

200007419

# Once, twice maybe, but not three times: Reheating *Xanthorrhoea australis* resin

Jeff Parr

Except as permitted under the Copyright Act 1968, copying this copyright material is prohibited without the permission of the copyright owner or its exclusive licensee or agent or by way of a licence from Copyright Agency Limited

Hafting is a process in which a handle is attached to a stone tool adding to its functionality and/or ease of use. This was normally achieved by using a resinous plant exudate as a fixative (Flood 1995:270) which was heated and then fashioned into place (Cribb and Cribb 1982:89). The resin may also have been reinforced with other materials such as grass, beeswax and fine sand (Cribb and Cribb 1982:89). A large range of stone tools have retained evidence of hafting in the form of resins long after separation or deterioration of handles due to taphonomic processes. These tools range in function from utilitarian and ceremonial uses to articles of trade. For example, backed blades, Bondi points, some eloueras, burrens and ground-edged axes were used to carry out a range of woodworking and food procurement tasks (McBryde 1975; McCarthy 1976; Kamminga 1977; Morwood and L'Oste Brown 1994; Flood 1995). Alternatively, leilira blades and Kimberley points often served important roles in ceremonial events and the latter is known as a significant item of trade (Tindale 1965; McCarthy 1976).

Latz (1995:66) has suggested that spinifex (*Triodia* spp.) resin is the strongest and most malleable of the cements obtained from plants within Australia. However this product was not available in all areas and, therefore, in some localities alternative plant exudates were used. For example, Ironwood (*Erythrophloeum chlorostachys* [Richardson 1988:58]), Sugarwood (*Myoporum platycarpum*), Cypress pine (*Callitrus collumellaris*), and Kurrajong (*Brachychiton populneus*) resins (Boot 1993:5) were used. Another such material, and the focus of this paper, is the resin from the Grass Tree *Xanthorrhoea* spp. (Maiden 1975:231). *Xanthorrhoea* which occurs throughout temperate zones of Australia (Holliday 1989) was a particularly important choice for this study due to its use as a control during previous attempts to accurately identify archaeological resin using Gas, Thin Layer and Ascending Paper Chromatography techniques (Bowden and Reynolds 1982; Boot 1993). In addition, *Xanthorrhoea* resin is also documented as an important item of trade (Cribb and Cribb 1982).

Identifying a resin's species of origin has been a recurring problem in Australian archaeology and the subject of limited but ongoing research. It has been suggested that resins can be distinguished from other residue types by their glassy appearance, physical attributes (Boot 1993: 4-5) and their solubility in some organic solvents (Bootle 1985:10). Nevertheless, identifying which genus or species of plant the resin came from is problematic. While previous studies have found that the identification of fresh and/or unused resin (in particular resin of *Xanthorrhoea*) was possible using Gas Chromatography (GC) (Reynolds and Bowden 1980; Bowden

and Reynolds 1982), identifying the species of resins on stone tools which have been used for hafting (i.e. heat-treated) is difficult (Bowden in Rosenfeld et al. 1981:90; Boot 1993:12). Bowden (in Rosenfeld et al. 1981) has suggested that this is possibly due to the loss of volatile components used for identification of resins as a result of heating.

Identification of the species of bonding materials used for hafting has the potential to resolve a number of temporal and spatial issues such as:

1. the clarification of questions relating to trade, technology and selectivity, and
2. whether or not these practices were continued over prolonged periods of time or were instead temporally distinctive.

For example, stratified archaeological deposits containing stone tools bearing different and/or specific resin species could provide a history of resin use and tool manufacture over time. Additionally, the trading of items, including resins, within Australia is well-documented (Thompson 1949; Berndt 1951; Cribb and Cribb 1982; Stanner 1933). By identifying resin species, mapping their distribution and comparing this data to known exchange systems, important information on trade, prestige and function could be established.

Bowden has suggested that the small quantities or lack of volatile material in archaeological samples of resins has made it difficult to determine their species of origin using GC (cited in Rosenfeld et al. 1981:92). An important question follows: If volatiles are lost as a result of heating during the hafting process, does the resin remain viable for reuse? Detecting stability or changes in the physical attributes of *Xanthorrhoea* resin (e.g. brittleness as a consequence of heating and/or reheating) may assist in such enquiries. Reports on clumps of resin found in archaeological sites have been interpreted as both caches for later use (Rosenfeld et al. 1981) and alternatively as discard from artefact repair (Jones and Johnson 1985b). Some issues which would benefit from such an enquiry include: Were clumps of resin carried about and heated time and time again or was a new piece required each time? How does this relate to the prestige of resin both within the immediate environment and externally as an item of trade?

The aims of this study are firstly to determine if the heating of *Xanthorrhoea australis* resin, to simulate the process of hafting, causes chemical changes through the loss of volatiles making species identification of archaeological samples by GC difficult. Secondly, to make visual observations detecting any alteration in the form of brittleness which could render the resin ineffective as a hafting cement after reheating.

## Material and methods

A GC unit was used to detect any loss of volatiles from the *Xanthorrhoea australis* resin samples after they had been reheated to a range of different temperatures. A dissecting

School of Resource Science and Management, Southern Cross University, PO Box 571, Lismore, NSW 2470, Australia.

Sample	No.	Weight (g)	2 <sup>nd</sup> HT. (sec)	3 <sup>rd</sup> HT. (sec)	Total
GC97A616	1	0.0097	0	0	0
GC97A617	2	0.0094	22.87	0	28.87
GC97A618	3	0.0097	45.42	0	45.42
GC97A619	4	0.0094	22.87	22.82	68.36

**Table 1** The GC process number, sample number with corresponding weights in grams, and duration of time in seconds that samples were exposed to heat (HT).

probe was used to apply pressure to each sample upon cooling. The resins from *Xanthorrhoea* spp. are relatively hard to break, therefore brittleness was measured by the ease with which the heated resin samples chipped or crumbled under pressure.

The sample of freshly extruded *Xanthorrhoea australis* resin came from near the Warby Ranges State Park, in Victoria. The collection was made in late summer-autumn of 1997, with the resin naturally extruding about 30 cm above the base of the trunk. The area had been fire free for approximately four years. This was an important factor in the use of this particular resin sample. For example, to accurately measure a gain or loss in any property it is usually the practice that the base reading from the control sample is as pristine as possible. If the sample had been exposed to flame prior to collection, some volatiles may have already been depleted, thus corrupting the results.

The resin was first crushed using a mortar and pestle. One piece of resin about the size of a match head, but significantly larger than the microscopic amounts required for GC (Bowden in Rosenfeld et al. 1981), was weighed (Table 1). This piece was diluted in 10 ml of absolute alcohol (ethanol) within a 10 ml glass flask and put aside to later represent sample 1 (a control for the experiment). Absolute alcohol was chosen because of its ability as an organic solvent to dissolve the hard *Xanthorrhoea* resin samples (Bootle 1985; Boot 1993).

Pieces of resin from which samples 2 and 3 were extracted were placed in a metal spatulate and heated over the flame of a Bunsen burner for different periods of time (Table 1). Sample 4 was exposed to heat for the same period of time as sample 2. In addition, this process was repeated on sample 4 one hour later and again approximately 48 hours later, allowing the sample to reset between heating. The extra heating was carried out to simulate the type of treatment the resin would receive if it were being transported from place to place or being cached for later reuse.

A portion from each heated sample was weighed on a top-loading balance to achieve uniformity with sample 1 (Table 1). Each sample was then diluted in 10 ml of ethanol in 25 ml glass flasks. The flasks were then left undisturbed to allow any undiluted particles to settle. Following this, 1.5 ml was extracted from just below the meniscus area of the solution and placed into pre-labelled rubber-stopped vials prior to GC analysis (Table 1). All observations (e.g. physical changes and odours) were recorded in a laboratory note-book as they occurred. Samples 1 to 4 were then placed in a GC unit (Varian Starr 3400) and a test sequence was run by Dan Alter, the senior professional officer, Department of Agronomy and Soil Science, University of New England Armidale (see Appendix for elution rates). The rates were then adjusted to achieve best results and a final sequence was run (see Figs 1, 2, 3 and 4 and Appendix for rates).

## Results

The resin was initially hard to break-up. The outside edges of the fractured resin were observed to be orange in colour and the inner parts dark red. Those samples which had been heated (i.e. 2, 3 and 4) released odours, each of which had some individuality. Heating duration and

sample weights are shown in Table 1.

### Sample 1

The control had some particles present that did not dissolve. A small amount of dark brown to black fine granular sediment was observed in the base of the flask. This solution of resin and ethanol became a light amber colour.

### Sample 2

When heated, this sample released an odour similar to a pleasant patchouli plant-type scent. The heating duration is recorded in Table 1. After resetting, the resin was about as hard as it had been before heating and broke into large pieces. The solution was a pink colour when the resin and ethanol were first mixed. However, after standing, the solution changed colour to a dark amber.

### Sample 3

This sample released a stronger aroma than sample 2. Although similar in odour, sample 3 had a dry or clogging effect on the nostrils if experienced too closely. At one stage of heating the flame came too close to the resin itself and ignition occurred. Unlike sample 2, sample 3 became brittle after resetting and broke into small pieces. The solution of resin and ethanol was recorded as a light red wine colour.

### Sample 4

This sample displayed the same characteristics as samples 2 and 3 as it went through the first two stages of the heating process. The third exposure to heat resulted in no detectable differences in odour. However the sample became very brittle on setting and broke into a more powder-like state. The solution of resin and ethanol became a dark red wine colour.

## Chromatograph results for

### Samples 1, 2, 3 and 4

A chromatograph shows the time individual constituents take to move through a column – this is called the elution rate. At the base of the chromatograph is a series of one minute graduations which are used to measure the elution rate. Each constituent of the dissolved resin is represented by a peak. The intensity of the peak indicates the proportions of the constituent present and the corresponding graduation gives its elution time. Standardised reference lists of elution times and associated substances can then be scanned to determine what each peak represents. The chromatograph results of samples 1, 2, 3 and 4 are represented in Figures 1, 2, 3 and 4 respectively.

The peak in the 4.5 minute area on the far left of all the chromatographs represents the elution rate of ethanol (Figs 1, 2, 3 and 4). The successive peaks up to about the 45 minute area represent the volatile component which is used in this and previous studies as a signature for the identification of

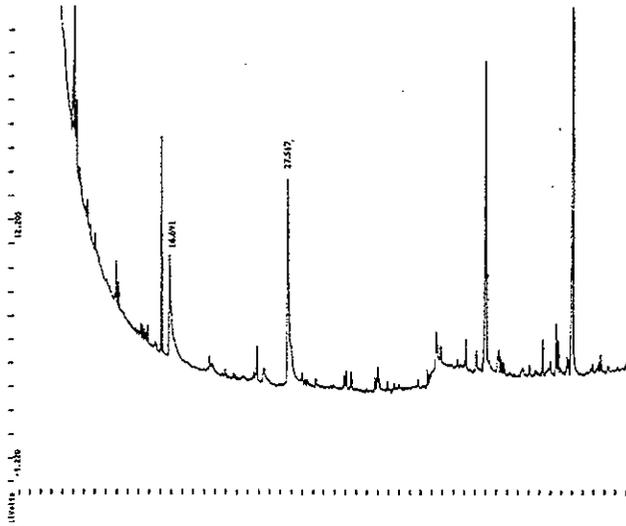


Figure 1 Gas Chromatography sequence readout for Sample 1.

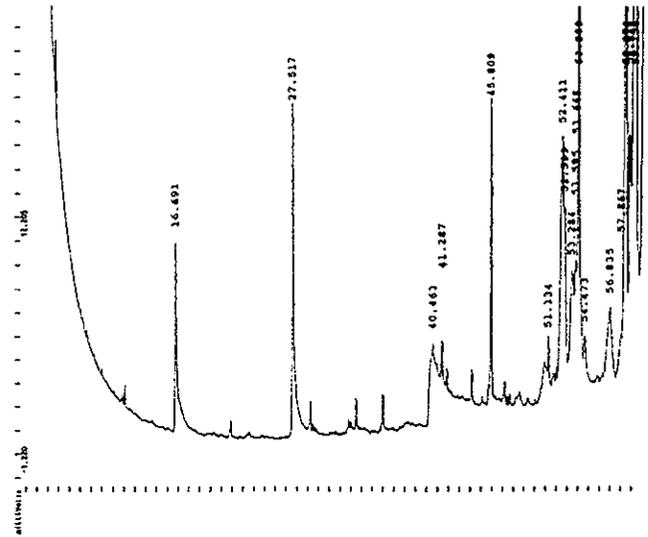


Figure 2 Gas Chromatography sequence readout for Sample 2.

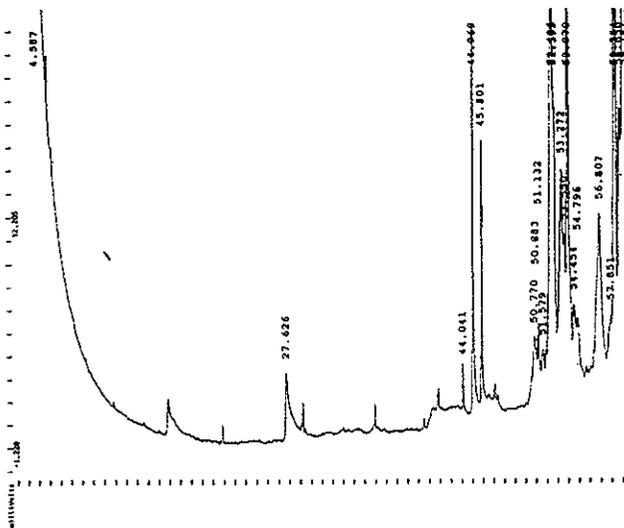


Figure 3 Gas Chromatography sequence readout for Sample 3.

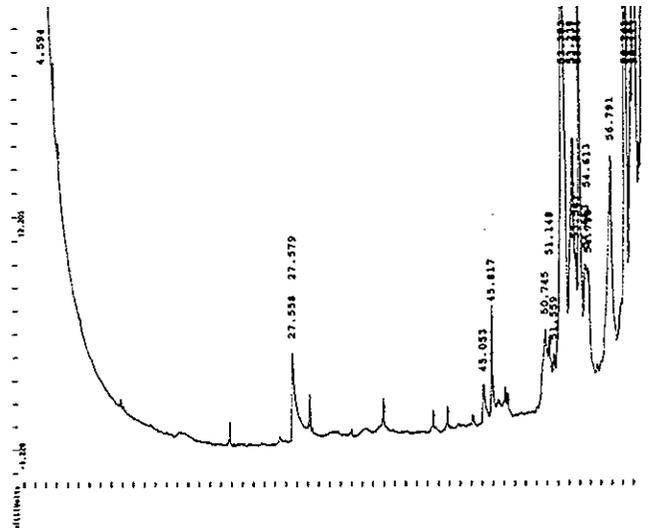


Figure 4 Gas Chromatography sequence readout for Sample 4.

resin (Figs 1, 2, 3 and 4). Therefore the detection of peak loss in this area is of greatest interest. Subsequent peaks represent waxes and possibly oxidation occurring, particularly in the heavy concentration of peaks towards the end of the chromatographs (Dan Alter pers. comm. 1997).

The control (sample 1), when put through a GC sequence demonstrated what an unheated sample of *Xanthorrhoea australis* resin looked like. That is, it provided a signature of the compounds present in the resin's natural state (Fig. 1). Subsequent alterations to these signatures shown in Figures 2, 3 and 4 are distinguished by the loss or reduction in peak size between the 15 minute and 45 minute zones. This is consistent with the loss of volatiles in relation to the application of heat during the experiment (Alter pers. comm. 1997). Later changes in peaks after the 45 minute area indicate that some form of chemical reaction was taking place such as oxidation (Alter pers. comm. 1997).

#### Physical Attributes of Samples 1, 2, 3 and 4

There was no apparent evidence of weakness in sample 2, however there was definite confirmation of physical

alteration in the form of brittleness in samples 3 and 4 as a result of exposure to heat. It was observed that, in these samples, the longer the resin was exposed to heat the more brittle it became (Table 1). Likewise, the advent of brittleness corresponds with the loss of volatiles and the increase in oxidation (Figs 2, 3 and 4).

#### Discussion

It is of interest that one-time Surgeon-General, John White, noted the pleasant odour and therapeutic properties of *Xanthorrhoea* spp. for chest congestion (Davis 1973:P-35) when the resin is burnt (Cribb and Cribb 1988:88). The odours released during the heating process were probably related to the loss of volatiles as verified by the changes in elution time peaks during the GC sequences.

As suggested in the results there is a definitive association between volatile loss, oxidation processes and the increased brittleness of *Xanthorrhoea* resin. During the probe test used to assess the brittleness of resin, sample 2 did not display any signs of weakening. Alternatively, samples 3 and 4 showed considerable evidence of deterioration. This is important

because it indicates that *Xanthorrhoea australis* resin would not be vigorous enough to withstand the pressures applied during tool use after it had been reheated.

Although the resin discussed is from a *Triodia* species, Tindale (1965) describes how Walpiri elders at Yuendumu removed and reset an adze flake in resin. It is reasonable to infer that many hafted artefacts would need repair work as a result of loosening, wear and breakage. This view is further supported by Jones and Johnson's (1985b) reports of resin discard from artefact repair. The fact that *Xanthorrhoea* resin was an important item of trade (Cribb and Cribb 1982) indicates that it must have been desirable and effective as a hafting cement. With this in mind, the inability of *Xanthorrhoea* resin to maintain its viability after reheating perhaps reflects that the prestige of this item outweighed any inconvenience in its use.

The results support the suspicions of Bowden (in Rosenfeld et al. 1981) that volatiles may be lost as a result of the heating process during the manufacture of hafted tools. Therefore to be able to identify the species of origin for archaeological resin samples, it would be necessary to use a control sample which had been preheated. This is based on the proposition that heating might simulate the chromatographs of archaeological samples. The main obstacle with this approach is in determining the duration of heating and/or the temperatures to be used for control samples.

If, following the methods applied in this experiment as a guide, heating duration are best kept to around 28.87 seconds (Table 1). If taken beyond this point they should not exceed 45.42 seconds (Table 1). This is because at least two distinctive volatile peaks should be present to make even a tentative identification of resins possible.

The chromatographs show that the main volatile peaks which can be used for the identification of *Xanthorrhoea australis* resin occur at the 11, 15, 16 and 27 minute positions respectively (Figs 1 and 2). After the 28.87 second heating period these peaks begin to drop out (Figs 1, 2 and 3). If the heating duration is extended to 45.42 seconds, only the remnants of the 16 and 27 minute peaks remain. Beyond a 45.42 second heating duration the 27 minute peak is the last of the original volatile peaks from which *Xanthorrhoea australis* resin could have been satisfactorily identified. Natural volatile loss with an increase in the age of resins (Bowden in Rosenfeld et al. 1981:92), contamination from mixing mediums, the long term exposure to ultraviolet light and chemical reactions with sediments, are additional variables which need to be considered.

Chromatographic techniques have not yet been able to reliably isolate Australian archaeological samples to species level (Bowden and Reynolds 1982:43; Boot 1993). Furthermore, some of the resin species known to have been used as hafting cements have component signatures which do not differentiate them from other species, even in fresh samples (Bowden and Reynolds 1982). For example, all *Xanthorrhoea* species contain similar chemical properties (Maiden 1975:231) but vary to a degree in volatile signatures,

some of which are difficult to distinguish even from eucalypts (Bowden and Reynolds 1982).

## Conclusions

To better understand the use of hafting cements, a more comprehensive examination, including the testing of other species and arbitrary components, needs to be undertaken. A database of chromatographs consisting of fresh (heated and unheated) samples of all species known to be used for hafting would be of benefit to further research.

It would also be of great benefit to be able to identify the individual chemical components of resins. The possibility of isolating and identifying the chemical structure of resin constituents using a mass spectrometer has been discussed by Dan Alter and myself as a future research area. This may isolate individually distinctive chemical components which, together with chromatography techniques, might then lead to more comprehensive identification.

The effects of exposure to the environment also needs to be considered. For example does the soil pH or ultraviolet light affect the chemical signature of a resin? Finally, testing for changes that might occur as a result of the addition of other materials to the resin to assist bonding should also be carried out.

This study has established that the heating of *Xanthorrhoea australis* resin does initiate the loss of volatiles and subsequent changes in the chemical signature, making the positive identification of this species from archaeological samples difficult when using Gas and/or other Chromatography techniques. There was also evidence of the physical depletion of *Xanthorrhoea australis* resin when heated. It was found that, the longer samples were exposed to heat the more brittle they became. Only the sample with the shortest exposure to heat seemed to have retained its integrity. This would indicate that it is unlikely that the resin of *Xanthorrhoea australis* could be reheated and still maintain its viability as a hafting cement. It is likely that because of their related properties much of the data accrued in this experiment is applicable to a range of different plant resins. Ultimately, although their methodologies are different in application, all chromatography techniques have similar principles. Therefore the results of this study should be pertinent to all forms of this type of analysis.

## Acknowledgements

I wish to thank Professor Prakash, Department of Botany University of New England for providing the funding for the chromatography. Matthew Gray kindly surrendered his laboratory space, his time and advice. I would also like to thank Dan Alter for his valuable advice and the processing of GC samples; Pat Watters for access to hafted artefacts at the UNE Museum; Mike Morwood who arranged access to the museum and gave a presentation on hafted artefacts; Wendy Beck for direction on literature searches and comments on an early draft of this paper; and Rowan Webb for advice on procedure. Many thanks to those who made encouraging

comments about presenting the results, particularly Terry Kelly for donating the resin sample and Loraine Watson for her invaluable assistance.

## References

- Berndt, R.M. 1951 Ceremonial exchange in western Arnhem Land. *Southwestern Journal of Anthropology* 7.
- Boot, P.G. 1993 Analysis of resins and other plant residues on stone artefacts from Graman, New South Wales. In B.L. Fankhauser and J.R. Bird (eds) *Archaeometry: Current Australian Research*, pp.3-12. Canberra: Prehistory Publications, RSPAS, ANU. *Occasional Papers in Prehistory*, No.22.
- Bootle, K.R. 1985 *Wood in Australia, Types, Properties and Uses*. Sydney: McGraw-Hill Book Company.
- Bowden, B.F. and Reynolds, B. 1982 The chromatographic analysis of ethnographic resins. *Australian Institute of Aboriginal Studies Newsletter* 17:41-2.
- Cribb, A.B. and Cribb, J.W. 1982 *Useful Wild Plants in Australia*. Sydney: Fontana Books.
- Cribb, A.B. and Cribb, J.W. 1988 *Wild Medicine in Australia*. Melbourne: Collins Publishers.
- Davis, F.A. 1973 *Taber's Cyclopedic Medical Dictionary*. Philadelphia: F.A. Davis Co.
- Flood, J. 1995 *Archaeology of the Dreamtime: The story of prehistoric Australia and its people*. Sydney: Angus and Robertson.
- Holliday, I. 1989 *A Field Guide to Australian Trees*. Sydney: Lansdowne Publishing Pty. Ltd.
- Jones, R. and Johnson, I. 1985b Rockshelter excavations, Nourlangie and Mt Brockman Massifs. In R. Jones (ed.) *Archaeological Research in Kakadu National Park*, pp.39-76. Canberra: Australian National Parks and Wildlife Service, Special Publication 13.
- Kamminga, J. 1982 *Over the Edge. Functional Analysis of Australian Stone Tools*. St Lucia: Anthropology Museum, University of Queensland. *Occasional Papers in Anthropology* 12.
- Latz, P.K. 1995 *Bushfires and Bushtucker: Aboriginal plant use in Central Australia*. Alice Springs: IAD Press.
- Maiden, J.H. 1975 [1889] *The Useful Native Plants of Australia*. Melbourne: Compendium Pty Ltd.
- McBryde, I. 1975 *Aboriginal Prehistory in New England*. Sydney: Sydney University Press.
- McCarthy, F.D. 1976 *Australian Aboriginal Stone Implements*. Sydney: Australian Museum Trust.
- Morwood, M.J. and L'Oste-Brown, S. 1994 Chronological change in stone artefact technology. In M.J. Morwood and D. Hobbs (eds) *Quinkan Prehistory*, pp.161-77. Brisbane: Anthropology Museum, University of Queensland. *Tempus* Vol. 3.
- Reynolds, B. and Bowden, B.F. 1980 The chromatographic analysis of gums and waxes used in Aboriginal artefacts. *COMA Bulletin* 23-7.
- Richardson, N. 1988 Selected filmography on Aboriginal woodworking. In J. Kamminga (ed.) *Wood Artefacts: A checklist of plant species utilised by Australian Aborigines*. *Australian Aboriginal Studies* 2:26-59.
- Rosenfeld, A., Horton, D. and Winter, J. 1981 *Early Man in North Queensland*. Canberra: Prehistory Publications, RSPAS, ANU. *Terra Australis* 6.
- Stanner, W.E.H. 1933 Ceremonial economics of the Mulluk Mulluk and Madngella tribes of the Daly River, North Australia. *Oceania* 4, nos 2 and 4.
- Thompson, D.F. 1949 *Economic Structure and the Ceremonial Exchange Cycle in Arnhem Land*. Melbourne: Macmillan.
- Tindale, N.B. 1965 Stone implement making among the Nakako, Ngadadjara and Pitjandjara of the Western Desert. *Records of the South Australian Museum* X:131-164.

## Appendix 1

### Test Sequence

:Method File	ALKN9X15.
Operator	:Dan Alter
Workstation	:MS-DOS 5
Software	:Star Chromatography Version 4
Instrument	:Varian Star #1
Column Specifications	:30m, 0.32mm, 57. polar, 25µ coating Econocap AT54 (Alltech).
Channel	:A=FID-A 10 Volt
Detector Type	:ADCB (10 Volts)
Bus Address	:16
Sample Rate	:10.00 Hz
Run Time	:60.002 min
Injection temperature	:280°C
Column temperature	:180°C to 275°C. 10°C per minute
Flow rate	:3.5ml per minute

### Run Sequence

:Method File	IONMASS.
Operator	:Dan Alter
Workstation	:MS-DOS 5
Software	:Star Chromatography Version 4
Instrument	:Varian Star #1
Column Specifications	:30m, 0.32mm, 57. polar, 25µ coating Econocap AT54 (Alltech).
Channel	:A=FID-A 10 Volt
Detector Type	:ADCB (10 Volts)
Bus Address	:16
Sample Rate	:10.00 Hz
Run Time	:60.002 min
Injection temperature	:220°C
Column Specifications	:30m, 0.32mm, 57. polar, 25µ coating Econocap AT54 (Alltech).
Column temperature	:60°C to 240°C. 3°C per minute
Flow rate	:1 ml per minute at 60°C