

## COMPOSITIONAL VARIATIONS IN AGED AND HEATED PISTACIA RESIN FOUND IN LATE BRONZE AGE CANAANITE AMPHORAE AND BOWLS FROM AMARNA, EGYPT\*

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*This study examines resinous deposits from the interior surfaces of sherds of imported Canaanite amphorae and locally produced bowls from the 18th Dynasty site of Tell el-Amarna, Egypt. Archaeological evidence indicates that the Canaanite amphorae were used for resin transport, whilst the bowls are associated with burning resin as incense. A number of characteristic triterpenoids identify all the resinous deposits from both vessel types as Pistacia spp. No other resins were observed and there was no evidence of mixing with oils or fats. The composition of the archaeological resins is more complex than that of modern pistacia resin, due to degradation and generation of new components. Experimental heating alters the relative abundance of the triterpenoid composition of modern pistacia resin. One component, the triterpenoid 28-norolean-17-en-3-one, is produced by such heating; however, an increase in its relative abundance in ancient samples is not matched by the archaeological evidence for heating. It is therefore not possible to use this component reliably to identify heated resin. However, additional unidentified components with a mass spectral base peak at  $m/z$  453 have been associated with seven (out of 10) bowls and are not observed in resins associated with Canaanite amphorae. It is proposed that these components are more reliable molecular indicators of heating.*

**KEYWORDS:** EGYPT, AMARNA, LATE BRONZE AGE, RESIDUE ANALYSIS, TRITERPENOID, PISTACIA, INCENSE, GAS CHROMATOGRAPHY – MASS SPECTROMETRY, CANAANITE AMPHORAE

### INTRODUCTION

In contrast to many other areas, the desert regions of Egypt have long been recognized for their often-exceptional organic preservation. One site with unusually well preserved material is Amarna, located in Middle Egypt. This site, dated to the 18th Dynasty of the New Kingdom,

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was largely occupied for a single generation under the Pharaoh Akhenaten (1364–1347 BC). Many pottery sherds from the recent excavations still show evidence of visible residues, often of a resinous appearance. Study of these sherds has indicated that the resin is often present as a deposit adhering to bowls traditionally associated, from pictorial evidence, with incense burning (Serpico 1996, 115). In support of this, some of these residues survive as darkened brittle deposits or are slightly charred in appearance (Serpico and White 2000, fig. 5). In addition, resin is also frequently present as a coating on the interior of ‘Canaanite’ amphorae (Serpico and White 2000, fig. 7). These large storage jars were widely used for the transport of goods throughout the eastern Mediterranean in the Late Bronze Age (Grace 1956; Leonard 1995). Notably, some of the amphorae found in Egypt were inscribed, probably when they first entered the country, with the name of the contents. Some with resin are labeled *sntr*, most often translated as incense (Serpico 1996). Although known centres of manufacture for the amphorae are very rare, recent petrological investigations support an origin in modern Israel for jars with this commodity (Bourriau *et al.* 2001). Gas chromatography – mass spectrometry (GC–MS) analysis of a selection of bowls and amphorae from Amarna, including inscribed examples, has shown that, on the basis of the molecular composition, this resin is from a species of *Pistacia* (Serpico and White 2000). The absence of other resins from Canaanite jars at Amarna indicates that resins such as frankincense (Evershed *et al.* 1997) were probably not available at that time (Serpico and White 2000). Interestingly, in a few instances, the pistacia resin adhering to Canaanite amphorae sherds also appears to have been burned, leading to the suggestion that the sherds had been re-used as makeshift censers (Serpico 1996, 128).

Some idea of the scale of the trade in this commodity can be ascertained from the 14th-century BC shipwreck discovered off the coast of south-west Turkey at Ulu Burun, where about 150 resin-filled Canaanite amphorae were present as part of the cargo. GC–MS examination of a number of these residues also established that the resin was that of *Pistacia* spp. (Mills and White 1989; Hairfield and Hairfield 1990; Haldane 1993; Pulak 1998). In addition, pistacia varnishes on sarcophagi, shabti boxes, canopic cases and tomb walls from other New Kingdom sites (Serpico and White 2001) indicate widespread and large-scale use. There is also some evidence of the use of pistacia resin in mummification, at least as early as the Third Intermediate Period (Kaup *et al.* 1994; Serpico and White 1998; Colomnini *et al.* 2000).

The genus *Pistacia* (family Anacardiaceae) has four Mediterranean species (*P. atlantica*, *P. khinjuk*, *P. lentiscus* and *P. terebinthus*), all of which may have been available in the past for the production of resin. Pistacia resin is also known as mastic, Chios (sometimes Chio or Chian) terpine, Cyprus balsam or terebinth (Mills and White 1989). Today, the resin is commercially produced on the island of Chios, and is used for chewing gum, varnish, sweets and cordials (Grieve 1994; Serpico 2000). Although there has been some debate about precise species identification and ancient use of cultivated forms (Padulosi *et al.* 1996; Serpico 2000), only *P. khinjuk* is native to modern Egypt. However, the resin-producing capability of these species varies, and it is thought that the most abundant source would have been *P. atlantica* (Mills and White 1989). Today, only the resin from the cultivated *P. lentiscus* is still commercially produced in large quantities. The resin is yielded by cutting the bark, and over a kilogram of the resulting pale yellow semi-liquid ‘tears’ can be produced per year (Serpico 2000).

Pistacia resin is largely composed of triterpenoids (indeed, the word ‘terpenoid’ is derived from ‘terebinth’), and the chemical composition of the modern resin has been studied by a number of workers (Barton and Seoane 1956; Seoane 1956; Monaco *et al.* 1973, 1974; Scrubis *et al.* 1975; Caputo *et al.* 1978, 1979; Mangoni *et al.* 1982; Monaco *et al.* 1982; Mills and White 1989; Marner *et al.* 1991; Papageorgiou *et al.* 1997). The methyl ester derivatives of the

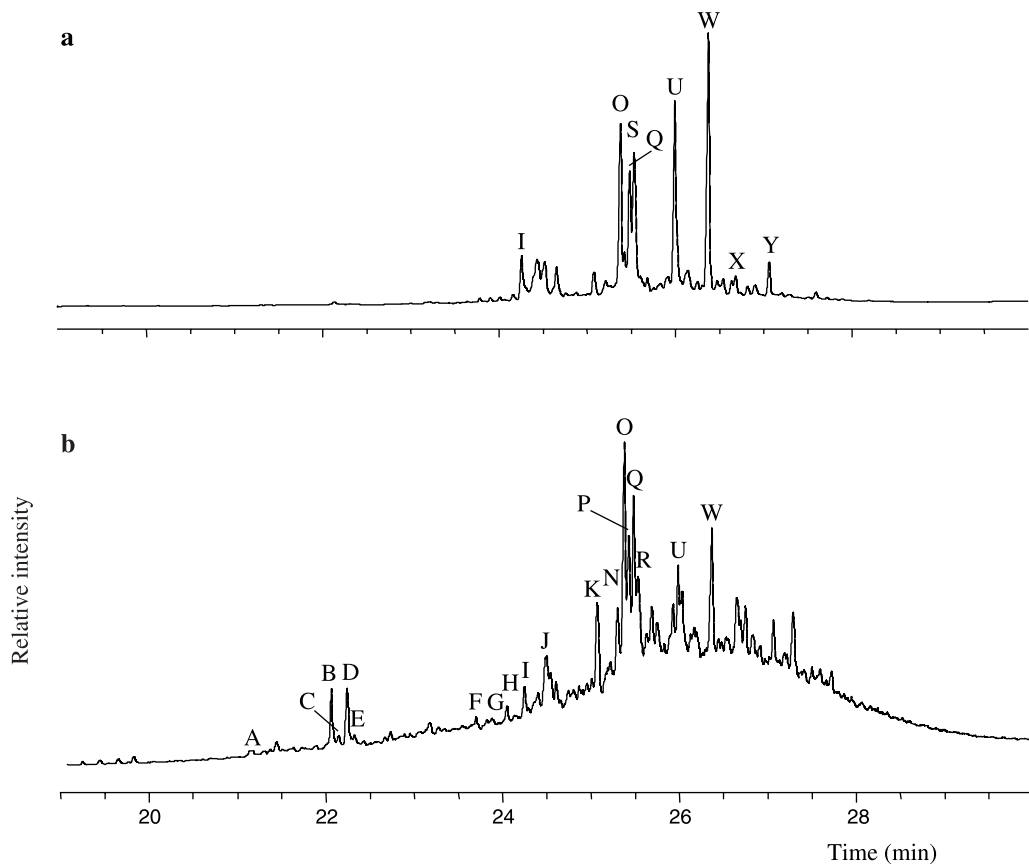


Figure 1 Partial chromatograms of (a) modern pistacia resin (Chios) and (b) visible residue from a Canaanite sherd (TA17#112) from Amarna, both derivatized with diazomethane. Molecular identification by GC-MS and retention times; for peak identification, see Table 2.

most abundant components of pistacia resin are methyl moronate (O), methyl oleanonate (Q), methyl isomasticadienonate (U) and methyl masticadienonate (W) (Fig. 1).

Defunctionalized terpenoids have been associated with the heating of natural resins, leading to aromatic, alkyl-substituted, dehydrogenated and decarboxylated compounds. Two carefully examined processes are the diterpenoid pitches produced by the destructive distillation of pine resin or wood (e.g., Evershed *et al.* 1985; Robinson *et al.* 1987; Reunanen *et al.* 1989) and the triterpenoid containing tar, produced by the destructive heating of birch bark (e.g., Charters *et al.* 1993; Reunanen *et al.* 1993; Regert *et al.* 1998; Aveling and Heron 1998, 1999). The extension of this work to pistacia has been examined by a few workers: Kaup *et al.* (1994) identified pistacia resin in the muscle tissue of an Early Ptolemaic mummy. Unfortunately, the molecular identities of the components were not provided, although the gas chromatogram appears similar to the data presented here (Fig. 1). However, the authors note that 'noroleanone' is a major component, and reveal a number of earlier eluting molecules not found in modern pistacia resin, which they label 'aromatized and skeleton products'. They speculate that these have been produced by a 'smouldering process'. Colombini *et al.* (2000) identify pistacia resin

from the solid mass within the thoracic and abdominal cavities of a seventh-century BC mummy. With archaeological evidence, they use the molecular evidence of oxidized and dehydrogenated triterpenoids, and the high abundance of 28-norolean-17-en-3-one (J), to suggest that the resin was heated prior to its use. Serpico and White (2000) suggest a correlation between pistacia resins described as charred, darkened and brittle from bowls traditionally associated with incense burning and the occurrence of 28-norolean-17-en-3-one (J), although quantified data is absent.

In the study by Serpico and White (2000), 32 samples from bowls and amphorae from Amarna were analysed. Archaeological evidence indicates that the Canaanite amphorae were used for transport of *Pistacia* spp. resin and the locally produced bowls as incense burners. However, the molecular identifications were limited to four components and two different methylation techniques were used (Serpico 1996, 567). Therefore, a further 40 samples consisting of 10 bowls and 30 Canaanite amphorae were taken for analysis. This study therefore aims to identify further visible and absorbed resinous residues, and to compare the effects of diagenetic degradation between modern and these ancient resins. Moreover, the use of the resin as incense indicated that a more comprehensive examination of the molecular identification and composition was needed to compare the thermal degradation and the generation of new components in modern pistacia resin when heated.

#### EXPERIMENTAL PROCEDURES

A number of sherds found during recent excavations at Amarna (seasons 1981–90) along with three samples from previously excavated Amarna vessels now in museum collections are examined here (Table 1). All visible residues were from the interior surfaces of Canaanite amphorae or from out-turned rim bowl sherds. Sub-samples were taken from one bowl, from one Canaanite sherd believed to have been re-used as a censer, where the resins had a visibly

Table 1 *The sample code, vessel type, Amarna provenance and description of the visible residues sampled in this study*

<i>Bowl sample code</i>	<i>Sample source</i>	<i>Amarna provenance</i>	<i>Notes</i>
MS132p	Complete vessel; used as censer	Petrie museum UC 19173	
MS84p	Complete vessel; used as censer	Petrie museum UC 24275	
TA65	Rim sherd; used as censer	WV	
TA8	Rim sherd; used as censer	SAT	
TA88	Base sherd; used as censer	WV	
TA89	Rim sherd; used as censer	WV	
TA96	Rim sherd	WV	
TA103	Rim sherd; used as censer	KN	
TA130	Rim sherd; used as censer	KN	
TA13, sub-sample 1	Rim and body sherd; used as censer	KN	Orange-coloured resin
TA13, sub-sample 2	Rim and body sherd; used as censer	KN	Interior portion of resin
TA13, sub-sample 3	Rim and body sherd; used as censer	KN	Brown-coloured resin

Table 1 (continued)

	<i>Sample source</i>	<i>Amarna provenance</i>	<i>Notes</i>
<i>Canaanite amphora sample code</i>			
MS134p	Body sherd	Ashmolean museum Ash 1925.597e H.O.1178	
TA106	Body sherd	SAT	
TA17# 112	Body sherd	SAT	
TA20# 93	Body sherd	SAT	
TA208# 90, sub-sample 1	Body sherd; used as censer	WV	Black-coloured resin
TA208# 90, sub-sample 2	Body sherd; used as censer	WV	Brown-coloured resin
TA208# 90, sub-sample 3	Body sherd; used as censer	WV	Orange/black-coloured resin
TA208# 90, sub-sample 4	Body sherd; used as censer	WV	Yellow-coloured resin
TA210	Body sherd	SAT	
TA224	Handle and body sherd	NC	
TA231	Rim sherd	WV	
TA232	Rim sherd	MC	
TA251, sub-sample 1	Rim sherd	SAT	Brown-coloured resin
TA251, sub-sample 2	Rim sherd	SAT	Interior portion of resin
TA251, sub-sample 3	Rim sherd	SAT	Brown-coloured resin
TA251, sub-sample 4	Rim sherd	SAT	
TA253	Body sherd	SAT	
TA26#111	Body sherd	SAT	
TA276, sub-sample 1	Shoulder sherd	CC	
TA276, sub-sample 2	Shoulder sherd	CC	
TA276, sub-sample 3	Shoulder sherd	CC	
TA288	Shoulder sherd	KN	
TA297	Body sherd	SAT	
TA3# 91	Body sherd	SAT	
TA30	Body sherd	SAT	
TA304	Shoulder sherd	CC	
TA305	Rim sherd	SAT	
TA306	Handle and body sherd	SAT	
TA307	Rim sherd	SAT	
TA308	Base sherd	SAT	
TA309	Body sherd	KN	
TA312	Body sherd	Panehsy's private house	
TA34# 94	Body sherd	SAT	
TA4	Body sherd	SAT	
TA5	Body sherd	SAT	
TA6, sub-sample 1	Rim sherd	SAT	
TA6, sub-sample 2	Rim sherd	SAT	
TA66, sub-sample 1	Base sherd	WV	
TA66, sub-sample 2	Base sherd	WV	
TA66, sub-sample 3	Base sherd	WV	
TA94	Shoulder and body sherd	MC	

CC = Central City, MC = Main City, NC = North City, KN = Kom el-Nana, SAT = Small Aten Temple, WV = Workmen's Village (as discussed in Frankfort and Pendlebury 1933; Pendlebury 1951; Serpico and White 2000). Canaanite amphora sherds are identified by shape and fabric (Serpico and White 2000).

different colour, and from four Canaanite amphorae sherds for comparison. Modern *Pistacia lentiscus* resin was obtained from Chios.

After dichloromethane (DCM) extraction of a portion (10–20 mg) of the visible residue, the carboxylic functionalities of the extracts were methylated using diazomethane in diethyl ether, after the method of Fales *et al.* (1973). Combined gas chromatography – mass spectrometry (GC–MS) was carried out using a Hewlett Packard 5890 series II GC connected to a 5972 series mass-selective detector. The GC was equipped with a splitless injector and fitted with a DB-1ht (J&W scientific) coated (0.1  $\mu\text{m}$ ) fused silica column (15 m  $\times$  0.32 mm i.d.). Helium was the carrier gas, with a constant head pressure of 1 psi and a flow rate of 1 ml  $\text{min}^{-1}$  at 50°C. The injector and interface were maintained at 300°C and 340°C respectively. The temperature of the oven was programmed from 50°C (2 min) to 340°C (12 min) at 10°C  $\text{min}^{-1}$ . The column was directly inserted into the ion source. Electron impact (EI) spectra were obtained at 70 eV, with full scan from  $m/z$  50 to 700.

To heat authentic pistacia resin, a methodology similar to that of Stott and Abbott (1995) for microscale pyrolysis was applied. Approximately 10 mg of the modern homogenized pistacia resin was placed into a melting point tube (1.16 mm i.d., 70 mm length) previously sealed at one end in a Bunsen flame and then sealed at the other end to retain any volatile products. Care was taken not to heat the resin at this stage. Separate tubes were then placed in a heated GC oven for 30 min each at different temperatures between 100°C and 400°C, at 50°C intervals. In addition, a sealed tube was unheated but prepared and extracted in an identical way to the heated tubes. Once cooled, the outer surfaces of the tubes were rinsed in DCM to remove any contamination due to handling. The tubes were then broken and the contents dissolved, with 15 min sonication in 1 ml DCM, a portion of which was then derivatized with diazomethane as above. In order to resolve peak co-elution, the GC–MS measured the peak areas on the basis of the mass spectral base peaks for the following components; 28-norolean-17-en-3-one,  $m/z$  163; methyl moronate,  $m/z$  189; methyl oleanonate,  $m/z$  203; 20,24-epoxy-25-hydroxy-dammaren-3-one,  $m/z$  143; unknowns (P and R),  $m/z$  143; methyl isomasticadienonate,  $m/z$  453; and methyl masticadienonate,  $m/z$  453.

## RESULTS AND DISCUSSION

### *The identification of Pistacia resin*

*Pistacia* resin was identified by the characteristic composition and distribution of triterpenoids, especially in comparison to modern authentic resins, as shown in Figure 1. All of the resin associated with Canaanite amphorae and bowls were identified as *Pistacia* spp. However, due to the natural variability of the resin it is not possible to distinguish the pistacia species on the basis of the triterpenoid composition or abundance. There was no evidence of any other resin or mixing with oils or fats. In addition, where the friable surface residue has been lost, pistacia resin was extracted from the interior few millimetres of the sherds, indicating the penetration of the resin into the ceramic fabric in a similar way to fatty acids, as observed by Stern *et al.* (2000).

The chromatogram (Fig. 1 (b)) of the archaeological residue is far more complex than that of the modern pistacia resin (Fig. 1 (a)). Although it must be acknowledged that compositional changes in the resin produced by the plants may have changed over time, the most likely cause is diagenetic degradation of the original resin. The presence of an unresolved complex mixture in the archaeological resins, which raises the chromatographic baseline at similar retention times to the triterpenoids, is attributed to degraded components that are not resolved into

discrete peaks. As noted by others (Mills and White 1994; van der Doelen *et al.* 1998), moronic acid (methyl ester O) is relatively stable and is therefore the most abundant triterpenoid in the ancient resin. Conversely, 18 $\alpha$ -oleanonate (methyl ester S), 3 $\alpha$ -acetoxy-isomasticadienolate (methyl ester X) and 3 $\alpha$ -acetoxy-masticadienolate (methyl ester Y) are only present in the modern resin. Minor components reported by others, such as methyl masticadienolate (Papageorgiou *et al.* 1997), tirucallol and  $\beta$ -amyryn (Mills and White 1989), were not observed in this study, presumably due to degradation, co-elution with major components or heterogeneity between different resins. There are additional components that are only present in the archaeological resin; all but two (P and R) of these components identified as discrete peaks are of shorter retention time than methyl moronate (O), indicating lower molecular weight and polarity due to loss of functionality (Table 2). One of these components, 28-norolean-17-en-3-one (J), can be formed from oleanonic acid (methyl ester Q) using a mechanism of decarboxylation followed by a hydrogen shift (Pastorova 1997, 104). Two components (P and R) are characteristic of aged triterpenoid varnishes (van der Doelen *et al.* 1998): they are present in the modern resin in trace amounts, but are of significant abundance in the archaeological samples. These compounds have a prominent base peak at  $m/z$  143 (Table 2), which is likely to originate from the side-chain of ocotillone-type molecules (van der Doelen *et al.* 1998). Unfortunately, they co-elute with other components, so that their absolute identification is not possible.

#### *Heating experiments and the use of Pistacia as incense*

Serpico and White (2000) suggest a correlation between those resins described as charred, darkened and brittle and the occurrence of 28-norolean-17-en-3-one (J). Figure 2 (a) shows the percentage areas of the base peaks for each of the major components from modern *Pistacia lentiscus* resin heated for 30 min at different temperatures. Although this rudimentary heating experiment cannot faithfully reproduce the heating in antiquity, an increase in the percentage composition of 28-norolean-17-en-3-one with increasing temperature is clearly seen. At the lower temperatures, all components are present and their compositions are similar to that of the unheated resin. Isomasticadienonic acid and masticadienonic acid are the first triterpenoids to be degraded at 300°C. At 400°C, of the components measured here, only 28-norolean-17-en-3-one survives. The unheated sample has the lowest amounts of 28-norolean-17-en-3-one, indicating no detectable molecular alteration due to the sealing of the melting point tube or during the analysis.

Other triterpenoids from the archaeological samples (28-nor-17,12-olean-dien-3-one (F) and 28-nor-12-olean-3-one (G)) were not observed in the modern heated samples, and the unknown components, P and R, were not shown to increase with heating. It is therefore likely that these are not affected by thermal degradation processes. Although the relative composition of 28-norolean-17-en-3-one increases with heating, unfortunately, when archaeological examples of censers and unheated amphorae are compared, there is no trend of increased 28-norolean-17-en-3-one (J) with the suggested use as censers (Fig. 2 (b)). In addition, there is considerable variation in the relative composition of the resins when sub-samples from the same sherd are analysed. Therefore, although this component is produced during heating, this does not reflect the archaeological evidence and is unlikely that it can be used as a 'biomarker for heating' in this archaeological context. One reason for this difference might be further loss of 28-norolean-17-en-3-one, either by volatilization—which is unlikely, given its molecular weight—or by subsequent diagenetic degradation. However, of interest is Figure 3, which shows the mass chromatogram produced from the  $m/z$  453 fragment ion of the pistacia residue



Table 2 Peak assignment, structure, molecular formulae, reference to identical literature or authentic standard data and mass spectral data for triterpenoids identified in this study

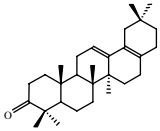
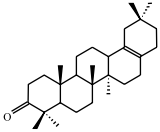
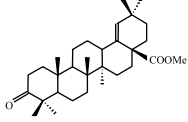
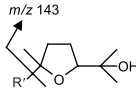
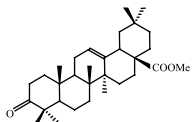
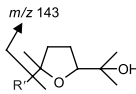
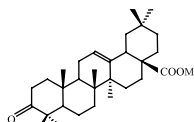
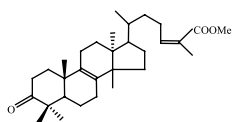
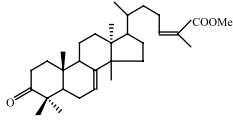
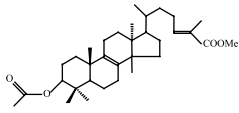
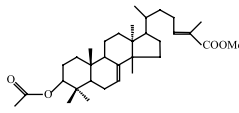
Peak	Assignment and structure	Formulae	Ref.*	M <sup>z</sup>	bp	Diagnostic and significant ions m/z (Relative abundance %)
A				370(27)	161	355(20), 341(20), 311(24), 299(29), 297(23), 267(30), 245(96), 205(41), 189(26), 173(91), 164(42), 161(100), 135(44), 109(45), 107(41), 81(61), 69(68)
B				358(31)	95	315(75), 297(8), 227(3), 205(41), 109(58), 107(42), 95(100), 81(65), 81(65), 67(57), 55(56)
C				374(33)	95	342(26), 327(11), 299(24), 207(19), 205(71), 189(28), 164(36), 147(40), 135(45), 121(47), 107(48), 95(100), 81(89), 55(86)
D				360(14)	95	343(6), 327(9), 317(48), 299(71), 191(57), 189(58), 135(57), 95(100), 81(79), 55(54)
E				384(20)	55	358(21), 340(19), 299(15), 189(77), 135(55), 121(64), 107(84), 95(89), 55(100)
F	28-norolean-12, 17-dien-3-one	C <sub>29</sub> H <sub>44</sub> O	1	408(100)	408	399(35), 393(18), 269(25), 241(40), 189(41), 133(56)
						
G	28-norolean-en-3-one	C <sub>29</sub> H <sub>46</sub> O		410		
H					424	440(20), 424(100), 409(11), 381(11), 255(75), 189(43), 163(63), 105(26)
I	28-norolean-en-3-one	C <sub>29</sub> H <sub>46</sub> O		410(7)	204	395(3), 205(21), 204(100), 191(19), 189(39), 175(15), 115(28), 55(17)
J	28-norolean-17-en-3-one	C <sub>29</sub> H <sub>46</sub> O	1, 2	410(20)	163	395(8), 191(65), 175(22), 163(100), 55(35)
						
K				466(22)	202	406(13), 391(13), 299(12), 239(18), 202(100), 187(16), 133(18), 132(23), 55(22)
N					407	466(52), 421(10), 407(100), 369(13), 255(24), 247(40), 215(32), 205(30), 189(60), 187(68), 133(80), 105(61), 95(63), 55(88)
O	Methyl moronate	C <sub>31</sub> H <sub>48</sub> O <sub>3</sub>	2, 4, 5	468(6)	189	453(1), 262(8), 249(21), 205(13), 203(29), 189(100), 119(23)
						

Table 2 (continued)

Peak	Assignment and structure	Formulae	Ref.*	$M^+$	bp	Diagnostic and significantions $m/z$ (Relative abundance %)
P	 $m/z$ 143				143	Co-elutes with O and Q
Q	Methyl oleanonate 	$C_{31}H_{48}O_3$	2, 4, 5	468(3)	203	453(1), 409(5), 262(27), 249(10), 203(100), 189(38), 133(20)
R	 $m/z$ 143				143	Co-elutes with Q
S	Methyl 18 $\alpha$ -oleanonate 	$C_{31}H_{48}O_3$	4	468	203	Identical mass spectra to Q, but later retention time
U	Methyl isomasticadienonate 	$C_{31}H_{48}O_3$	4, 5	468(13)	453	453(100), 435(9), 421(29), 393(10), 257(34), 121(43), 95(66), 81(32), 55(57)
W	Methyl masticadienonate 	$C_{31}H_{48}O_3$	3, 4, 5	468	453	Identical mass spectra to U, but later retention time
X	Methyl 3 $\alpha$ -acetoxy-isomasticadienolate 	$C_{33}H_{52}O_4$	4	512(3)	437	453(2), 437(100), 241(18), 189(30), 127(30), 95(55), 55(41)
Y	Methyl 3 $\alpha$ -acetoxy-masticadienolate 	$C_{33}H_{52}O_4$	4	512	437	Identical mass spectra to X, but later retention time

\* 1 = Pastorova (1997), 2 = Budzikiewicz *et al.* (1963), 3 = authentic standard, 4 = Papageorgiou *et al.* (1997), 5 = Mills and White (1989).

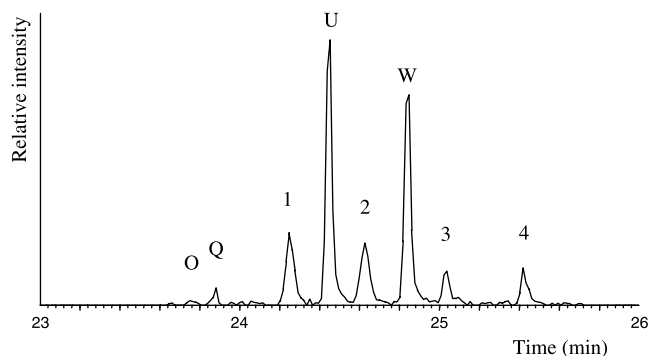


Figure 3 Partial mass chromatograms of  $m/z$  453 of extract from bowl sherd TA130.

from the inner surface of a locally produced bowl (TA130). In addition to methyl moronate (O), methyl oleanonate (Q), methyl isomasticadienonate (U) and methyl masticadienonate (W), other peaks are seen at  $m/z$  453 (peaks 1–4, Fig. 3). These additional peaks have been found in seven (MS132p, TA65, TA8, TA88, TA103, TA130 and TA13) out of 10 bowls, and are not observed in any of the pistacia residues from Canaanite amphorae or a suspected Canaanite sherd believed to have been re-used as a censer (TA208#90). Of interest is sherd TA96 (bowl), which did not show any archaeological evidence for heating. Due to co-elution with other components and their low abundance, the molecular structure of these additional components has not been identified, although they are likely to be isomers of isomasticadienonic and masticadienonic acids. However, when modern *Pistacia lentiscus* resin was heated, the additional  $m/z$  453 peaks were observed at 250°C and 300°C, but at 400°C they had disappeared. This could be indicative of a smouldering process, but further experimental work will be required to establish the conditions of heating, such as the duration and temperatures employed. However, it appears likely that the composition of the resin is changed during heating, and that in some circumstances the multiple  $m/z$  453 peaks are preserved in the archaeological record, whilst the increased 28-norolean-17-en-3-one may not be retained.

#### CONCLUSIONS

A number of characteristic triterpenoids identify all the visible and ceramic absorbed resinous deposits associated with Canaanite amphorae and locally produced bowls as *Pistacia* spp. resin. Archaeological evidence indicates that the Canaanite amphorae were used for transport and the locally produced bowls as incense burners. The terpenoid compositions of the archaeological samples are far more complex than that of the modern resin, due to diagenetic degradation of the archaeological resin. This process removes some components found in the modern resin and generates novel triterpenoids. No other resin types were observed and there was no evidence of mixing with oils or fats. Experimental heating of modern pistacia resin results in a relative increase of 28-norolean-17-en-3-one and the production of a number of unidentified components with a mass spectral base peak at  $m/z$  453. However, the relative abundance of 28-norolean-17-en-3-one from these archaeological samples does not match the archaeological evidence for the heating of the associated sherds. Nevertheless, the components with a mass spectral base peak at  $m/z$  453 are associated with locally produced bowls and are not observed in Canaanite amphorae.

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