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Gas chromatography/mass spectrometry and pyrolysis-gas chromatography/mass spectrometry for the chemical characterisation of modern and archaeological figs (*Ficus carica*)

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ABSTRACT

Gas chromatography/mass spectrometry (GC/MS) after alkaline hydrolysis, solvent extraction and trimethylsilylation, and analytical pyrolysis using hexamethyldisilazane (HMDS) for in situ derivatisation followed by gas chromatographic/mass spectrometric analysis (Pyrolysis-silylation-GC/MS) were used to investigate the hydrolysable and soluble constituents, and the polymerised macromolecules of an archaeological fig (*Ficus carica*) recovered in Zaragoza (Spain), as well as of modern figs. The main aim was to study the compositional alterations undergone by the fig tissues in a particular archaeological environment: the fig was in a vessel and covered by a layer of a mixture of orpiment and gypsum. A comparison between the GC/MS results from modern and archaeological figs revealed that degradative reactions took place, leading to the disappearance/depletion of reactive (unsaturated fatty acids) and sensitive compounds (phytosterols and triterpenes). Py-silylation-GC/MS data provided evidence of a significant degradation of the saccharide and lipid components of the fig tissue, which left a residue enriched in polyphenols and polyesters.

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1. Introduction

Botanical remains such as seeds, fruits, cereals, vegetable fibres and wood tools are important archaeological findings. These remains are easily susceptible to attack by fungi, bacteria and insects, as well as by chemical processes due to the burial/conservation environments. For this reason, botanical remains are rare at archaeological sites. However, particular environmental conditions, such as very dry or cold and waterlogged conditions, allow botanical remains to survive biological and chemical attack. Microscopic analysis of the morphology and chemical analyses of the composition can provide not only information on the diagenetic alterations undergone by the botanical materials in an archaeological context, but can also provide information for the recovery and future conservation of these remains. To date most chemical research has been undertaken on remains of a fossil origin, mainly to obtain geological information for the reconstruction of paleoecological and depositional environments, and for the preservation of organic matter [1–7]. The work that has been carried out on archaeological botanical remains has mainly concerned the study of wood [8–14], while other types of findings have rarely been considered [15–17].

In this study we investigated the chemical composition of an archaeological fig recovered in Zaragoza (Spain), in an Islamic context dating back to the 11th century AD. The fig was found inside a small glazed ceramic pot, which was possibly part of a chemical preparation for pigment or medical purposes. The fig remains were preserved in a very particular environment, given that they were recovered from a small (65 mm high, maximum diameter of 66 mm) glazed ceramic vessel and covered by a layer of inorganic compounds, a mixture of orpiment (arsenic sulphide, As_2S_3) and gypsum (calcium sulphate, $CaSO_4{\cdot}2H_2O$) [18].

The main aim of this study was to chemically characterise the fig remains and to gain information on the diagenetic alterations undergone by the fig tissues in this archaeological environment.

Figs, like other fruits, are complex plant materials containing small organic molecules (acyl-lipids, waxes, phytosterols, carotenoids and triterpenes) and biopolymers [19,20]. The biopolymers consist mainly of cellulose, hemicellulose, pectins, lignin and polyphenols [20]. Due to the complex chemical composition of vegetable tissues, we used analytical techniques based on gas chromatography/mass spectrometry (GC/MS) to determine and compare the molecular composition of the archaeological fig and of modern specimens. GC/MS after alkaline hydrolysis, solvent extraction and trimethylsilylation were used to investigate

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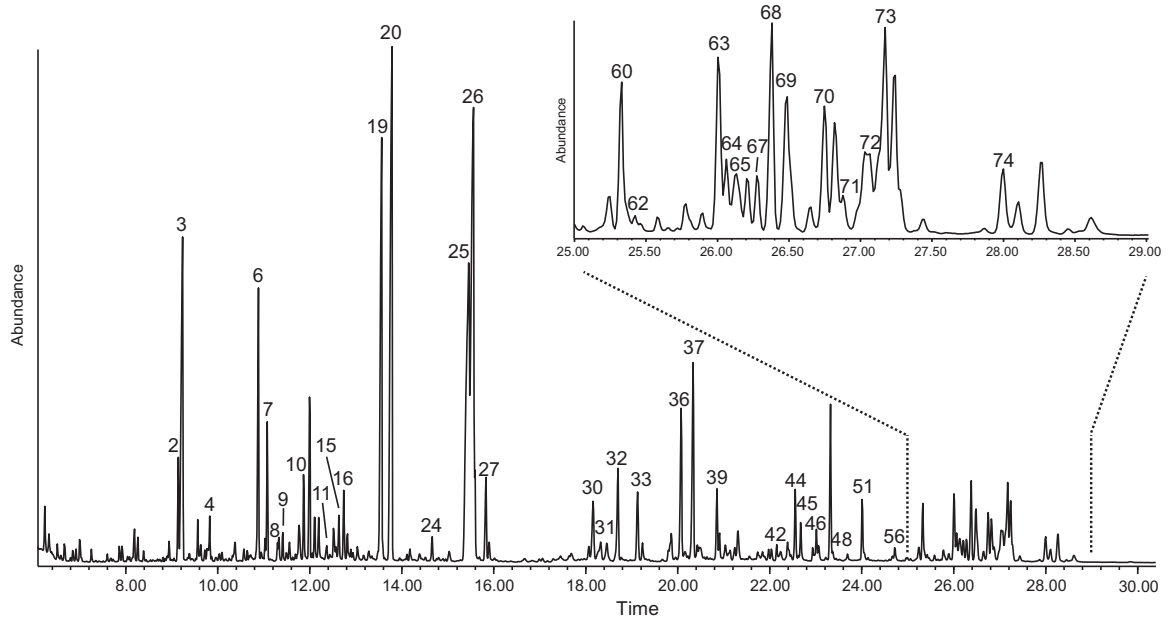

Fig. 1. TIC chromatogram of the hydrolysable and soluble components of a modern fig specimen after derivatisation with BSTFA. Peak identification is reported in Table 1.

the hydrolysable and soluble constituents. The highly polymerised macromolecules were studied through analytical pyrolysis using in situ thermally-assisted derivatisation followed by gas chromatographic/mass spectrometric analysis (Py-GC/MS). In the literature, many papers report on the Py-GC/MS analysis of complex macromolecules in samples of botanical origin [21], thus confirming the reliability and potentiality of this technique. Although in the literature the application of in situ derivatisation methods of the pyrolysis products is limited, it can be performed to increase the volatility of pyrolysis products for GC/MS analysis, thus improving the analytical response by accelerating the transfer of the products to the GC column and limiting the possibility of thermal degradation. In particular, hexamethyldisilazane (HMDS) was selected as the silylating agent as it is efficient in adapting polar and non-volatile compounds for gas chromatographic analysis: numerous classes of natural organic substances such as lipids, lignin, polysaccharides and terpenoids [22–26] have been studied using HMDS as a silylating agent.

2. Samples and materials

Chemicals. All solvents were Carlo Erba (Milan, Italy) pesticide analysis grade. *n*-Hexadecane (internal standard, IS_1), tridecanoic acid, (internal standard, IS_2), hydrochloric acid (HCl), potassium hydroxide (KOH), hexamethyldisilazane (HMDS) and N,O-bis(trimethyl)silyltrifluoro-acetamide (BSTFA) containing 1% trimethylchlorosilane, were purchased from Sigma–Aldrich (Milan, Italy).

Standards. Dodecanoic acid (lauric), tetradecanoic acid (myristic), hexadecanoic acid (palmitic), octadecanoic acid (stearic), (Z)-9-octadecenoic acid (oleic), (Z)-11-eicosenoic acid (gondoic), (Z)-13-docosenoic acid (erucic), (Z,Z)-9,12-octadecadienoic acid (linoleic), (Z,Z,Z)-9,12,15-octadecatrienoic acid (linolenic), octanedioic acid (suberic), nonanedioic acid (azelaic), decanedioic acid (sebacic), and cholesterol (cholest-5-en-3β-ol) were supplied by Sigma (St. Louis, MO, USA), all with a purity >99%. Lupeol (lup-20(29)-en-3β-ol, purity >98%), β-sitosterol (5-Stigmasten-3β-ol, purity >95%), stigmasterol (3β-hydroxy-24-ethyl-5,22-cholestadiene, purity roughly 95%) were supplied by Sigma (St. Louis, MO, USA). α-amyrin (urs-12-en-3-ol) was supplied by Extransyntese (France) with a purity >99%.

Archaeological samples. Archaeological microsamples were collected under a stereoscopic microscope. The fruit microsamples were then crushed and homogenised in an agate mortar for the chromatographic analyses.

Modern fig specimens. Fresh fruits from the dark-purple common fig (*Ficus carica L.*) were collected in Pisa (Italy) and Zaragoza (Spain) in November 2009. The figs were dried in an oven at 105 °C for 15 h, and were finely cut and homogenised before the analyses.

3. Methods and instrumentation

GC/MS. The analytical procedure used to investigate the soluble and saponifiable components can be summarized as follows: sample (1–3 mg) was subjected to alkaline hydrolysis by adding 1 ml of hydro-alcoholic KOH (KOH in CH_3OH (10 wt.%)/KOH in H_2O (10 wt.%), 2:3), and heating at 60 °C for 3 h. After hydrolysis, neutral organic components were extracted with *n*-hexane (3 × 500 μl) and, after acidification with hydrochloric acid (10 M; to pH 2), the acidic organic components were extracted with diethyl ether (3 × 500 μl). The *n*-hexane and ether fractions were mixed, evaporated to dryness under a gentle stream of nitrogen and subjected to trimethylsilylation. This was achieved by mixing the dried aliquots with a derivatization internal standard solution (5 μl of tridecanoic acid solution, 140 $\mu g\,g^{-1}$) and then they were derivatised with 20 μl of BSTFA (at 60 °C, 30 min), using 150 μl *iso*-octane as the solvent. After adding 10 μl of *n*-hexadecane solution (80 $\mu g\,g^{-1}$) as an internal standard for the injection, 2 μl of the solution were analysed by GC–MS. For the gas chromatographic separation, a 6890N GC System Gas Chromatograph (Agilent Technologies) coupled with a 5975 Mass Selective Detector (Agilent Technologies) single quadrupole mass spectrometer equipped with a PTV injector was used. The PTV injector was equipped with a glass PTV liner (multi baffle, deactivated, 1.5 mm, Agilent Technologies). The mass spectrometer was operated in EI positive mode (70 eV, scanning *m*/*z* 50–700). The MS transfer line temperature was 280 °C; the MS ion source temperature was kept at 230 °C and the MS quadrupole temperature at

Table 1
Compounds identified by GC/MS in the modern fig specimen and in the archaeological fig. Numbers refer to the peak numbers in the chromatograms shown in Figs. 1 and 3.

n.	Compound	Modern fig	Archaeological fig
1	Arsenic acid-3TMS		X
2	2-Hydroxy-3-phenylpropionic acid-2TMS	X	
3	ST_1 (hexadecane)	X	X
4	Dodecanoic acid-TMS	X	X
5	Octanedioic acid-2TMS		X
6	ST_2 (tridecanoic acid-TMS)	X	X
7	Isovanillic acid-2TMS	X	X
8	m-Coumaric acid-2TMS	X	
9	Nonanedioic acid-2TMS	X	X
10	Tetradecanoic acid-TMS	X	X
11	Decanedioic acid-2TMS	X	
12	Pentadecanoic acid (branched isomer)-TMS		X
13	Pentadecanoic acid (branched isomer)-TMS		X
14	Pentadecanoic acid-TMS		X
15	Gluconic acid, 2,3,5,6-tetrakis-O-(trimethylsilyl)-, lactone	X	
16	Gluconic acid, 2,3,5,6-tetrakis-O-(trimethylsilyl)-, lactone isomer	X	
17	p-Coumaric acid-2TMS		X
18	Sulfur (S8)		X
19	9-Hexadecenoic acid-TMS	X	
20	Hexadecanoic acid-TMS	X	X
21	Isoferulic acid-2TMS		X
22	Heptadecanoic acid (branched isomer)-TMS		X
23	Heptadecanoic acid (branched isomer)-TMS		X
24	Heptadecanoic acid-TMS	X	X
25	9,12-Octadecadienoic acid-TMS	X	
26	9-Octadecenoic acid-TMS	X	X
27	Octadecanoic acid-TMS	X	X
28	Nonadecanoic acid-TMS		X
29	1-Eicosanol-TMS		X
30	ω-Hydroxy-hexadecanoic acid-2TMS	X	X
31	11-Eicosenoic acid-TMS	X	
32	Eicosanoic acid-TMS	X	X
33	10,16-Dihydroxy-methylhexadecanoate-2TMS	X	
34	Heneicosanoic acid-TMS		X
35	1-Docosanol-TMS		X
36	ω-Hydroxy-octadecenoic acid-2TMS	X	X
37	Coeluition of, 9-, 8-, 7-, 6-, 5-hydroxy,ω-hydroxy-hexadecanoic acid-3TMS	X	X
38	ω-Hydroxy-octadecanoic acid-2TMS		X
39	Docosanoic acid-TMS	X	X
40	Tricosanoic acid-TMS		X
41	1-Tetracosanol-TMS		X
42	9,10,18-Trihydroxy-methyloctadecanoate-3TMS	X	
43	ω-Hydroxy-eicosanoic acid-2TMS		X
44	Tetracosanoic acid-TMS	X	X
45	9,10-Epoxy-18hydroxy-octadecanoic acid-3TMS (Identified as corresponding methoxyhydrin compound)[a]	X	
46	9,10,18-Trihydroxy-octadecanoic acid-4TMS	X	
47	Pentacosanoic acid-TMS		X
48	1-Hexacosanol-TMS	X	X
49	ω-Hydroxy-docosanoic acid-TMS		X
50	Coprostanol-TMS		X
51	Hexacosanoic acid-TMS	X	X
52	Epicoprostanol-TMS		X
53	Coprostan-3-one		X
54	Cholesterol-TMS		X
55	Cholestanol-TMS		X
56	1-Octacosanol-TMS	X	X
57	ω-Hydroxy tetracosanoic acid-TMS		X
58	3,12-Dihydroxy-cholan-24-oic acid-methyl ester-2TMS		X
59	Ergosterol-TMS		X
60	Octacosanoic acid-TMS	X	X
61	24-Ethylcoprostanol-TMS		X
62	Stigmasterol-TMS	X	
63	β-Amyrin-TMS	X	
64	β-Sitosterol-TMS	X	X
65	Parkeol-TMS	X	
66	Stigmastanol-TMS		X
67	α-Amyrin-TMS	X	X
68	Lupeol-TMS	X	
69	Parkeyl acetate	X	
70	β-Amyrin acetate	X	
71	Tricontanoic acid-TMS	X	
72	α-amyrin acetate	X	
73	Lupeol acetate	X	
74	Psi-Taraxasterol-TMS	X	

[a]The epoxy compounds were converted into corresponding methoxyhydrin compounds during hydrolysis in the presence of methanol.

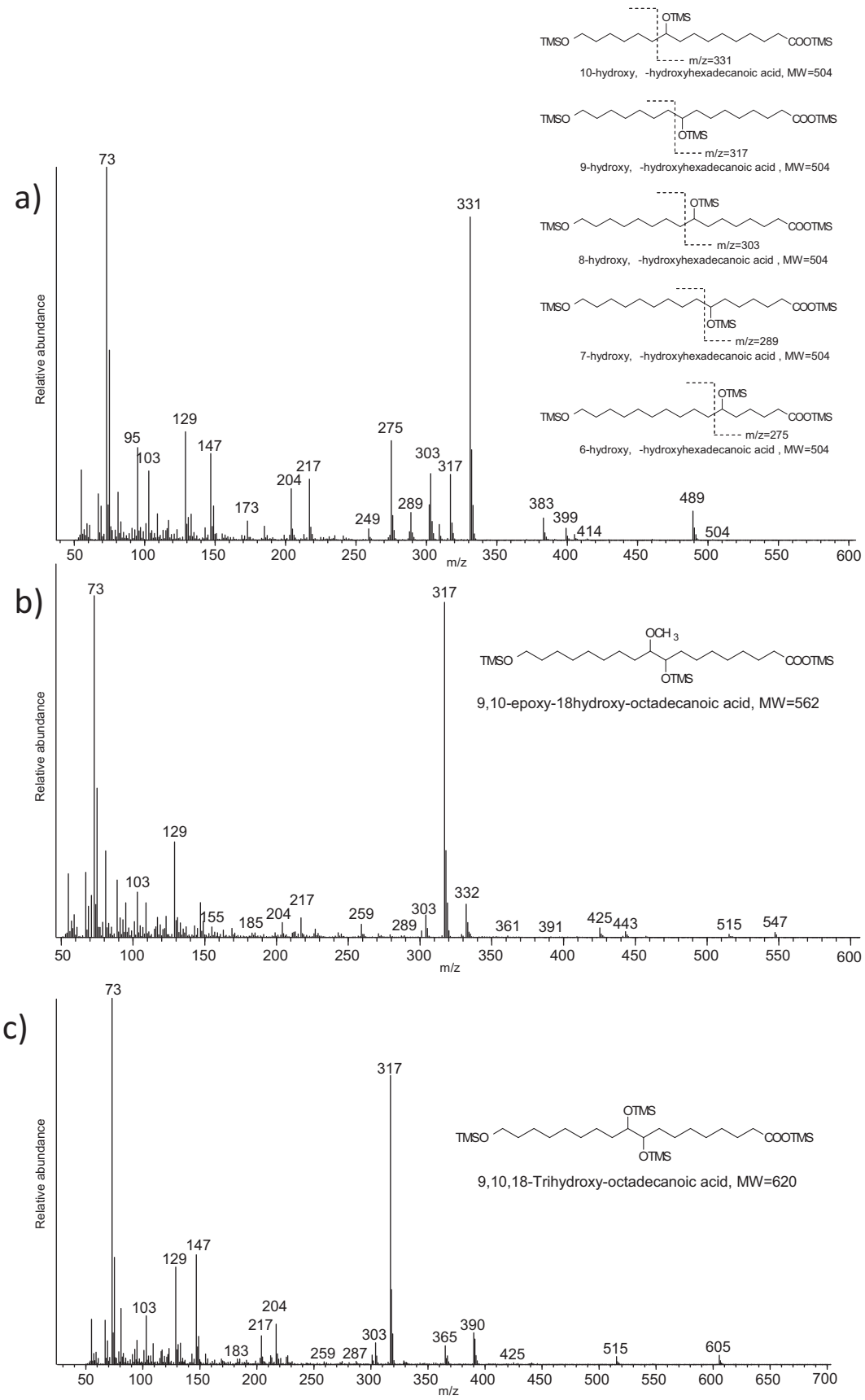

Fig. 2. Mass spectrum of TMS derivatives of 10-, 9-, 8-, 7- and 6-hydroxy,ω-hydroxy-hexadecanoic acids (coeluted mass spectrum) (a); 9,10-epoxy-18hydroxy-octadecanoic acid identified as corresponding methoxyhydrin compound (b); and 9,10,18-trihydroxy-octadecanoic acid (c).

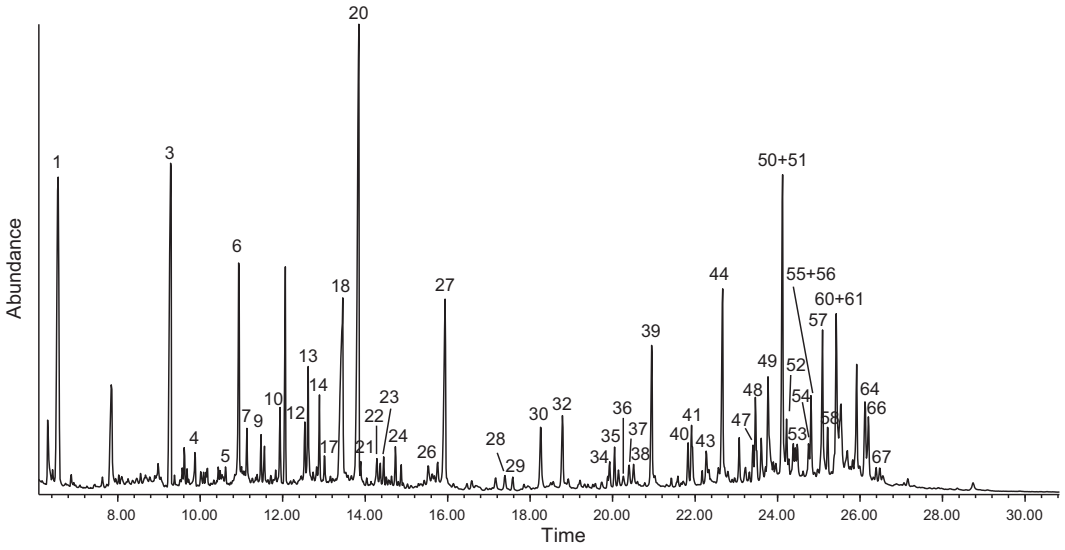

Fig. 3. TIC chromatogram of the hydrolysable and soluble components of the archaeological fig after derivatisation with BSTFA. Peak identification is reported in Table 1.

150 °C. For the gas chromatographic separation, an HP-5MS fused silica capillary column (5% diphenyl–95% dimethyl-polysiloxane, 30 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, Agilent Technologies, Palo Alto, CA, USA) coupled with a deactivated silica pre-column (2 m × 0.32 mm i.d., J&W Scientific Agilent Technologies, Palo Alto, CA, USA) using a quartz press fit (press-fit connector 0.32 mm–0.25 mm, Agilent Technologies, Switzerland), was used. The PTV injector was used in splitless (purge valve time 0.7 min) mode at 280 °C. The chromatographic conditions were programmed as follows: 80 °C, isothermal for 2 min, 10 °C/min up to 200 °C, 200 °C, isothermal for 3 min, 10 °C/min up to 280 °C, 280 °C, isothermal for 3 min, 20 °C/min up to 300 °C, and 300 °C, isothermal for 30 min. The carrier gas was used in the constant flow mode (He, purity 99.9995%) at 1.2 ml/min.

Py-GC/MS. The sample (a few micrograms) was placed in a quartz tube, admixed with 5 μl hexamethyldisilazane (HMDS) and pyrolysed at 550 °C (pyrolysis time: 20 s). The pyrolyser (CDS Pyroprobe 5000 series) was coupled online with a 6890N GC System Gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled with a 5973 Mass Selective Detector (Agilent Technologies, Palo Alto, CA, USA) single quadrupole mass spectrometer. The pyrolyser interface was kept at 180 °C, the transfer line at 300 °C, and the valve oven at 290 °C. The mass spectrometer was operated in EI positive mode (70 eV, scanning *m*/*z* 50–650). The MS transfer line temperature was 280 °C; the MS ion source temperature was kept at 230 °C and the MS quadrupole temperature at 150 °C. For the gas chromatographic separation, an HP-5MS fused silica capillary column (5% diphenyl–95% dimethyl-polysiloxane, 30 m × 0.25 mm i.d., J&W Scientific Agilent Technologies, USA) with a de-activated silica precolumn (2 m × 0.32 mm i.d., J&W Scientific Agilent Technologies, USA) was used. The split-splitless injector was used in split mode at 300 °C, with a split ratio of between 1:10 and 1:20, depending on the sample dimensions. The injector was equipped with a glass liner (single taper, deactivated, 4 mm ID, Agilent Technologies). The chromatographic conditions were as follows: 30 °C isothermal for 8 min, 10 °C/min up to 240 °C and isothermal for 3 min, 20 °C/min up to 300 °C and isothermal for 30 min. The carrier gas (He, purity 99.9995%) was used in the constant flow mode at 1.0 ml/min.

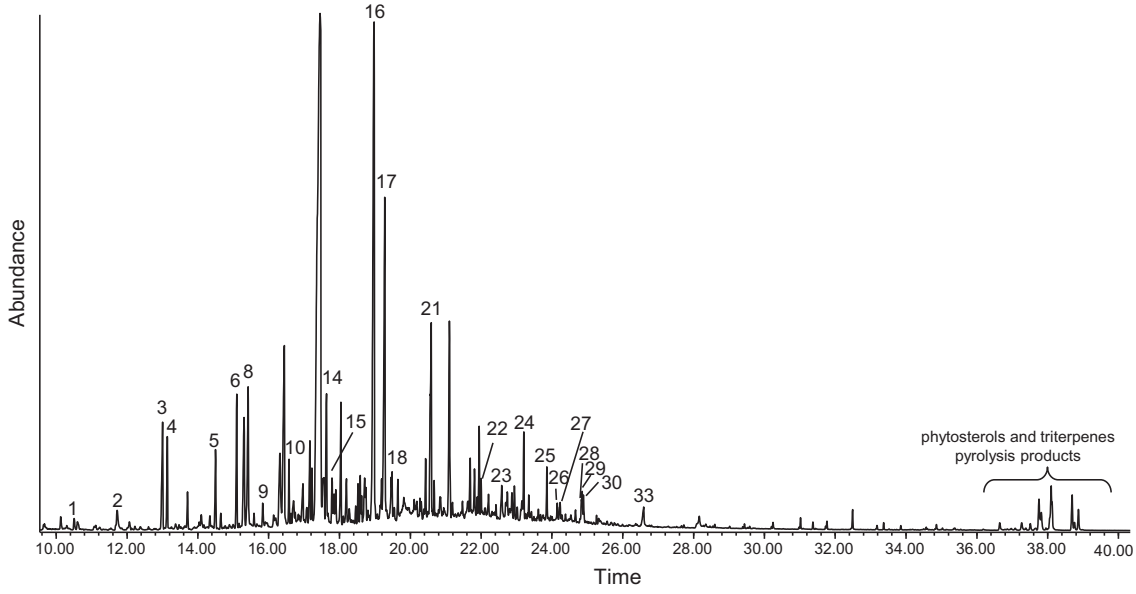

Fig. 4. Py(HMDS)-GC/MS profile of a modern fig specimen. Peak identification is reported in Table 2.

Table 2
Compounds identified by Py(HMDS)-GC/MS in the modern fig specimen and in the archaeological fig and their possible origin (S, saccharides; P, polyphenols). Numbers refer to the peak numbers in the pyrogram shown in Figs. 4 and 5.

n.	Compound	Possible source	Modern fig	Archaeological fig
1	Isovaleric acid-TMS		X	X
2	Valeric acid-TMS		X	X
3	Ethyleneglycol-2TMS	S	X	X
4	2-Furanmethanol-TMS	S	X	X
5	Phenol-TMS	P	X	X
6	2-Hydroxypropanoic acid-2TMS (lactic acid)	S	X	X
7	Caproic acid-TMS			X
8	2-Hydroxyethanoic acid-2TMS (glycolic acid)	S	X	X
9	o-Cresol-TMS	P	X	X
10	p-Cresol-TMS	P	X	X
11	Phenylmethanol-TMS			X
12	Arsenous acid-3TMS			X
13	Heptanoic acid-TMS			X
14	Resorcinol-2TMS	P	X	X
15	2-methoxyphenol-TMS (guaiacol)	P	X	X
16	Glycerol-3TMS		X	X
17	o-Pyrocatechol-2TMS	P	X	X
18	Nonanoic acid-TMS		X	X
19	4-Hydroxy-3-methoxybenzaldehyde-2TMS (vanillin)	P		X
20	4-Hydroxy-3-methoxypropenylbenzene-TMS (isoeugenol)	P		X
21	Sugar derivative	S	X	
22	Pyrogallol-3TMS	P	X	X
23	Sugar derivative	S	X	
24	Sugar derivative	S	X	
25	Sugar derivative	S	X	
26	Levoglucosan-3TMS	S	X	X
27	Sugar derivative	S	X	
28	Sugar derivative	S	X	
29	Sugar derivative	S	X	
30	Sugar derivative	S	X	
31	4-Hydroxy-3-methoxybenzoic acid-2TMS (vanillic acid)	P		X
32	Tetradecanoic acid-TMS			X
33	Hexadecanoic acid-TMS		X	X
34	Octadecanoic acid-TMS			X
35	Eicosanoic acid TMS			X
36	Docosanoic acid TMS			X
37	Chol-3-en-24oic acid-TMS			X
38	Tetracosanoic acid-TMS			X
39	Coprostanol-TMS			X
40	Cholesterol-TMS			X
	Phytosterols and triterpenes pyrolysis products		X	

GC/MS and Py-GC/MS analyses were repeated three times and the peak assignments were performed on the basis of the analysis of available authentic standards, by interpretation of mass spectra, comparison with mass spectral libraries (NIST 2.0 and Wiley275) and with published mass spectra.

4. Results and discussion

Fig. 1 shows the gas chromatogram of the modern fig, and Table 1 lists the compounds identified by GC/MS. The hydrolysable and soluble components of the modern fig specimens are mainly made up by saturated (C_{12}–C_{30} peaking at C_{16}) and unsaturated ($C_{16:1}$, $C_{18:2}$, $C_{18:1}$, $C_{20:1}$) even carbon-numbered monocarboxylic fatty acids, together with mono- and poly-hydroxymonocarboxylic and epoxy fatty acids. Fig. 2 shows some exemplificative mass spectra. The first mass spectrum corresponds to the mass spectrum of a co-elution mixture of five hydroxy acids with the same molecular weight: 10-, 9-, 8-, 7- and 6-hydroxy,ω-hydroxy-hexadecanoic acids. The peaks at *m*/*z* 331, 317, 303, 289 and 275 are due to the fragmentation (shown in Fig. 2a) from the α-cleavage relative to the trimethylsilyloxy ether group [27] of the various co-eluted hydroxy acids.

Plant sterols, namely stigmasterol and β-sitosterol, and triterpenes such as β-amyrin, α-amyrin, lupeol, parkeol and their acetates are also evident. The results are in good agreement with the literature, with all the identified compounds usually found in the plant membranes [23,28,29] and fig fruit and tree components [30]. The cuticular membranes such as cutin and suberin, made up of tridimensional biopolyesters, are particularly rich in mono- and poly-hydroxy and epoxy fatty acids [28,31].

Fig. 3 shows the gas chromatogram of the archaeological fig and Table 1 lists the compounds identified by GC/MS. The GC/MS analysis of the hydrolysable and soluble fractions of the archaeological fig revealed some compositional differences between the modern and ancient figs. Unsaturated fatty acids were practically absent and, in terms of phytosterols and triterpenes, only β-sitosterol and α-amyrin were evident; probably because they are among the major components of fig fruit [30]. This highlights that degradative reactions took place leading to the disappearance of reactive and sensitive compounds. Unsaturated and especially polyunsaturated fatty acids easily undergo oxidation at the double bonds via radical reactions, with the inclusion of oxygen in the acyl chain and carbon–carbon bond cleavage. As far as phytosterols are concerned, although they are very common compounds in the plant world, their tendency to oxidation and the fact that they are usually present in plant lipids in a low abundance, means that they rarely can be found in archaeological findings. The presence of arsenic acid and sulfur in the gas chromatogram of the archaeological sample can be explained by considering that they formed from the arsenic sulphide of the original sample in the acidification with HCl during the sample pre-treatment. A series of sterols, namely coprostanol,

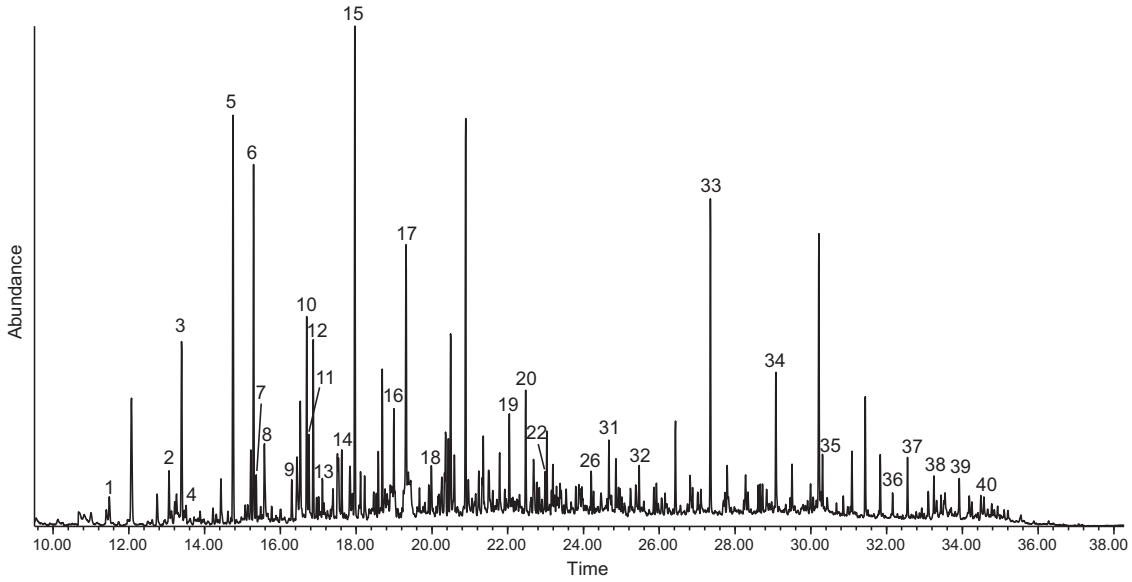

Fig. 5. Py(HMDS)-GC/MS profile of the archaeological fig. Peak identification is reported in Table 2.

epicoprostanol, coprostanone, cholesterol, cholestanol, ergosterol, 24-ethylcoprostanol and stigmastanol, were also evident. These compounds clearly highlight the presence of faecal matter, since they are considered as characteristic biomarkers of such matter [32–34]. The relative high abundance of coprostanol in the sample seems to suggest a human origin of the faecal matter [32,33]. These results might indicate that faecal matter was deliberately added to the fig in the small vessel or otherwise it may have come from sewage pollution. Actually, the analysis of samples collected from the mouth of the pot showed the presence of the same compounds reinforcing the hypothesis relative to an extraneous contamination.

The main pyrolysis products present in the pyrogram of the modern fig specimen are of a saccharide and phenolic nature (Fig. 4). Table 2 lists the compounds identified by Py-GC/MS in the modern figs. These pyrolysis products can be correlated to biopolymers such as cellulose, hemicellulose, pectins, lignin and polyphenols, which are the main constituents of fruits. Glycerol, released in the pyrolysis process from triacylglycerols, and pyrolysis products from phytosterols and triterpenes, all linkable to the lipid fraction of the fig, are well evident in the pyrogram.

In the pyrogram of the archaeological fig (Fig. 5 and Table 2 list the peaks identified), the distribution of the phenolic compounds is similar to that of the modern fig, although the relative abundance of the various compounds is different. The pyrogram is dominated by guaiacol.

There was a considerable reduction in the saccharide and lipid pyrolysis products. This provides evidence of a substantial degradation of the saccharide and lipid components of the fig tissue which leaves a residue enriched in polyphenols. In any case, levoglucosan (1,6-anhydro-β-D-glucopyranose), which is a well-known cellulose pyrolysis marker, is clear in the pyrogram, suggesting that part of the cellulose had been preserved.

The presence of faecal matter, already highlighted by GC/MS analysis, was confirmed by Py-GC/MS, with peaks due to cholenoic acid, coprostanol and cholesterol, which are evident in the pyrogram.

5. Conclusions

GC/MS and Py-GC/MS investigations on modern figs revealed the presence of soluble and saponifiable fractions mainly made up of lipid (monocarboxylic fatty acids, hydroxy-fatty acids and phytosterols) and terpenoid compounds, and a polymeric fraction made up of polysaccharides and polyphenols. Analysis of the archaeological fig revealed that the fig tissue was a residue enriched in polyphenols and polyesters. This means that in the archaeological environment several reactions took place that led to the disappearance/depletion of reactive unsaturated fatty acids and sensitive compounds such as phytosterols, triterpenes and polysaccharides.

A similar behaviour has been found in the study by analytical pyrolysis of waterlogged archaeological wood [14] as well as archaeological seeds [16] that shown to undergo an extensive loss of polysaccharides. The anoxic condition in the first case and the arid environment in the second one limited the action of microorganisms and a consequent extensive degradation. In our case, the presence of the inorganic layer (orpiment and gypsum), which may ensure anoxic conditions, and the poisonous properties and the toxicity of the arsenic to insects, bacteria, and fungi may probably have favoured the preservation of the organic matter.

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