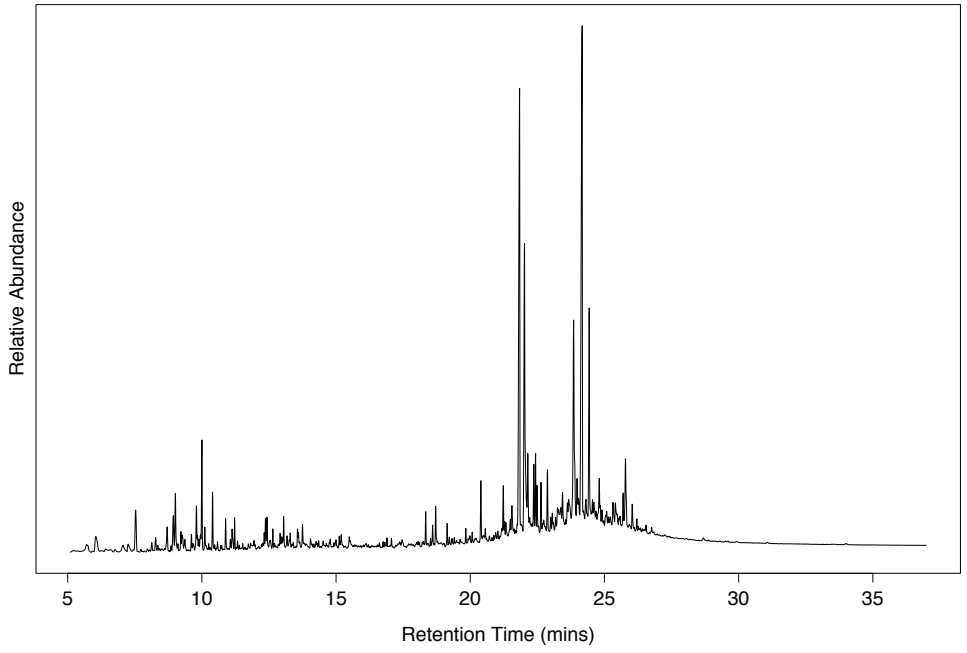
PRM07 | 1923.87.193





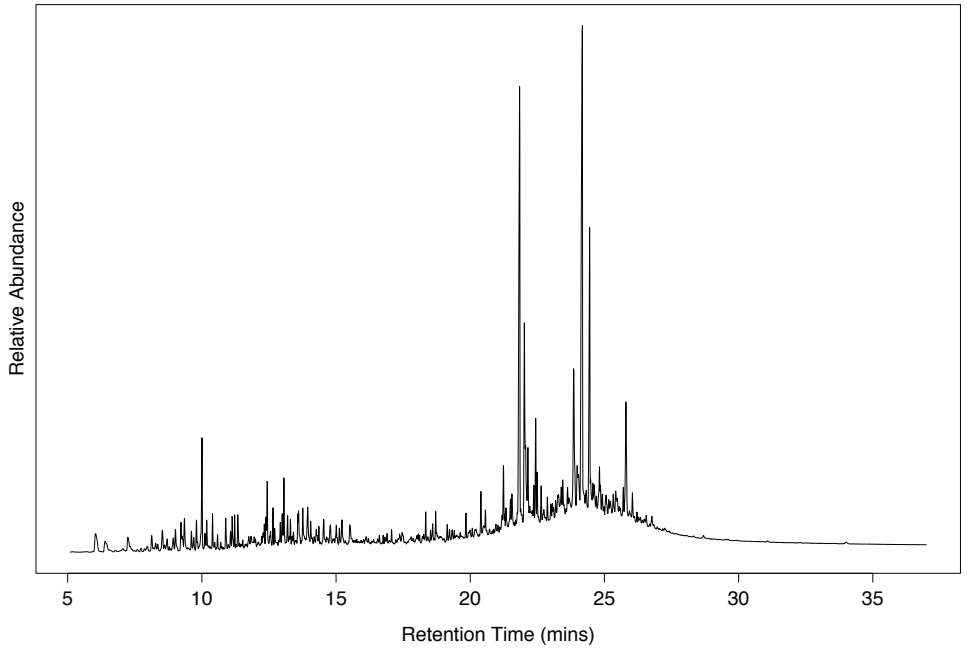
PRM08 | 1923.87.194



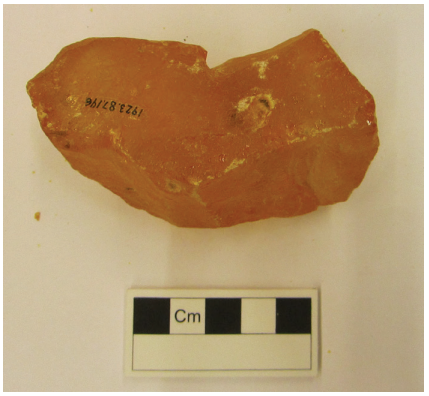


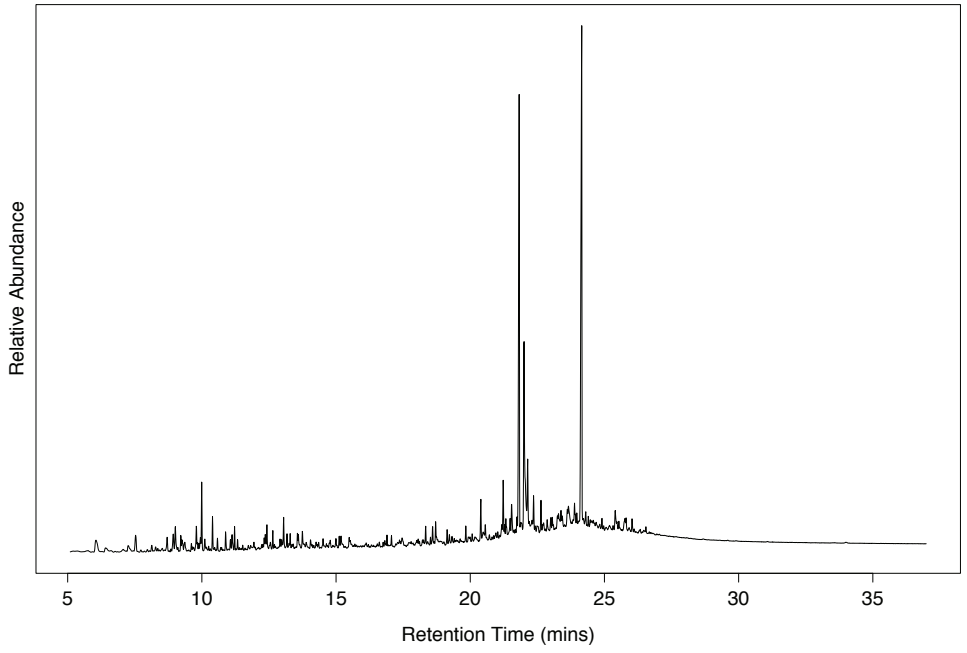
PRM09 | 1923.87.195





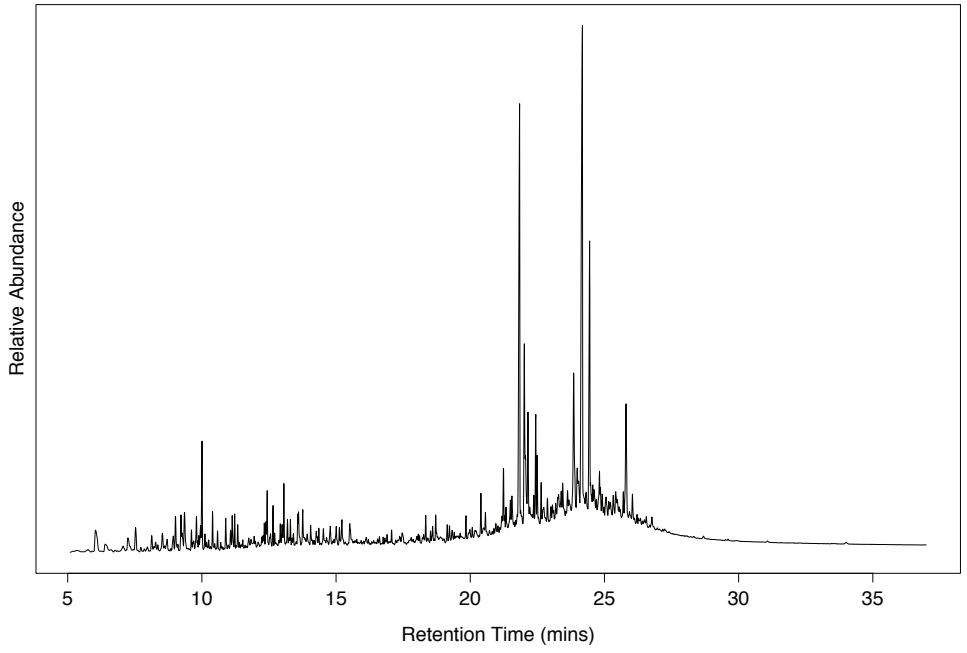
PRM10 | 1923.87.196





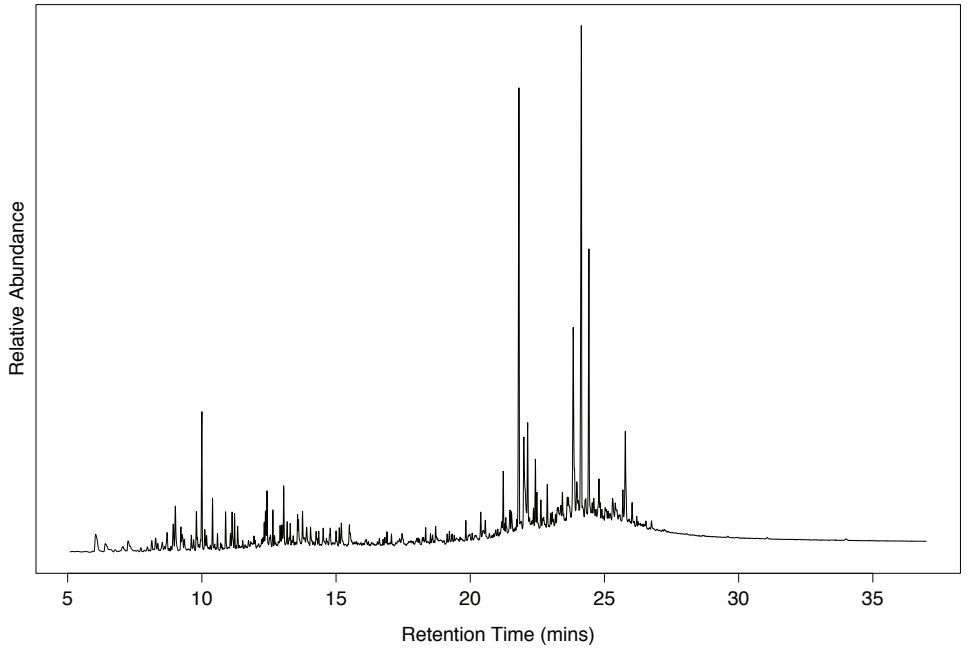
PRM11 | 1923.87.197





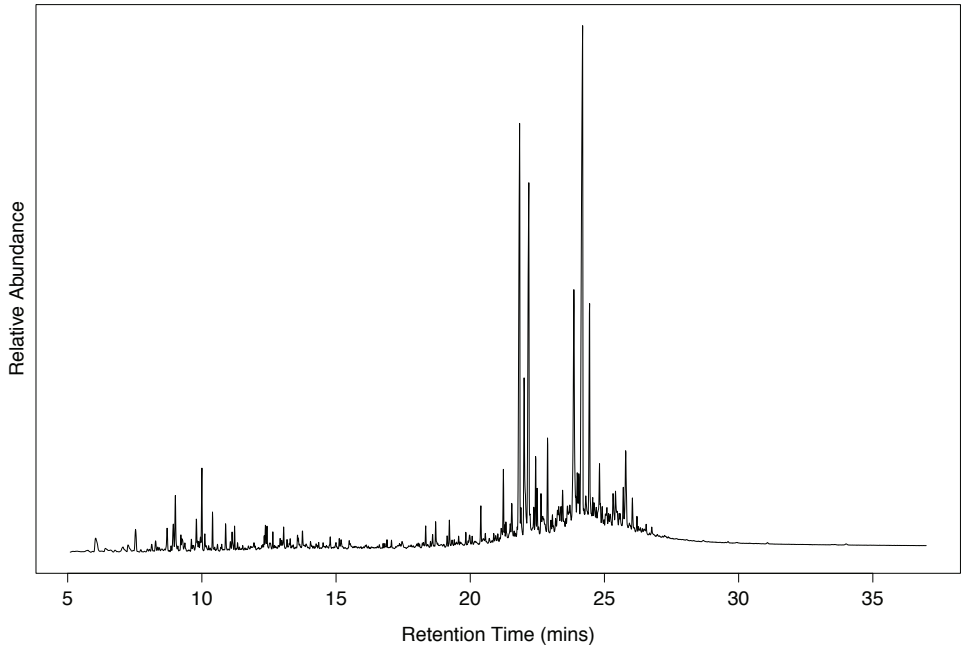
PRM12 | 1923.87.199



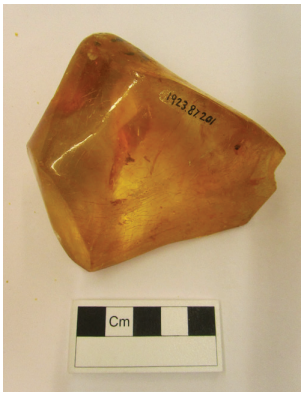


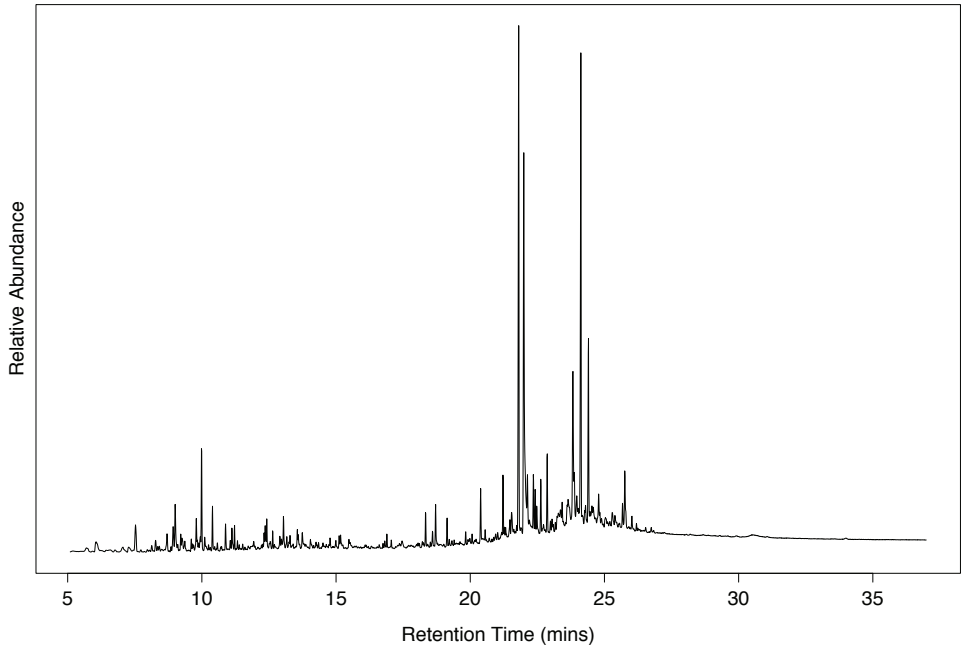
PRM13 | 1923.87.200





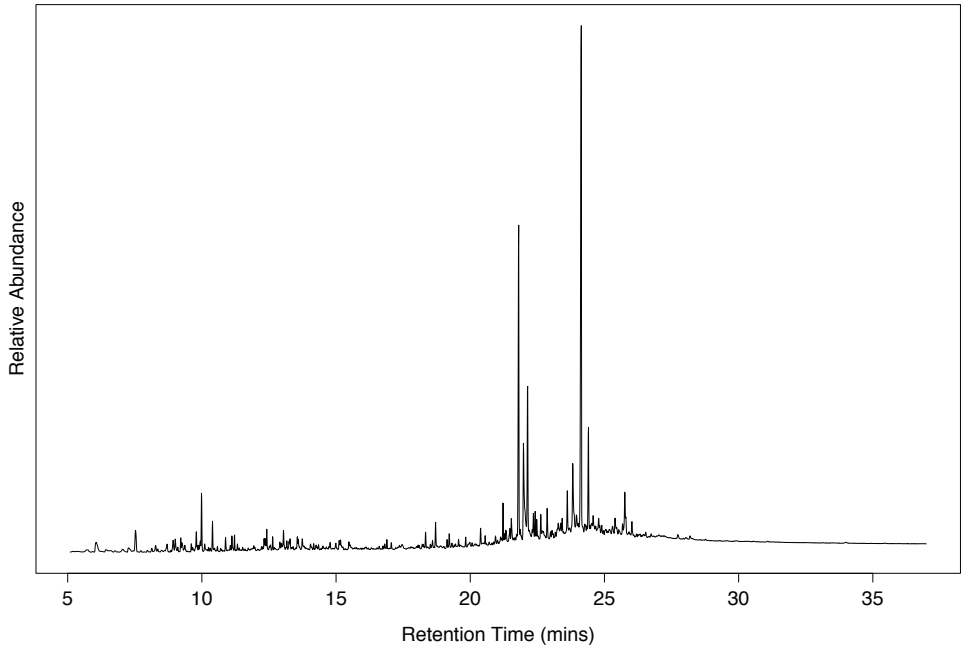
PRM14 | 1923.87.201



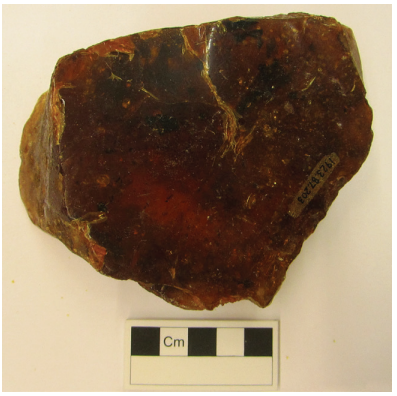


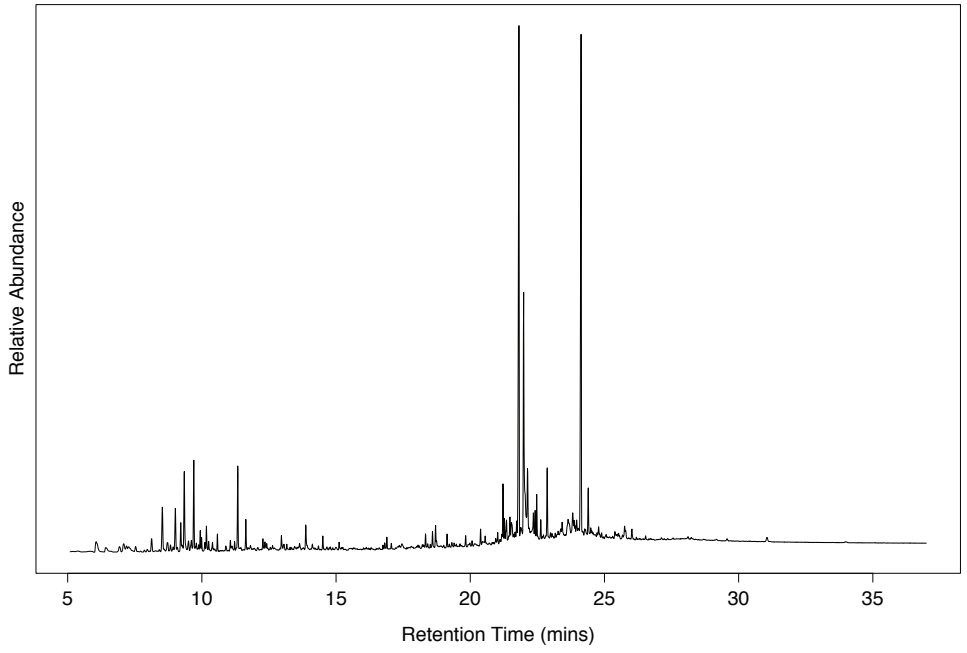
PRM15 | 1923.87.202



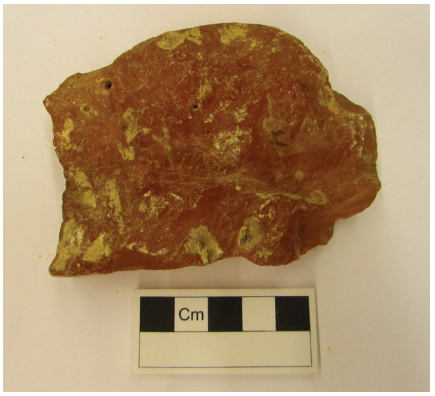


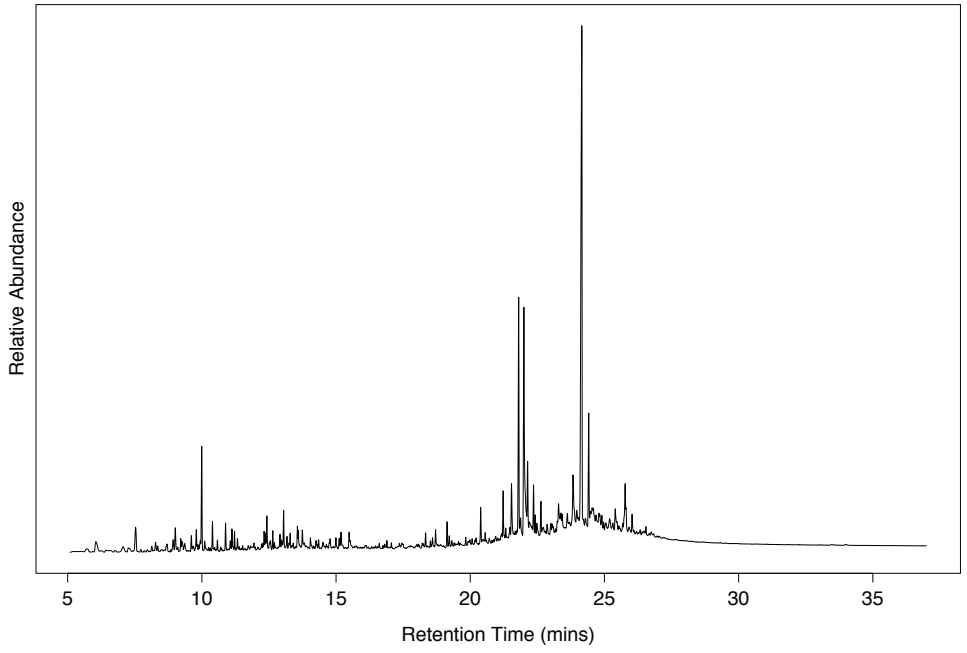
PRM16 | 1923.87.203





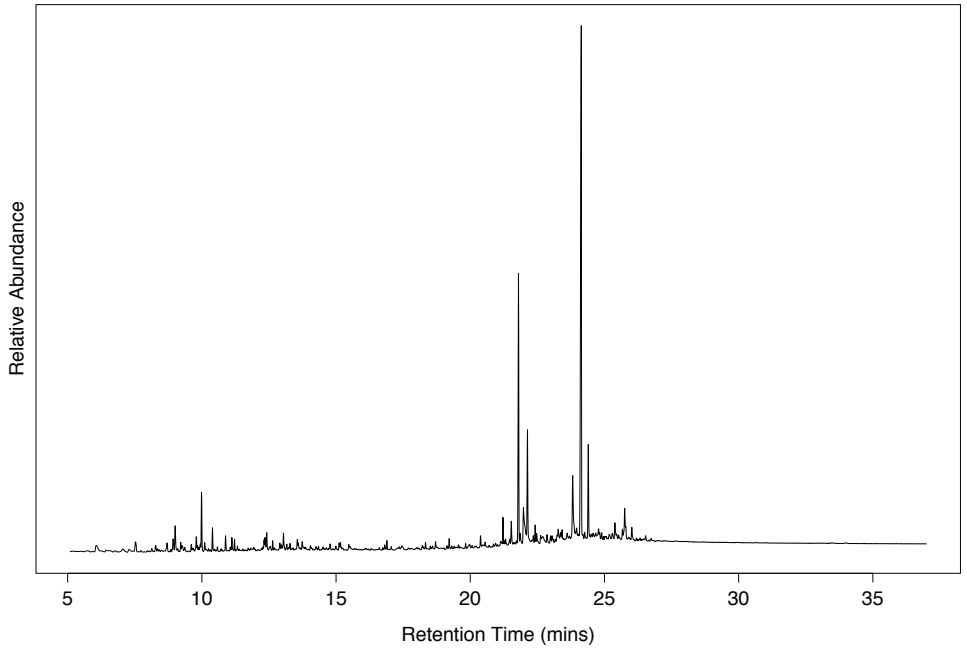
PRM17 | 1923.87.204





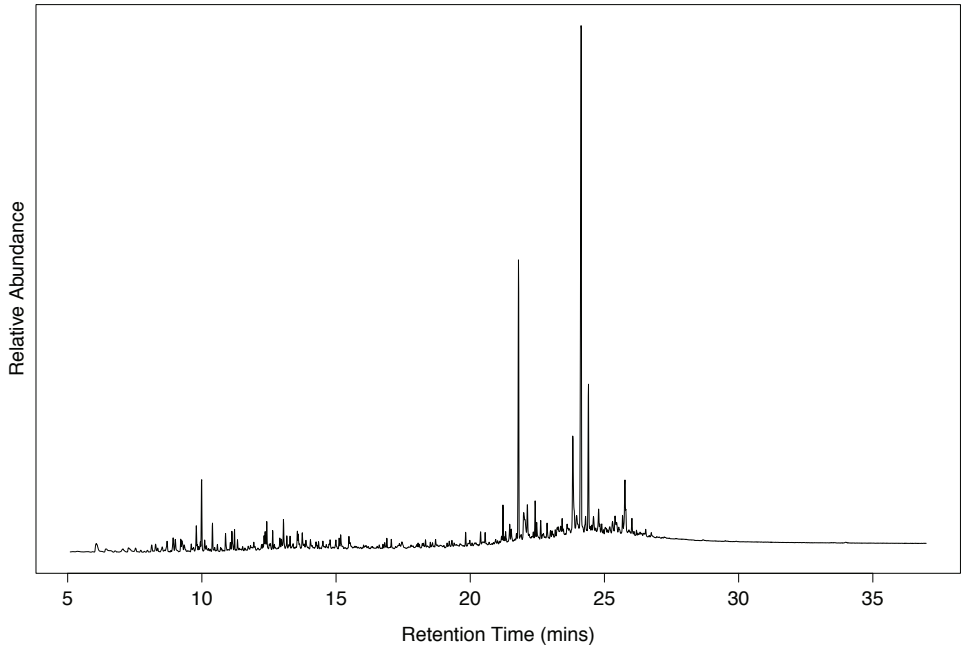
PRM18 | 1923.87.205



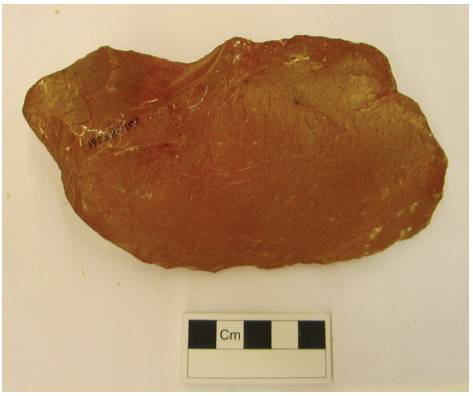


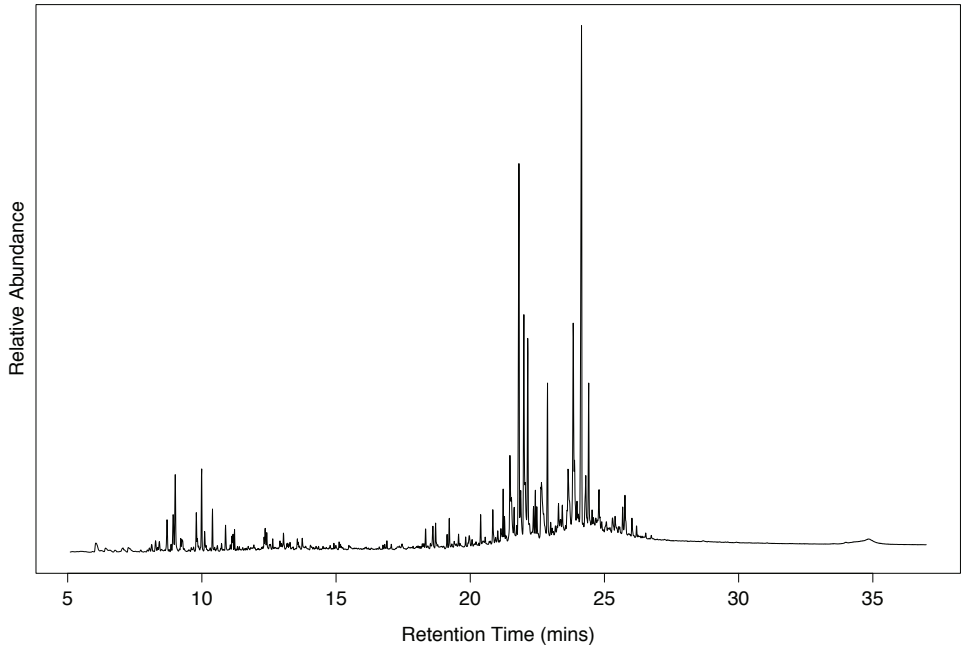
PRM19 | 1923.87.206





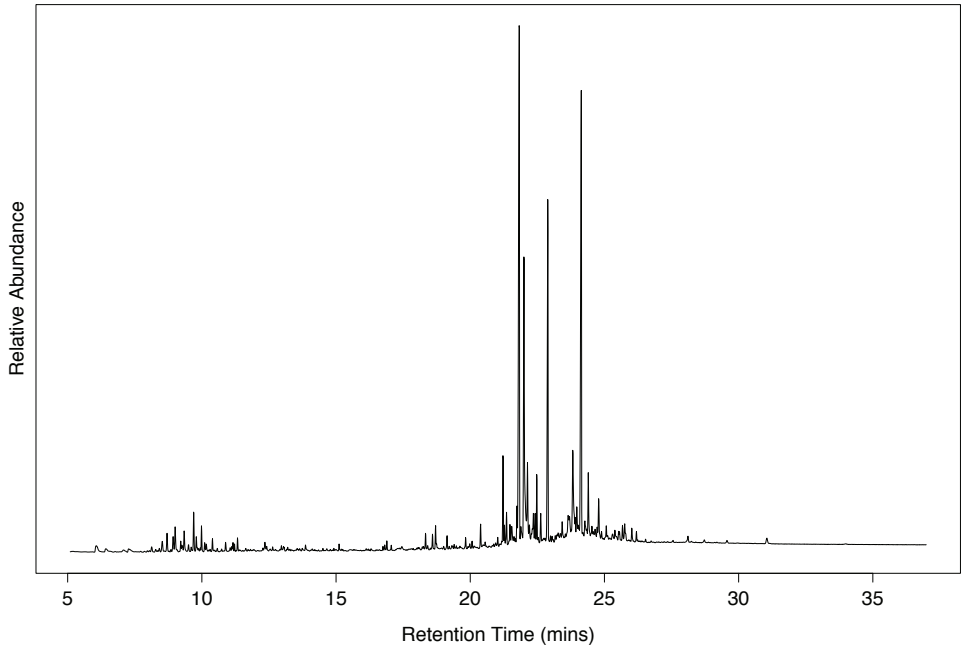
PRM20 | 1923.87.207





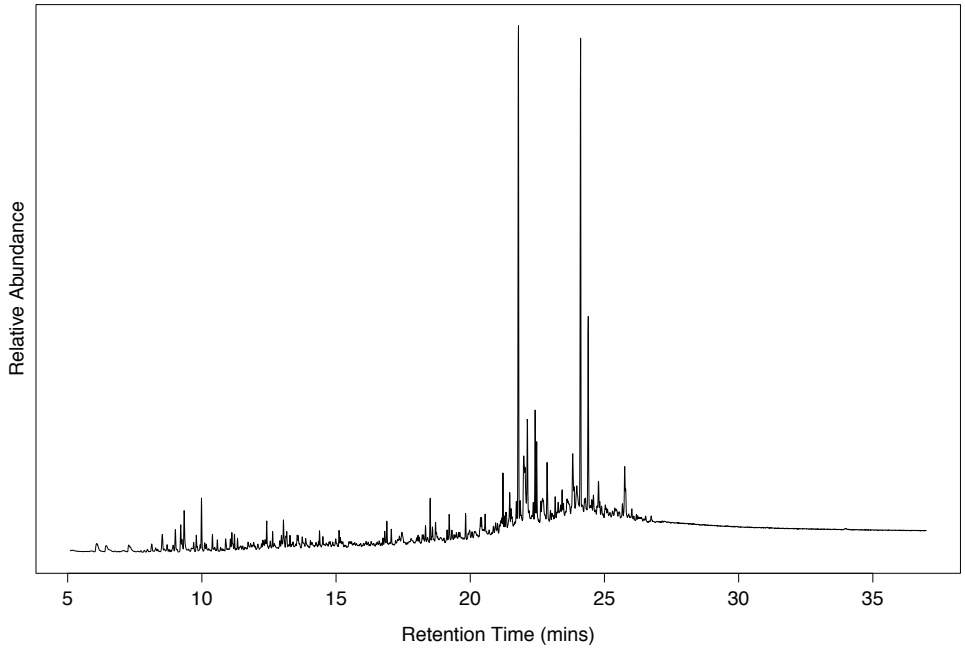
PRM21 | 1923.87.192.1





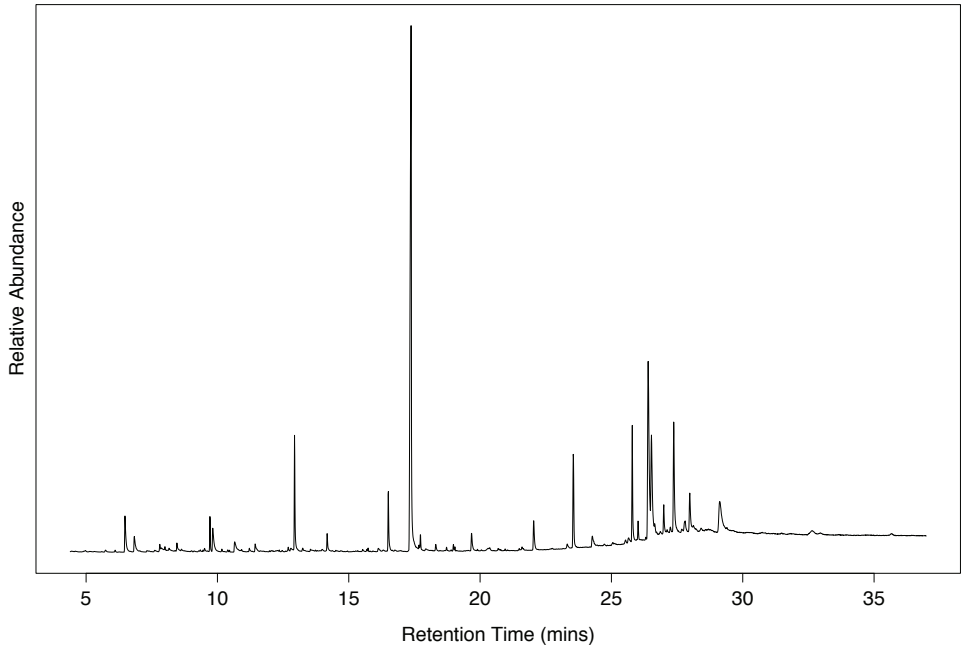
PRM22 | 1923.86.320





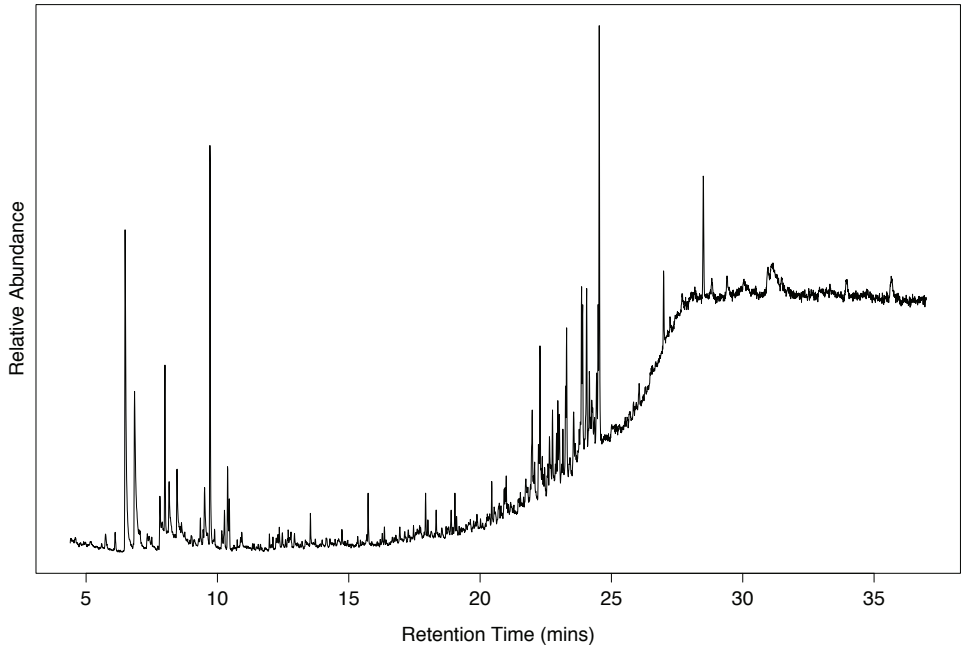
PRM23 | 1914.38.3





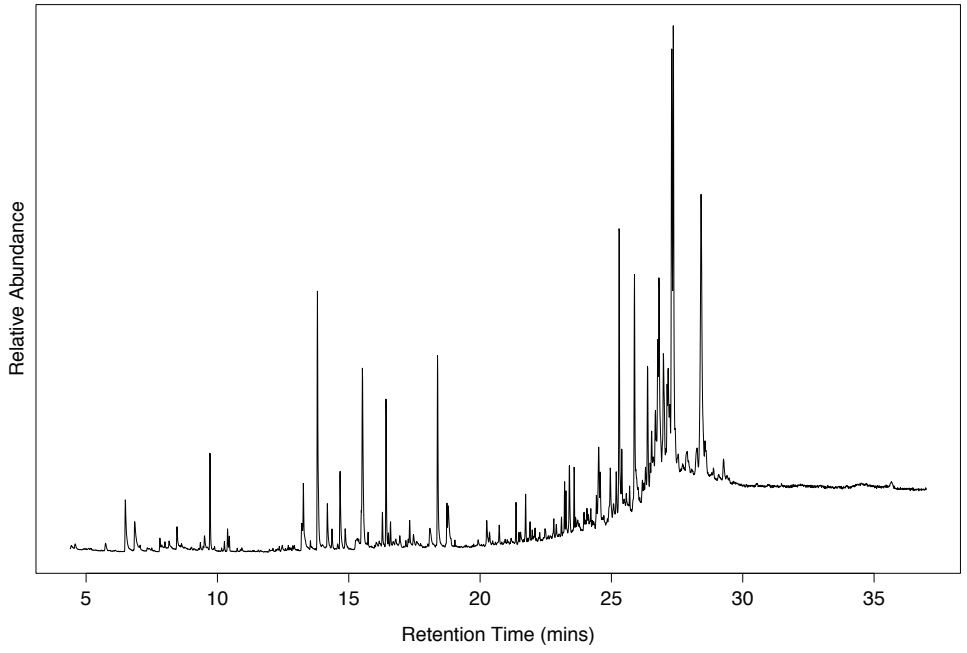
PRM24 | 1898.75.53





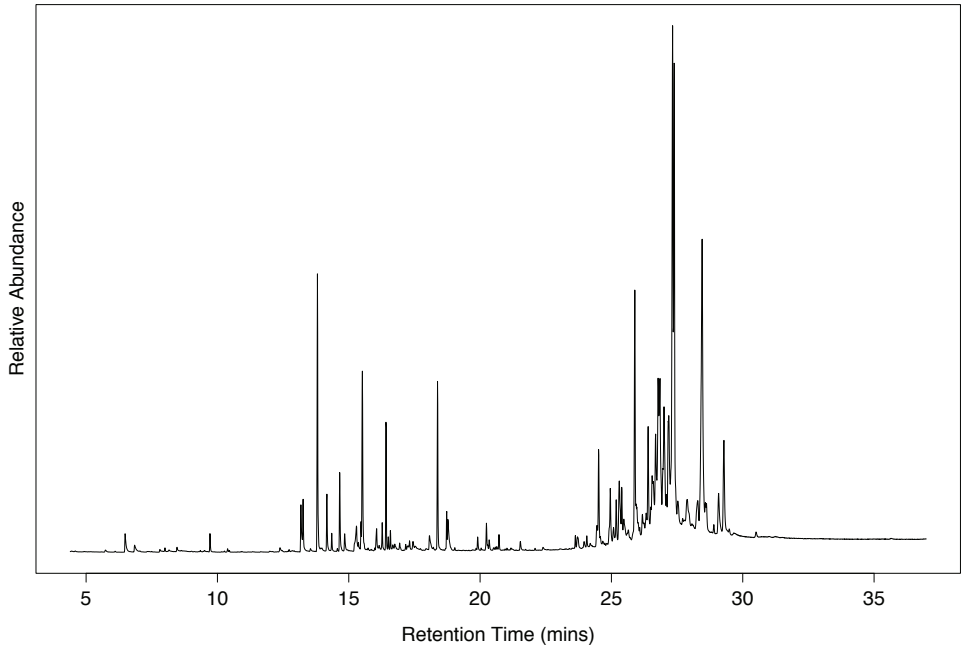
PRM25 | 1924.63.11





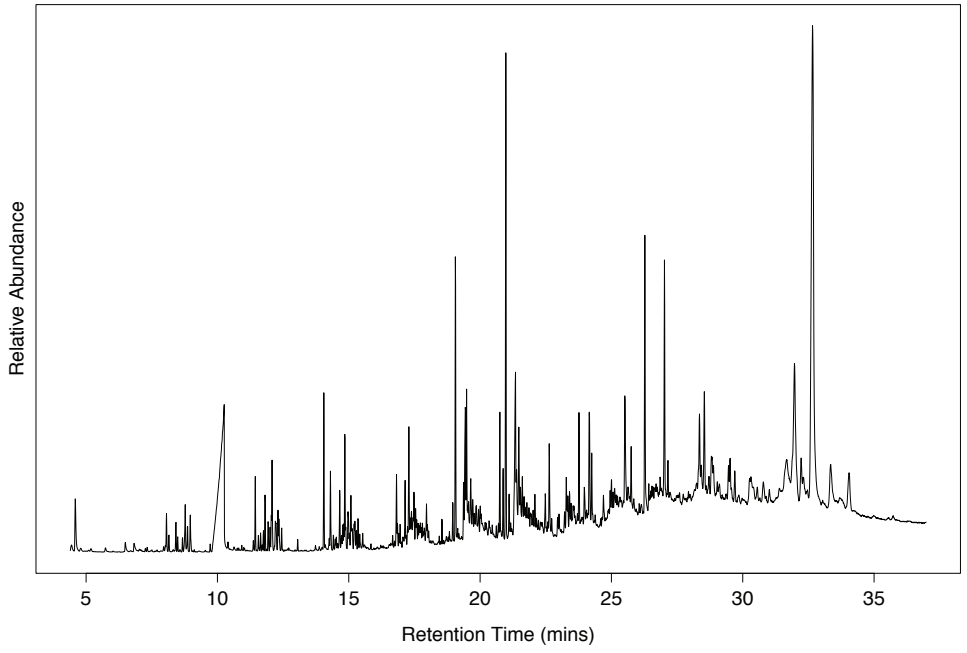
PRM26 | 1924.33.42(1924.63.12)





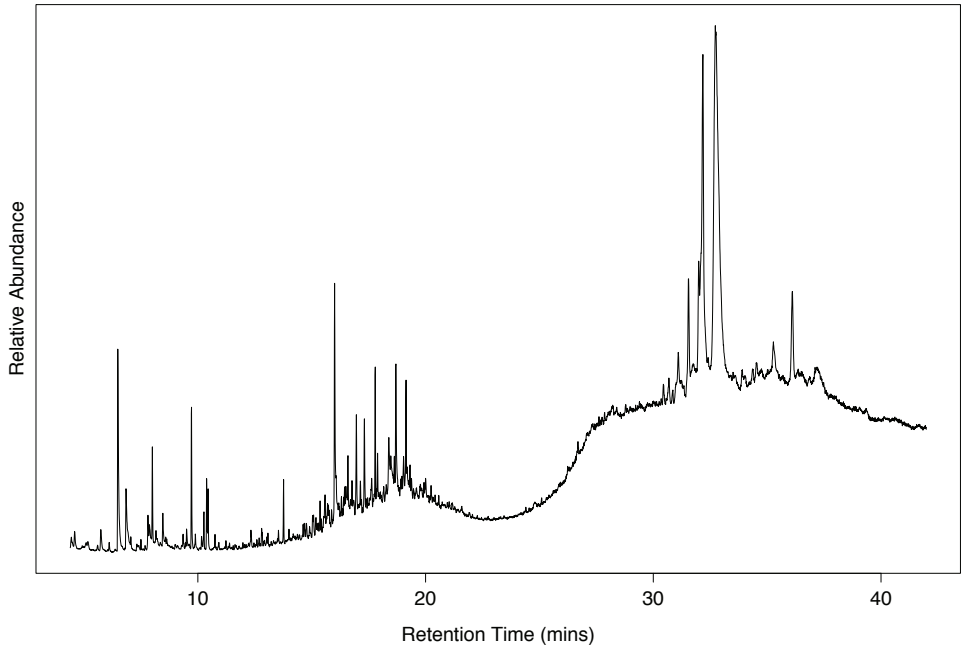
PRM27 | 1908.70.93 .1-4





PRM28 | 1908.70.94 .1-4





PRM29 | 1931.86.335



