# 6. Analysis of modern oils and experimental perfumes

The comparison of archaeological residues with modern materials is essential to interpreting the results of lipid residue analysis carried out on archaeological ceramics (e.g. Evershed *et al*., 1997a; Evershed *et al*., 1999; Mottram *et al*., 1999; Peters *et al*., 2005, 322-352; Pollard *et al*., 2007, 148). During this study two areas of analysis of modern materials were used to further characterise ancient residues.

The first area of experimentation was the analysis of modern oils and beeswax by GC-C-IRMS with the aim of providing a small database against which to compare archaeological residues containing fat or oil. The second line of enquiry was designed to investigate the potential for detecting ancient perfumed oils in the archaeological record.

## 6.1 GC-C-IRMS analysis of modern oils and waxes

### *6.1.i Modern oils*

Compound specific stable isotope analysis has been used since the mid 1980s to identify the source materials of archaeological fats using the stable isotopic signatures of fatty acids (Hastorf & DeNiro, 1985; Evershed *et al*., 1994; Evershed *et al*., 1997a; Evershed *et al*., 1997b; Dudd & Evershed 1998; Evershed, 1998; Evershed *et al*., 1999; Evershed *et al*., 2001; Copley *et al*., 2003; Craig *et al*., 2004; Copley *et al*., 2005a; Copley *et al*., 2005b; Copley *et al*., 2005c; Craig *et al*., 2007; Spangenberg *et al*., 2006). However, although

this analysis allows the identification of animal adipose fats and fish oils from different species and can distinguish between adipose fats and dairy fats, distinguishing plant oils from animal fats and fish oils has not been widely investigated.

Both documentary and archaeological evidence show that the transport and storage of plant oils was widespread in the eastern Mediterranean during the LBA (Knapp, 1991; Shelmerdine, 1985; Haldane, 1993; Negbi & Negbi, 1993; Cline, 1994; Serpico & White, 2000b; Hadjisavvas, 2003; Palmer, 2003; South & Steel, 2007). However oil residues remaining in ceramic vessels are usually degraded and appear to have the same molecular composition as other fats. Without exceptional preservation, or the recovery of specific biomarkers for specific plant oils, such as ricinoleic acid from castor oil (Mills & White, 1999, 33; Gunstone, 2004, 3), or the presence of plant sterols such as β-sitosterol (Gunstone, 2004, 23-32) it is impossible to identify residues as plant oils.

GC-C-IRMS of modern oils has become a routine procedure for confirming the purity of olive oil (Spangenberg *et al*., 1998; Woodbury *et al*., 1998a; Woodbury *et al*., 1998b). In modern olive oil, as in most plant oils, $C_{18:1}$ is very abundant while $C_{18:0}$ is often present in very low abundances (Gunstone, 2004, table 1.1, 4). However in archaeological material $C_{18:1}$ is usually depleted and may be missing completely. This is a problem when trying to compare the $\delta^{13}C$ values for individual fatty acids in archaeological residues with those in modern oils.

Some $C_{18:0}$ is usually present in fresh plant oils bound into triacylglycerols and is released by saponification. The question then arises as to whether this $C_{18:0}$ could be used in GC-C-IRMS analysis to provide a modern analogue for the $C_{18:0}$ present in archaeological oils. In other words, can the $\delta^{13}C$ values of $C_{18:0}$ released from triacylglycerols in modern oils by saponification be legitimately compared with $C_{18:0}$ present in archaeological material. There are several points at which isotopic effects may occur in the formation of triacylglycerols in modern oils and in the preparation of the oils for analysis. Similarly any archaeological oil samples will have been altered chemically over time. The question which must be considered is whether these 'life histories' can be considered equivalent in terms of isotopic effects and the resultant isotopic fractionation.

Firstly, studies of plant physiology indicate that $C_{18:0}$, whether free fatty acid or bound in acylglycerols, is all manufactured by the same biosynthetic pathway. Synthesis is usually *de novo* from acetyl-coenzyme A (acetyl-CoA) and involves the action of acetyl-CoA carboxylase and fatty acid synthetase (Hitchcock & Nichols, 1971, 124-128; Harwood, 1998; Knutson & Knauf, 1998). Incorporation of all fatty acids, including $C_{18:0}$, into acylglycerols is achieved by the action of fatty acid transferases via the Kennedy pathway (Hitchcock & Nichols, 1971, 178-179; Harwood, 1998; Knutson & Knauf, 1998; Stobart *et al*., 1998). These processes are the same for all plants; the different isotope effects observed in the tissues of $C_3$, $C_4$ and CAM plants occurs at an earlier stage during photosynthesis (O'Leary, 1981; Hoefs, 1997, 41-42 ; Lajtha & Michener,

1994, 1-4; Fry, 2006, 62-66; Pollard *et al*., 2007, 172), and not during the formation of fatty acids or acylglycerols.

Both archaeological and modern oils will have been formed by these processes. There is no reason to believe that plants produced oils of significantly different molecular composition during the LBA, certainly not outside the natural variation due to normal changes in growing conditions. Therefore the proportion of free $C_{18:0}$ in the original material and the proportion of $C_{18:0}$ bound into acylglycerols will have been similar in both the modern oils and the archaeological oils when fresh. So the isotopic signature of both modern and fresh ancient oils would be similar allowing for the differences in pre- and post-industrial atmospheric carbon.

This leaves the question of possible isotope effects introduced during degradation processes for the archaeological samples and during sample preparation of modern oils. Isotope effects occur in kinetic reactions or when a closed system reaches dynamic equilibrium and isotopic exchange reactions are involved (Hoefs, 1997, 5). Kinetic isotope effects only occur when a process is incomplete and unidirectional (*eg.* evaporation, dissociation, diffusion and many biological processes) (Hoefs, 1997, 10). During sample preparation in the laboratory saponification is carried out in such a way that all acylglycerols are hydrolysed. This is a reaction taken to completion in a closed system and no fractionation should result in this case. One study which compared modern oils with archaeological fats (Spangenberg *et al*., 2006) used saponification for the preparation of the modern oils. These modern oils were not analysed

specially for comparison with archaeological samples but had been analysed in a study which looked at the authentication of oils using stable isotope analysis (Spangenberg & Ogrinc, 2001). The implications of the preparation methods were not discussed in either study.

The fractionation of archaeological fats arising from degradation processes taking place in the burial environment is poorly researched but is generally considered to be negligible on the basis of the one published study (Evershed *et al*., 1999; Evershed *et al*., 2002). This is a problem common to all stable isotope analysis of archaeological fats and the generally accepted approach is to assume that no fractionation occurs as the result of burial or sample preparation (*eg*. Hastorf & DeNiro, 1985; Evershed *et al*., 1994; Evershed *et al*., 1997b; Dudd & Evershed 1998; Evershed *et al*., 2001; Copley *et al*., 2003; Craig *et al*., 2004; Copley *et al*., 2005a; Copley *et al*., 2005b; Copley *et al*., 2005c; Craig *et al*., 2007; Spangenberg *et al*., 2006). On this basis, the comparison of $\delta^{13}C$ values for fatty acids in saponified modern oils and archaeological fats should be a valid exercise.

All the modern samples in this study were corrected for the industrial burning of fossil fuels by +1.6‰ to allow a comparison with archaeological fats (Friedli *et al*., 1986; Heaton, 1999; Spangenberg *et al*., 2006). Similarly data from the literature on animal fats had also been corrected, most using a correction of +1.2‰ according to the source papers (Evershed *et al*., 1997; Dudd *et al*., 1999; Evershed *et al*., 2001), while the fish oils were corrected by an unknown amount (Craig *et al*., 2007). Although different corrections had been made, the

measurements of these values were made at different times separated by least 10 years during which time the $^{13}C/^{12}C$ ratio in atmospheric $CO_2$ will have changed considerably. This is apparent from the steep fall in values of $\delta^{13}C$ recorded in this area of the curve by Friedli *et al*. (1986). This may be a source of uncertainty when comparing stable isotope ratios of modern materials with archaeological samples. It is not always recorded in the literature how this correction is made or if it has been made at all (*eg.* in Mottram *et al*., 1999; Copley *et al*., 2005d).

All the oils analysed in this study were from $C_3$ plants because the main (although not only) $C_4$ plant oils in use today are maize oil and millet oil. Maize oil would not have been available in the LBA eastern Mediterranean and, although there is evidence that millet was grown, there appears to be little evidence of it being used as a source of oil (Shaw & Nicholson, 1995, 16-17; Serpico & White, 2000b; Serpico, 2001; Wetterstrom & Murray, 2001; Megaloudi, 2006, 38-49, 46-48). Oil was used extensively during the LBA across the eastern Mediterranean (Knapp, 1991). It is listed in the tablets from Pylos and Knossos in the context of perfume making and may possibly be olive oil (Shelmerdine, 1985, 24, 33-34) although there is some debate about the type of oil being used and whether more than one type is listed (Shelmerdine, 1985, 17-39). Documentary evidence from the reign of Thutmosis III (*c.*1467-1413) records that he brought home ‘sweet’ and ‘green’ oils as booty from Syria and a selection of oils from Cyprus, *Hatti*-land (the Hittite area of central Turkey), Babylonia, the northern Levant and Syro-Palestine, and Syria is mentioned in a papyrus from *c.*1200 (Knapp, 1991).

The evidence for the use of plant oils during the LBA and earlier is largely archaeological, from seed and pollen analyses and the discovery of oil processing installations, or textual (including pictorial) rather than molecular. Evidence of the presence of olive (*Olea europaea L.*) wood and fruit can be traced back to the Palaeolithic in the Near East (Serpico & White, 2000b) and the cultivation of olives may date back to the Chalcolithic Period (3700 – 3500BC) in the area around the Dead Sea (Serpico & White, 2000b). Archaeological evidence for the pressing of olives to produce oil has been found from Chalcolithic sites in Israel (Serpico & White, 2000b) and the oil was certainly in use by the LBA in the Aegean, Cyprus, Egypt, and throughout the Syria/Israel/Palestine area (Knapp, 1991; Serpico & White, 2000b; Hadjisavvas, 2003, Megaloudi, 2006, 58-59). Almonds shells (*Prunus dulcis*, *Prunus amygdalus*) have been found in Greece at sites from the Palaeolithic onwards (Haldane, 1993; Megaloudi, 2006, 66), as well as in Turkey and on other sites across the eastern Mediterranean (Haldane, 1993). In the LBA they have been recorded at the site of Amarna in Egypt (Serpico & White, 2000b), in Tutankhamun's tomb (Hepper, 1990, 62-63), on the LBA shipwreck at Ulu Burun (Haldane, 1993) and on Cyprus (Haldane, 1993). Almonds could have been used for oil manufacture but generally the shells are only found in small quantities (Hepper, 1990, 62-63; Haldane, 1993; Serpico & White, 2000b) and the almond was not attested as an oil plant until classical times (Theophrastus, 1916, Treatise on Odours, 16; Manniche, 1999, 30). Sesame oil (from *Sesamum indicum L.*) may have been used in LBA Egypt but the identification of sesame in the archaeological record during this period is controversial (Serpico & White, 2000b). It was possibly mentioned in Linear B tablets and

seeds have been identified in LBA Greece (Megaloudi, 2006, 56-57). Moringa oil (from *Moringa peregrina*) was cited as an oil source from early times but again is unconfirmed as a LBA product (Serpico & White, 2000b). Both the flax plant (*Linum usitatissimum*), which produces linseed oil and the castor oil plant (*Ricinus communis L.*) have a long history of cultivation in the eastern Mediterranean. The seeds of both plants have been found in Predynastic Egypt (Serpico & White, 2000b) and flax was cultivated in Greece from the Late Neolithic period (Megaloudi, 2006, 59), although the flax plant may have been grown for the production of fibre rather than oil (Serpico & White, 2000b).

Taking into account which modern oils were easily available and trying to include oils which might have been in use during the LBA in the eastern Mediterranean, the first batch of samples included almond oil (*Hermitage Oil*, USA), moringa oil (*Essentialoilsonline.co.uk* 100% pure, cold pressed, refined moringa oil), three samples of olive oil (*Carapelli firenze* Italian extra virgin olive oil, cold pressed; *Sainsbury's* Greek extra virgin olive oil, cold pressed; *Iliada Kalamata* Greek extra virgin olive oil, cold pressed, from first pressing), sesame oil (*Meridian* unrefined, cold pressed, Mexican sesame oil), and walnut oil (*Sainsbury's* walnut oil). This batch of samples also included a sample of argan oil (*Belazu Morrocan* argan oil, cold pressed). Although this was not one of the oils in use in the LBA eastern Mediterranean, the seeds of *Argania spinosa* have traditionally been pressed for oil extraction in south western Morocco (Charrouf & Guillaume, 1999) and the oil was included here to give additional information on the isotopic signatures of plant oils. The second batch of samples included a further sample of moringa oil from a different source

(*Fragrant Earth*), castor oil (*Care*+ virgin castor oil) and flax/linseed oil (*GranoVita* organic, cold pressed flax oil). The second sample of moringa oil was included after confirming the results of the first analysis where moringa oil produced a $\delta^{13}C_{16:0}$ value which took it outside the group formed by the other oils (fig. 7.43 and fig. 7.53).

Two drops of each oil were saponified using Method A (Chapter 5, p119-120). As these were modern materials it was necessary to use a more vigorous method of saponification than that finally recommended for archaeological material in order to completely saponify the oils. This prevents any isotope effects associated with the saponification process by taking the reaction to completion. The saponified oils were then methylated and sent for analysis by GC-C-IRMS as described in Chapter 5 (p122-123). Before sending the oil samples for GC-C-IRMS they were analysed by GC to check that all acylglycerols had been broken down by the saponification procedure, and that methylation was also complete.

### *6.1.ii Modern waxes*

Beeswax was present in many of the samples of RLWm ware from Boğazköy analysed in a previous study (Knappett *et al*., 2005; Steele, 2004, 56-64; Steele *et al*., 2007) and in similar samples from both Boğazköy and Kuşakli analysed for this study (p161ff.). Degraded beeswax usually contains $C_{16:0}$ which is a degradation product of the palmitic acid wax esters which form a substantial proportion of the fresh wax (p157ff.). However several of the sherds which

yielded biomarkers for degraded beeswax, including $C_{16:0}$, also yielded a series of fatty acids which suggested the presence of a fat or oil in addition to the wax (p203-204).

In order to attempt to determine whether these residues represented a mixture of beeswax and a fat or oil, unsaponified samples of the archaeological residues were sent for GC-C-IRMS analysis (p119). However a comparison modern material was then needed. The only available published determination of $\delta^{13}C$ values for fatty acids in beeswax measured the $\delta^{13}C_{16:0}$ value of a sample of 100 year old beeswax (Evershed *et al*., 1997b) giving a value of −22.8‰. No determination of $\delta^{13}C_{18:0}$ in beeswax has been reported, probably as there is very little $C_{18:0}$ present, most of it being bound up in esters (Tulloch, 1971; Tulloch & Hoffman, 1972; Garnier *et al*., 2002; Bonaduce & Colombini, 2004; Namdar *et al*., 2007).

In order to try and avoid beeswax from hives where the bees have been fed with sugar (possibly from a $C_4$ source such as sugar cane) and wax which had been adulterated with other material such as paraffin, and to obtain a wax as near as possible to a comb wax, two examples of honey containing intact honey comb were used as modern reference material. Wax 1 was obtained from "*Honeycomb*" chunk comb honey (packed by *Honeycomb Co. Ltd*, Lancaster, UK) produced in Hungary and purchased in a glass jar. Wax 2 was obtained from "*Borage Herbal Comb Honey*" "gathered from the borage fields of North Yorkshire" (*Bee Health Manufacturing*, Bridlington, E. Yorkshire, UK), purchased in a plastic box. Samples of the comb were removed from each

product using a clean scalpel and spatula, trying to remove as little honey as possible with the wax. The samples were allowed to drain on clean watch glasses. They were then heated in cleaned pyrex beakers to approximately 60°C. At this stage the waxes started to melt and form a layer on top of any remaining honey. After cooling this layer was removed leaving the honey behind. This produced waxes which were not uniform in colour but varied from golden yellow to brown and were significantly darker than commercially available beeswax. Wax 2 contained more dark wax than wax 1.

A pinhead sized piece of each wax was solvent extracted using 2:1 v/v DCM:methanol and analysed by GC as described in Chapter 5 (p113-115). Both samples contained material which was not soluble in DCM:methanol which was left as a white solid residue after solvent extraction. The purpose of this analysis was to check the waxes for possible adulteration. For GC-C-IRMS analysis, pinhead sized samples were removed from each wax sample and saponified using Method A (p119-120). They were then methylated and sent for GC-C-IRMS analysis as described in Chapter 5 (p122-123).

## 6.2 Experimental perfumed oils

It is clear from both archaeological and documentary evidence that there was a considerable trade in plant oils, olive oil in particular, across the eastern Mediterranean (Bergoffen, 1991; Knapp, 1991; Haldane, 1993; Hadjisavvas, 2003; Palmer, 2003). Transport and storage of oils in bulk was usually carried out in amphorae, stirrup jars or pithoi. Data on the volume of these containers

is not readily available although some of the large storage pithoi found at Kalavasos on Cyprus and the large stirrup jars found at Knossos and Mallia on Crete would together have contained tens to hundreds of thousands of litres of oil (Knapp, 1991). The Canaanite amphorae found at the site of the Ulu Burun shipwreck come in three sizes: large with a capacity of *c*.26.7 litres, medium at *c*.13 litres and small with a volume of *c*.6.7 litres (Pulak, 1997).

An estimation of the volumes of the RLWm ware vessels recorded in Eriksson's catalogue (Eriksson, 1993, 173-275) and South & Steel (2007) (see p130-132 for methodology and p320-322 for detailed results) produced volumes between 0.2 litres and 3.1 litres, although South and Steel (2007) do record volumes of 5.5 litres for exceptionally large pilgrim flasks. In general, the volumes of RLWm ware are all smaller than the sizes of vessels used for transporting or storing for example olive oil. In addition, RLWm ware vessels are not generally found in large amounts in one place. Even at Kalavasos on Cyprus, where nearly 700 sherds and 46 complete vessels were discovered, the sherds made up only 0.7% of the LBA sherds (South & Steel, 2007). There was more imported Aegean pottery in the total ceramic assemblage (1.8% of the total) than RLWm ware (South & Steel, 2007) (see Appendix 2 for notes on pottery quantification). This scarcity in itself indicates that the contents of RLWm ware vessels were probably commodities which were not part of a bulk trade but rather more valuable. The contexts of RLWm ware finds – predominantly in tombs and temples – also point to a commodity with 'added value'.

The shape of the common forms, with very restricted necks, suggests the contents were a liquid. The valuable liquid commodities of the LBA were fine wines, medicinal mixtures and perfumed oils (Knapp, 1991), and the results of previous residue analysis which indicates the contents were an oil or fat (Steele, 2004; Knappett *et al*., 2005; Steele *et al*., 2007), point to some mixture in an oily base.

Documentary evidence shows that the trade or exchange of perfumed oils was taking place routinely during the LBA (Bergoffen, 1991; Knapp, 1991; Palmer, 2003). The Linear B tablets from Knossos and Pylos give lists of supplies for perfume makers which indicate that perfume manufacture was well organised and carried out on a relatively large scale (Shelmerdine, 1985). Specialty oil from Cyprus was received by Thutmosis' III troops in Sinai (Bergoffen, 1991), oils from Cyprus, Turkey, the Levant and Babylonia are recorded in Egyptian documents (Knapp, 1991), rulers of Egypt and Cyprus exchanged gifts of perfumed oils in both directions (Knapp, 1991) and oils are recorded as part of the marriage gifts exchanged at royal weddings (Knapp, 1991).

Before the use of distillation to extract aromatic compounds from herbs, spices, woods and resins, most 'perfumes' were manufactured by steeping the aromatic ingredients in fat, oil, wine, water, honey or fruit paste with or without heating (Shelmerdine, 1985, 12-13; Manniche, 1999, 10). To a professional perfumier these are not perfumes, which are always prepared by distillation, but scented mixtures or preparations (Serpico, pers. comm.). Few recipes survive from the LBA. Middle Assyrian tablets from the reign of Tukulti-Ninurtas I (1243-

1207BC) do give a few recipes (Shelmerdine, 1985, 11, 15-16), and an Egyptian tomb painting probably from the reign of Thutmosis IV (1397-1384) shows what may be manufacture of solid perfume balls (Shelmerdine, 1985, 16). The Linear B tablets record ingredients used for perfume making and finished perfumes but not any recipes (Shelmerdine, 1985, 11). Most of the recipes which are still available to us come from later Egyptian writings such as the recipes on the east wall of the 'laboratory' in the Ptolemaic temple at Edfu (Manniche, 1999, 27, 29, 37-41) ($4^{th}$ – $1^{st}$ centuries AD), and from the classical writers such as Theophrastus ($4^{th}$ – $3^{rd}$ centuries BC), Dioscorides ($1^{st}$ century AD) and Pliny ($1^{st}$ century AD). However the methods employed for steeping fragrant substances to produce perfumes seems to remain essentially unchanged from the Middle Assyrian tablets to the $1^{st}$ century AD, although the details vary (Shelmerdine, 1985, 15), and it seems probable that these methods were very similar to the methods used in most places during the LBA to produce perfumed oils.

Despite two claims, one from Cyprus (Belgiorno, 2004, 27-28; Karageorghis, 2004; Lentini, 2004; Molyva, 2005; Morgan, 2005) and one from the Aegean (Tzedakis & Martlew, 1999), that Middle Bronze Age (MBA) perfume factories have been discovered and traces of ancient perfumes recovered, very little work has been done on how ancient perfumes might be detected, what materials might be identified and whether it is possible after several thousand years to detect substances as volatile as perfume ingredients. The potential for contamination from modern materials is high as so many modern creams, cleansing products, cleaning materials etc are highly perfumed.

In both the cases cited above it is perfectly possible that most of the ingredients attributed to ancient perfumes are in fact modern ingredients. For example, at least one of the aromatic ingredients identified, citrus bergamot, cannot have been part of a MBA perfume as neither plant which might be identified as such was present in the MBA eastern Mediterranean. The first is *Citrus aurantium ssp. bergamia*. It is not very clear when citrus plants were first introduced into the Mediterranean. The citron (*Citrus medica*) was the earliest to be recorded and may be described by Theophrastus in the 4th century BC (Dalby, 2003, 88). Lemons (*Citrus limon*) may be depicted in Roman wall paintings from the early Empire and is found in written sources from the 2nd century AD (Dalby, 2003, 88), while bitter oranges (*Citrus aurantium sp.*) are not recorded until the expansion of Arab influence in the 9th century AD (Morris, 1999, 40). The second plant sometimes referred to as bergamot is *Monarda didyma,* a native of North America (Bremness, 1990, 61). However bergamot oil *is* a common ingredient in modern sun creams and oils (Jellin *et al*., 2000, 106). This calls into question the results of both studies.

To try and determine whether looking for ancient perfumes might be a feasible undertaking and to identify some biomarkers for ancient perfume ingredients, some basic experiments were carried out. Single ingredient perfumed oils were manufactured using traditional methods as far as possible and the results analysed by GC-MS. When using ancient texts as sources of information on aromatic and other ingredients the many potential lexicographical problems must be considered as, at the very least, the identification of these ingredients may not be secure.

Although Theophrastus in his ‘On Odours’ mentions almond, balanos, sesame and olive oil as base materials for perfumes (Theophrastus, 1916, IV.13-16), olive oil (*Sainsbury’s Extra Virgin* olive oil) was chosen as a base due to its availability and relatively low cost. Dioscorides and Theophrastus both mention a preliminary steeping of the oils with astringent spices aspalathus, cyperus and ginger-grass which makes them more receptive to the required perfume (Dioscorides, 1933, eg recipes in sections I.53, 55, 66; Theophrastus, 1916, IV.16-20; Shelmerdine, 1985, 13) and the use of coriander in the same way has been deduced from the Pylos tablets (Shelmerdine, 1985, 22). Heat may be applied at this stage. After this a variety of methods are used including mixing the aromatics with water or wine and heating (maceration), mixing the crushed aromatics directly with the oil with or without heating, repeating some or all of these processes with more of the same aromatic ingredients or with different ingredients. The perfume may be strained at any stage and is usually strained at the end of the process. Some recipes are extremely complex as, for example, the recipe for Hekenu unguent recorded at Edfu which took 365 days and about 2.5 kg dry ingredients and 2.2 litres liquids to produce about 500 ml of the perfume (Manniche, 1999, 37-41).

To simplify the analyses and make sure that any biomarkers were attributed to the correct aromatic, only single aromatic ingredients were used in each preparation. These were chosen partly on the basis of common ingredients mentioned in ancient texts (Theophrastus, 1916; Shelmerdine, 1985) or discovered in archaeological contexts (Hepper, 1990; Bass, 1991; Haldane, 1993) and partly on ease of availability. Coriander seeds (*Suma Moroccan*

coriander seed), rosemary and sage leaves (grown in a local garden), rose petals (harvested from a local garden), frankincense and myrrh resins (*Neal's Yard*) were chosen as the ingredients for experimental oil preparation.

Coriander is mentioned as an ingredient supplied to perfume makers in the Pylos tablets (Shelmerdine, 1985, 17-18) and coriander seeds have been found for example in Tutankhamun's tomb (Hepper, 1990, 57) and on the Ulu Burun (Haldane, 1993). Rose and sage are mentioned in the context of perfumed oils in the Pylos tablets, finished oils being described as rose-scented (Shelmerdine, 1985, 21, 25) and sage-scented (Shelmerdine, 1985, 25, 29). Tablets from Knossos mention myrrh (Shelmerdine, 1985, 23), two of the Amarna letters mention oil of myrrh (Knapp, 1991) and it was identified in a Middle Kingdom jar from Dhashur in Egypt (Serpico & White, 2000c). Frankincense has been tentatively identified in Tutankhamun's tomb (Hepper, 1990, 20) and has been identified in Egyptian materials dating from both before and after the LBA (Evershed *et al*., 1997c; Mathe *et al*., 2004). Rosemary is not attested in either LBA documents or the archaeological record but is an aromatic plant from the Mediterranean.

The methods described by ancient authors were adapted and combined with modern methods for producing aromatic, medicinal and culinary oils. Sources used for creating the methods used here were Theophrastus (1916), Dioscorides (1933), Little (1980), Shelmerdine (1985), Bremness (1990), Schwartz (1996) and Manniche (1999).

Frankincense and myrrh oils were produced using only one method (method 1). Coriander was initially produced using two different methods (methods 1 and 2) to test whether the oil produced was dependent on the method used for the preparation. Rose oil, which needs more gentle preparation to conserve the fragrance of the petals, and rosemary and sage oils were prepared using method 3.

Method 1: *c.*5g of the crushed or bruised aromatic was covered with 40ml olive oil and warmed to about 120°C. The mixture was maintained at that temperature for 15 minutes then allowed to cool and transferred into a sealed jar. It was then left to steep for several days, up to two weeks. The oil was then strained into a clean container. This process was repeated twice more with the same oil and at this point all three oils smelt strongly of the aromatic ingredients.

Method 2: Following the ancient recipes described by Dioscorides (*eg*. I.66) and Theophrastus (*eg*. V.29), coriander oil only was also prepared by covering *c*.5g crushed coriander seeds with 40ml of cold de-ionised water, bringing to the boil and boiling until reduced to approximately half its original volume. This was then decanted into a clean container, sealed and left to steep for a few days. The mixture was then strained. The aromatic liquid was mixed with 40ml olive oil and heated until the water had evaporated off, cooled and decanted into a sealed container. The whole process was repeated once more with the same oil. At this stage it appeared that the method made little difference to either the

aroma, as perceived by the human nose, or the results of GC-MS analysis of the oils, so this method was abandoned as being too time consuming.

Method 3: To prepare rose oil 200ml olive oil was warmed gently over a water bath to about 40°C and 10g rose petals (*Rosa rugosa*) added (Theophrastus, 1916, V.26; Dioscorides, 1933, I.53; Manniche, 1999, 79-80). This was then cooled and left to steep overnight and the oil strained into a clean container. Leaving for longer than this encouraged mould to form and several batches were discarded as a result. The process was repeated four more times with the same oil to achieve an oil which smelt of roses, although the smell of this oil was always somewhat musty. Rosemary and sage oils were prepared using exactly the same method but starting with 40g rosemary leaves for 300ml oil and 35g sage leaves for 500ml oil. The differences in volumes and weights of ingredients used depended partially on the volume occupied by a given weight of aromatic – rose petals for example occupy a much larger volume than the same weight of rosemary leaves. The other limiting factor was the availability of each aromatic – for example the rose petals were only available in large quantities for a few weeks in June each year. After three steepings both rosemary and sage oils smelt strongly of the aromatic ingredients.

For all oils a sample was retained for analysis after each steeping so that each stage of the manufacture could be recorded. Control samples of the base oil were also prepared using the same methods but adding no aromatic ingredients. However this was only carried out up to the second steeping stage. These samples were also analysed by GC-MS.

Control samples consisting of the olive oil alone were prepared using methods 1 and 2 to determine what effect, if any, the preparation techniques had on the oil itself. Unfortunately these were not continued beyond the first steeping for either method, an experiment which might have proved instructive had it been continued.

For GC-MS analysis one drop of each oil was taken from the batch being analysed. This was dissolved in DCM-methanol (2:1 v/v) and derivatised using BSTFA as described in Chapter 5 (p112). This sample was then blown down and dissolved in DCM for analysis in the GC-MS. The GC-MS operating conditions were as described in Chapter 5 (p115-116). One drop of each oil was also taken for saponification and further GC-MS analysis. Method A (p119-120) was used for the saponification as these are modern samples and therefore much more concentrated than archaeological residues and required a more vigorous process to ensure complete saponification. The non-saponifiable and saponifiable fractions were analysed by GC-MS as above.

During the preparation of these oils it was difficult to be consistent in the methods for preparing each oil, particularly between different oils and different steepings of the same oil. Consequently the time each oil was left to steep and the exact amounts of aromatic ingredients added to a given quantity of oil was somewhat variable. This was due to constraints of other work and the availability of some fresh ingredients. However, although a more consistent approach would have been preferable it would not have altered the results significantly (p299-303). Any repeat of these experiments or further

experimentation was made impossible by the failure of the GC-MS in March 2007 and the lack of GC-MS facilities thereafter.