Chemical curing in alkyd paints: An evaluation via FT-IR and NMR spectroscopies

G. Bartolozzi et al. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 118 (2014) 520–525

oil paint made by *Winsor & Newton*, French ultramarine (PB29)

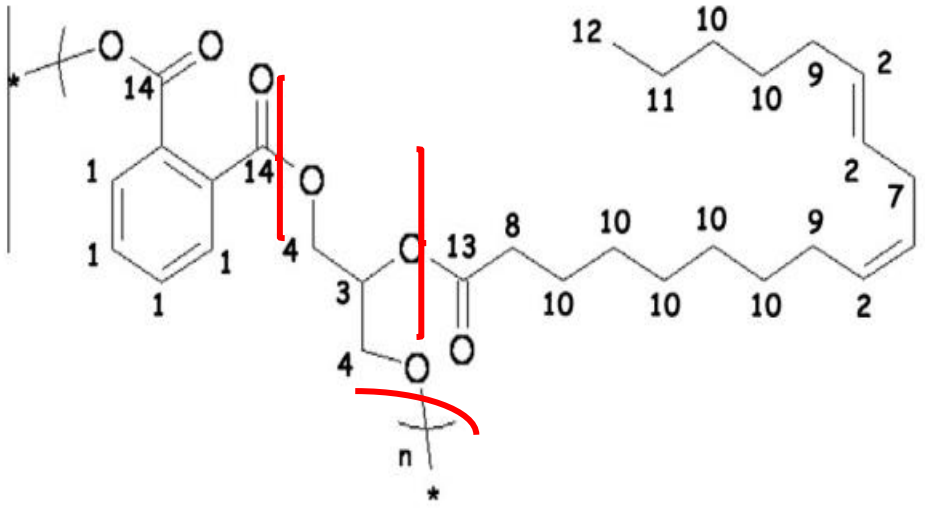


Fig. 4. Structure of a generic alkyd resin; the numbers correspond to the different types of H or C as reported in Table 2.

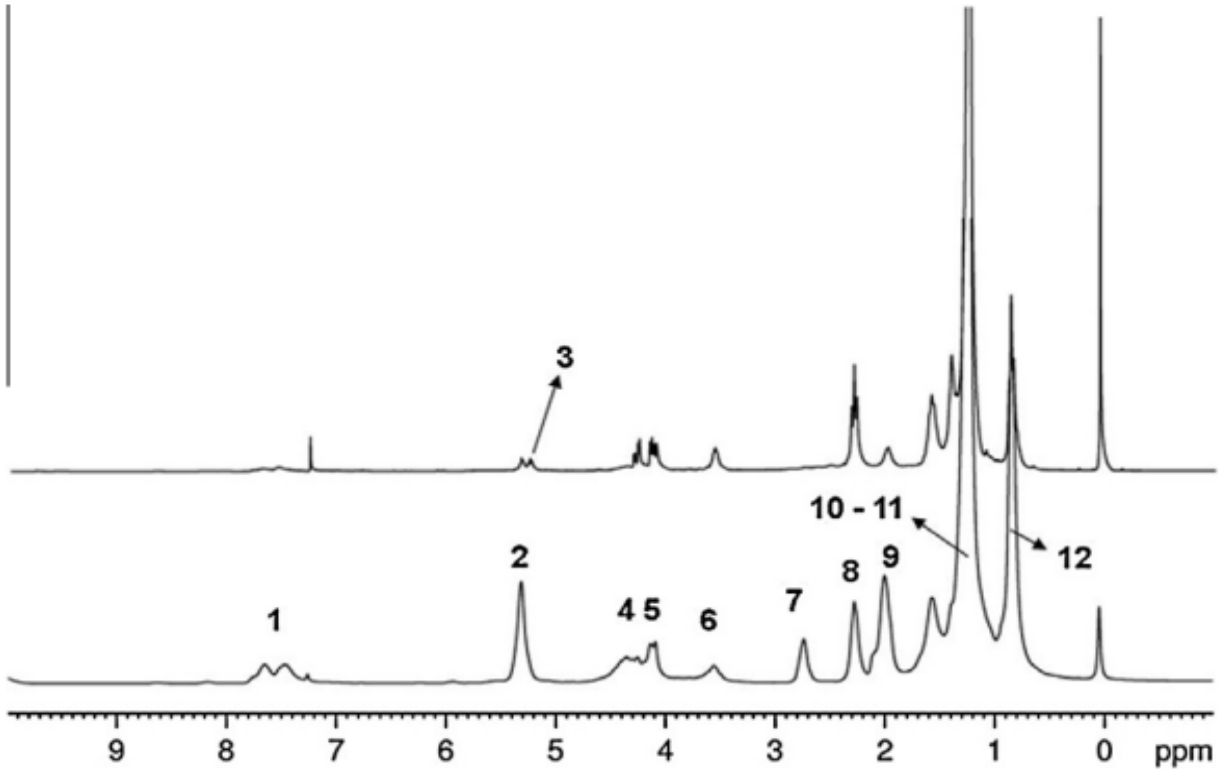


Fig. 5. ^{1}H NMR spectra of t_0 (bottom) and t_9 (10 weeks) of French Ultramarine extracts in chloroform. Peak numbers are in agreement with Table 2 and Fig. 4.

Table 2
Chemical shift (δ) of the main ^{1}H and ^{13}C NMR resonances (see Fig. 4) in the t_0 sample extracted in $CDCl_3$ [25–28].

	Δ		Group	Assignment
	^{1}H	^{13}C		
1	7.8–7.4	131.7–129.9; 129.5–128.5	*Ph*CO	Aromatic phthalate
2	5.31	129.9; 129.7; 128.3; 128.1; 127.9; 127.8	*CH=CH*	Unsaturated vinyl protons
3	5.25	69.0	*CH*OCOR	Triglycerides
4	4.34–4.18	62.8	CH_2OCOR	Triglycerides
5	4.34–4.13	62.4	CH_2OCOR	1,2-diglycerides
6	3.57	71.9	CH_2OH	1,2-diglycerides
7	2.76	25.6	CH=CHCH_2CH=CH	Diallyl
8	2.30	34.1	CH_2COOR	Mono- and diesters
9	2.00	27.2	CH_2CH=CH	Unsaturated fatty acids
10	1.37–1.20	30–28.8; 31.9; 31.5	$(CH_2)_x$	Fatty acids and diacids
11	1.37–1.20	22.7–22.6	C-n-1 CH_2CH_3	Acyl chains
12	0.91–0.87	14.2	CH_3	Acyl chains
13		173.9–172.5	CH2*C*OOR	Aliphatic carbonyl ester
14		168.0–166.0	Ph*C*OOR	

Φυσική ξήρανση 96 h. Χημική μετατροπή 70 d, έναρξη διαδικασίας γήρανσης (ageing).

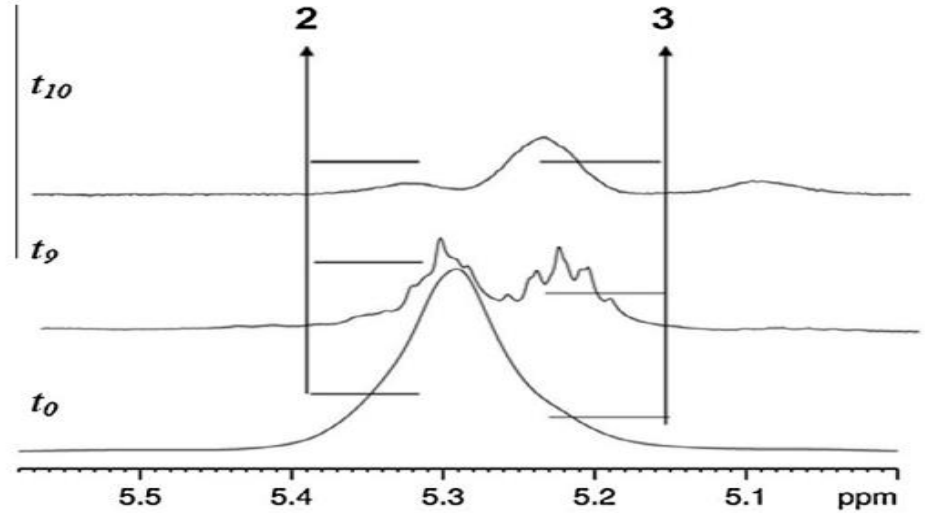


Fig. 6. Progressive decrease in the signal due to the vinyl proton (2) in ^{1}H NMR spectra over one year of ageing.

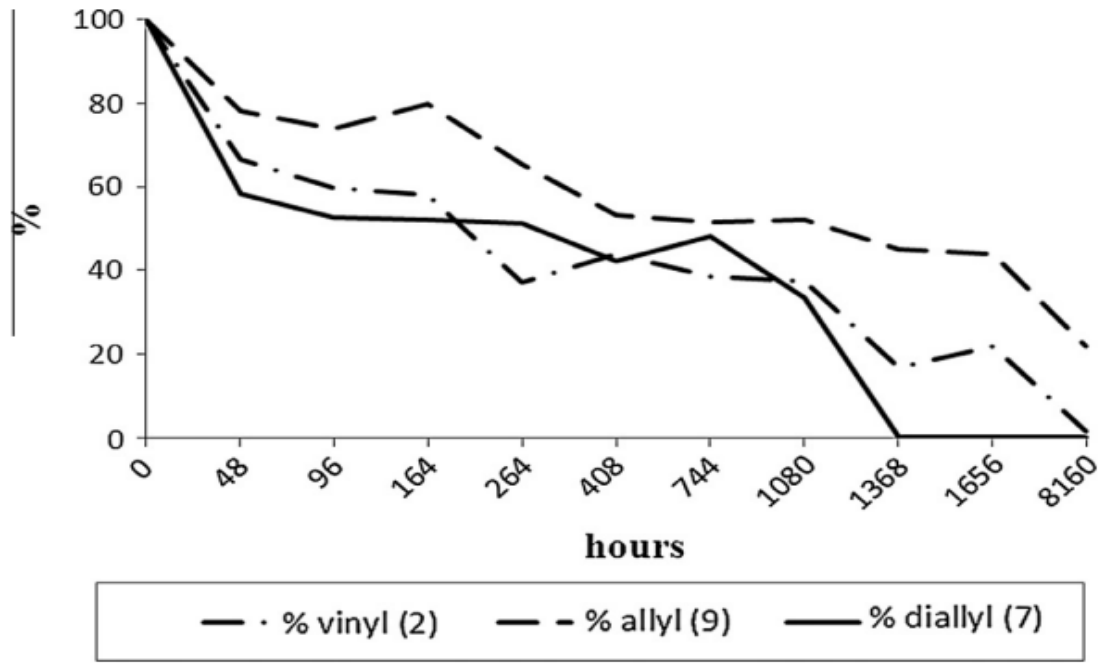


Fig. 7. Percentage decrease in vinyl protons (peak 2), in the double allyl protons (peak 7), in allyl protons (peak 9) in ^{1}H NMR spectra over 1 year.

Development of brewing science in (and since) the late 19th century: Molecular profiles of 110–130 year old beers

Sebastian Meier etc.

Food Chemistry 183 (2015) 227–234

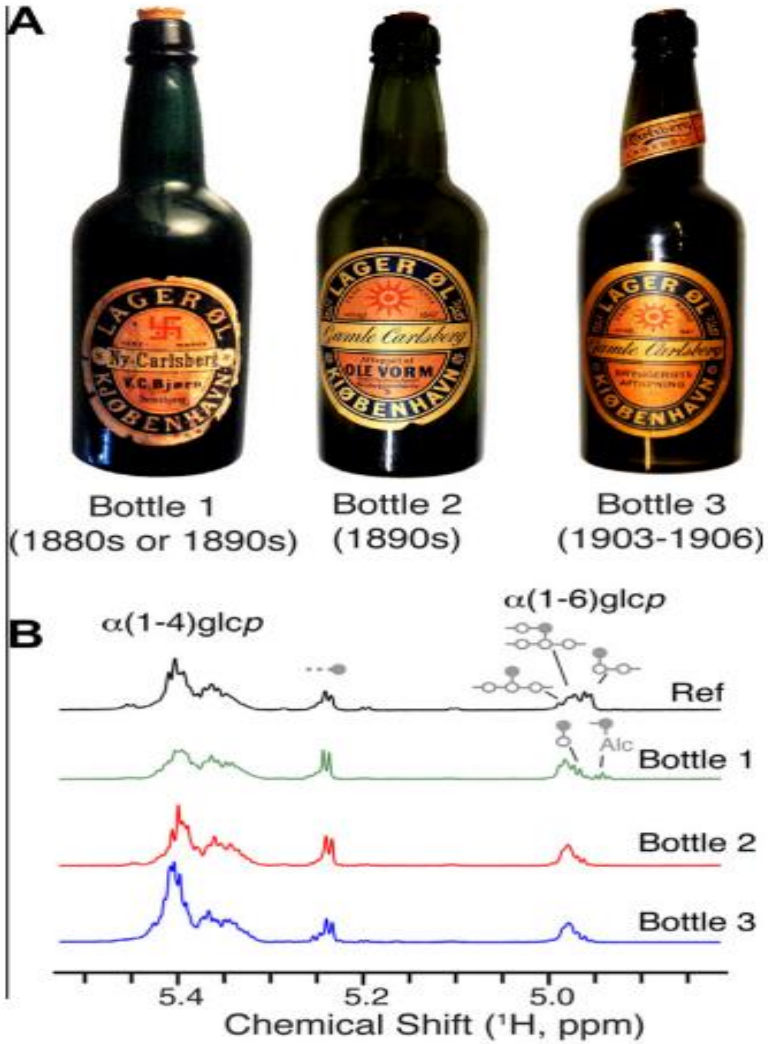
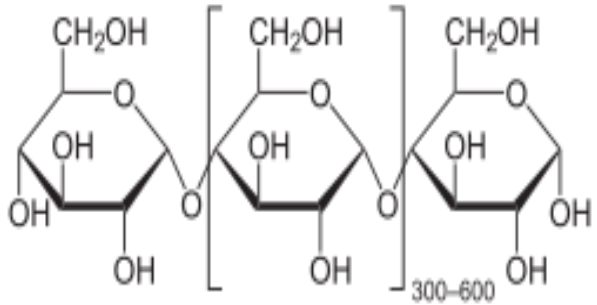


Fig. 1. (A) Historic bottles from the Carlsberg Museum bottle collection filled with original lager beer. Time ranges for their filling were deduced from the names of fillers given on the labels. (B) ^{1}H NMR spectrum of the spectral region containing α-anomeric sugar signals from starch fragments in the present-day reference and historic beer samples of the bottles shown in (A). The hump at 5.35 ppm results from α(1–4) signals near branch points. Horizontal lines designate α-(1–4)glycosidic bonds, vertical lines designate α-(1–6) glycosidic bonds and circles designate glucopyranosyl units, where the filled circle yields the signal in a structural motif indicated by open circles. (C) ^{1}H NMR spectrum of the aliphatic spectral region. (D) ^{1}H NMR spectrum of the aromatic spectral region. Residual d_2-acetate signal derives from addition of d_3-acetate for stabilizing sample pH and internal referencing. The ^{1}H NMR spectra are normalized relative to the d2-acetate signal.



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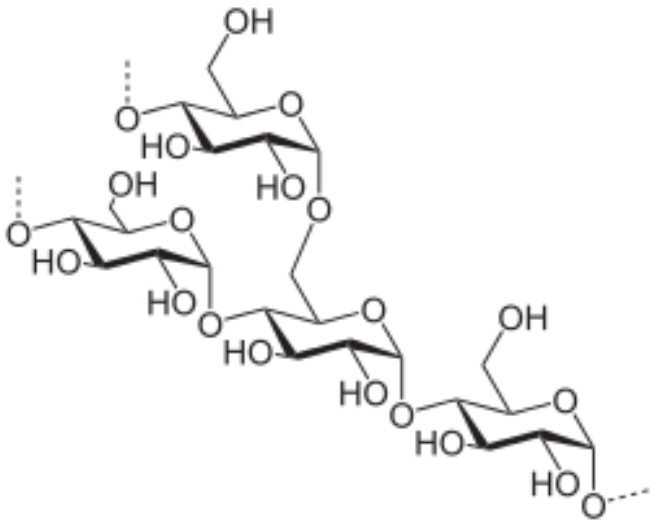

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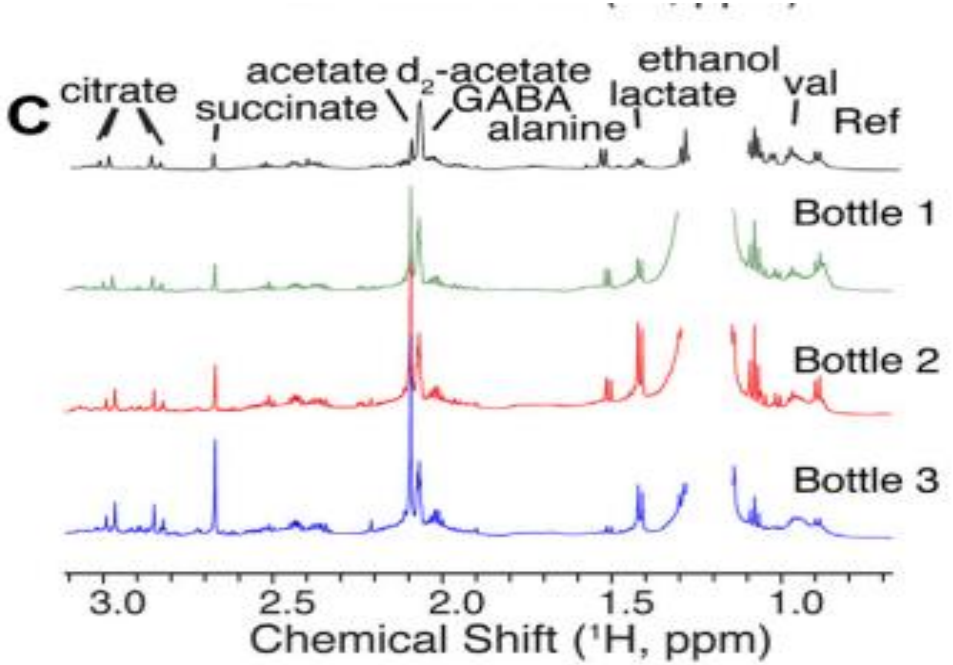

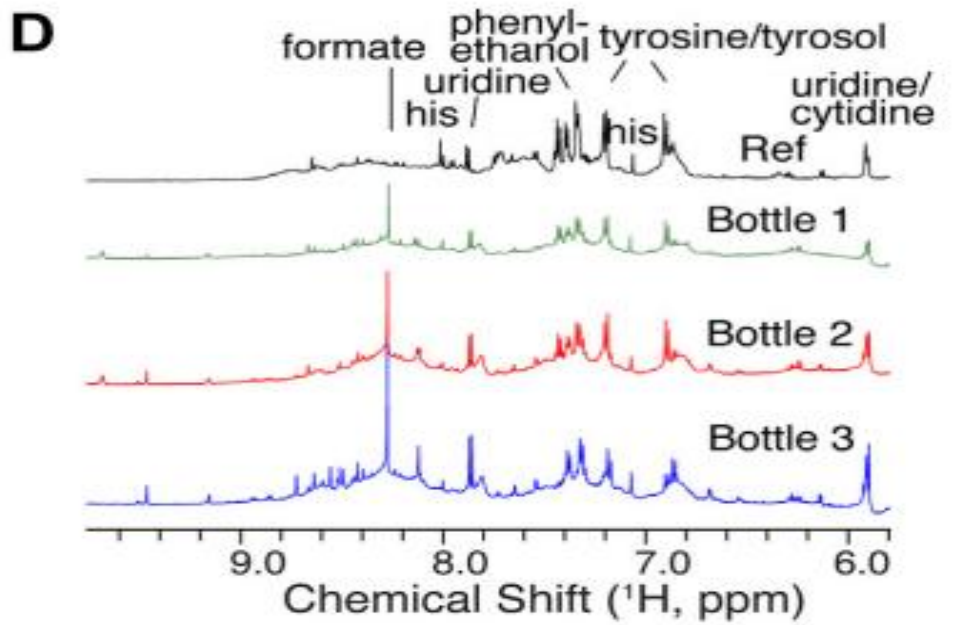

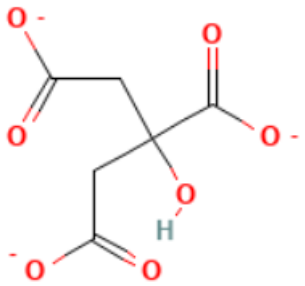

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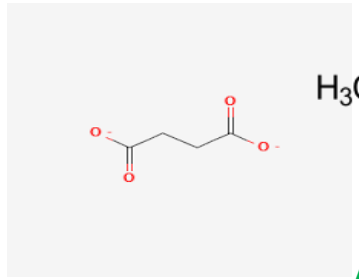

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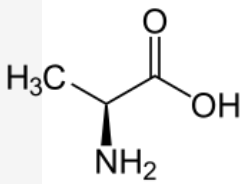

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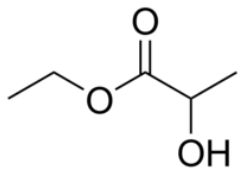

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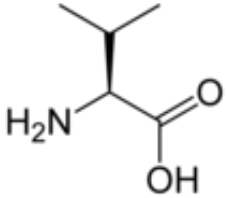

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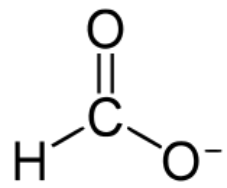

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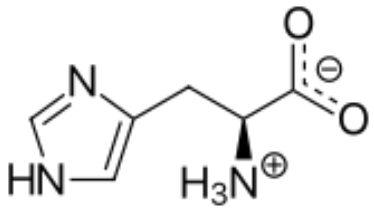

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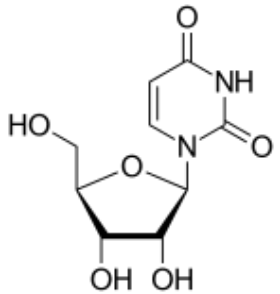

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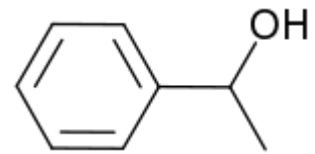

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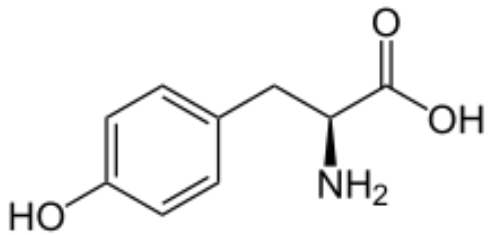

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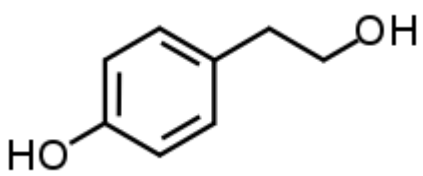

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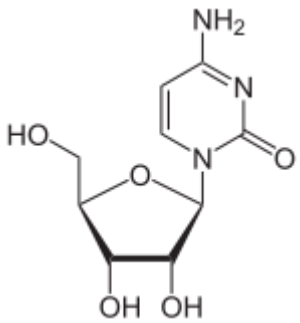

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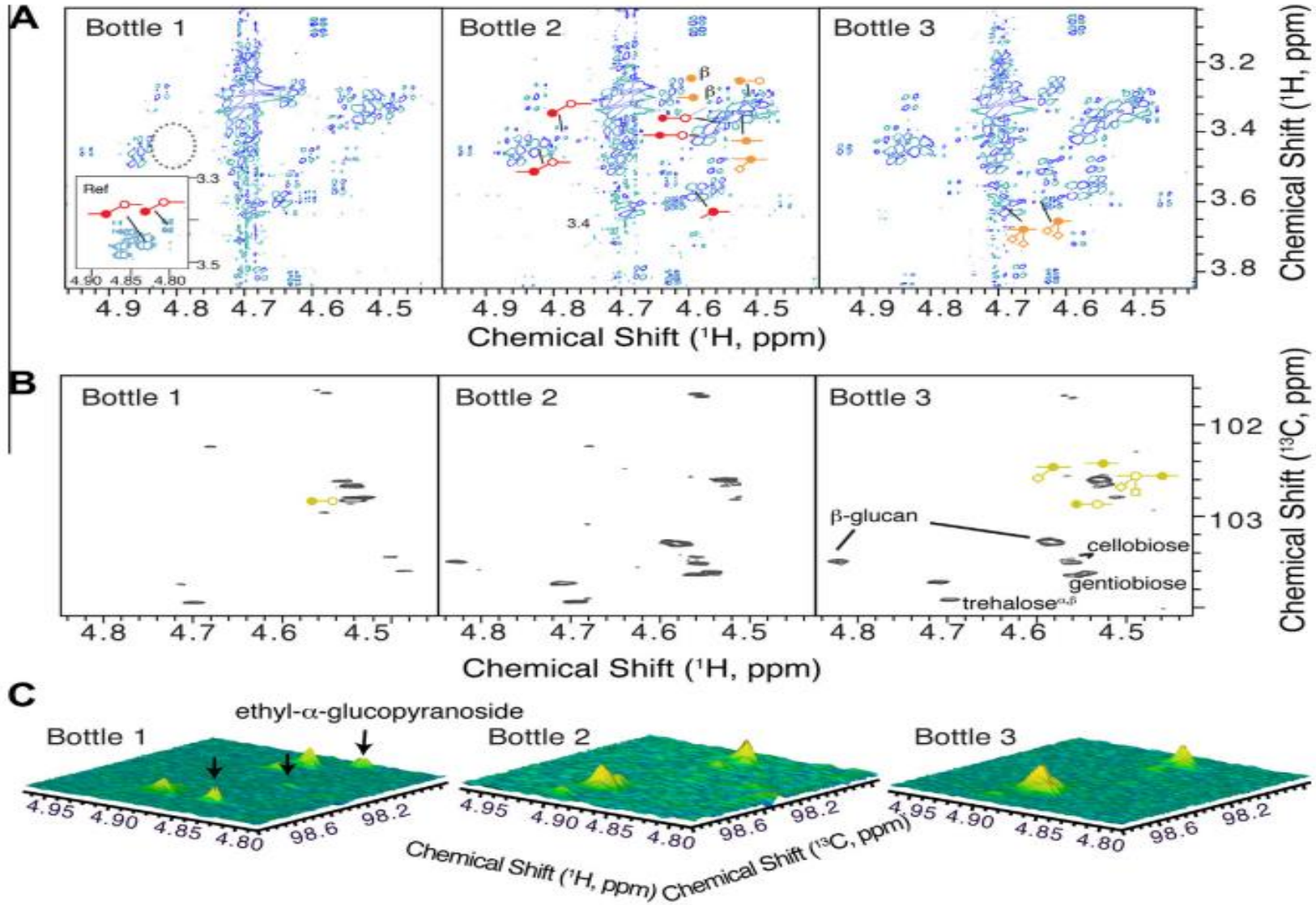
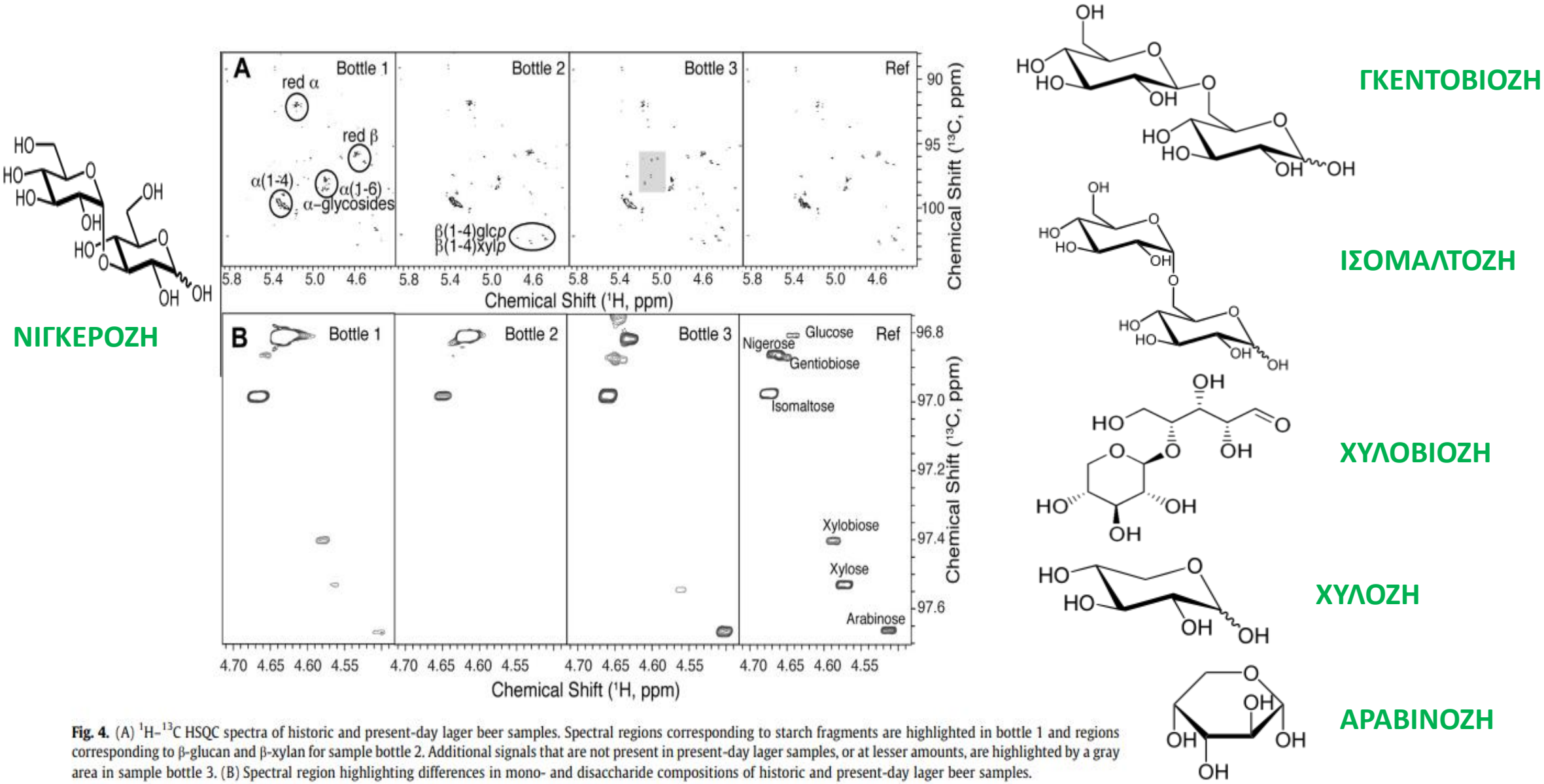


Fig. 3. (A) $^{1}H-^{1}H$-COSY and (B) $^{1}H-^{13}C$ HSQC spectra of barley cell wall polysaccharides in the historic beer samples. In depictions of arabinoxylan fragments (orange), squares designate arabinofuranosyl units, circles designate xylopyranosyl-units, horizontal lines indicate β-(1–4) glycosidic bonds, vertical lines indicate α-(1–2) glycosidic bonds, and diagonal lines indicate α-(1–3) glycosidic bonds. In depiction of β-glucan structures (red), circles designate glucopyranosyl units, horizontal lines indicate β-(1–4) glycosidic and diagonal lines indicate β-(1–3) glycosidic bonds. (C) Presence of alcoholic α-glycosides in beer from bottle 1 at $^{1}H-^{13}C$ HSQC spectral positions indicated by arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



ΝΙΓΚΕΡΟΖΗ

ΓΚΕΝΤΟΒΙΟΖΗ

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ΧΥΛΟΖΗ

ΑΡΑΒΙΝΟΖΗ

Fig. 4. (A) ^{1}H–^{13}C HSQC spectra of historic and present-day lager beer samples. Spectral regions corresponding to starch fragments are highlighted in bottle 1 and regions corresponding to β-glucan and β-xylan for sample bottle 2. Additional signals that are not present in present-day lager samples, or at lesser amounts, are highlighted by a gray area in sample bottle 3. (B) Spectral region highlighting differences in mono- and disaccharide compositions of historic and present-day lager beer samples.

ΣΥΜΠΕΡΑΣΜΑ: ΥΔΑΤΑΝΘΡΑΚΕΣ ΣΤΑΘΕΡΟΙ ΑΠΟ ΤΟΝ 19ο ΑΙΩΝΑ ΣΕ ΧΗΜΙΚΕΣ, ΕΝΖΥΜΑΤΙΚΕΣ ΚΑΙ ΜΙΚΡΟΒΙΑΚΕΣ ΕΠΙΔΡΑΣΕΙΣ. ΕΣΤΕΡΕΣ ΚΑΙ ΑΛΔΕΥΔΕΣ ΥΦΙΣΤΑΝΤΑΙ ΧΗΜΙΚΕΣ ΜΕΤΑΒΟΛΕΣ.

CHEMICAL ANALYSIS OF ORGANIC RESIDUES FOUND IN HELLENISTIC TIME AMPHORAE FROM SE BULGARIA

B. Zlateva[a*] and M. Rangelov[b]

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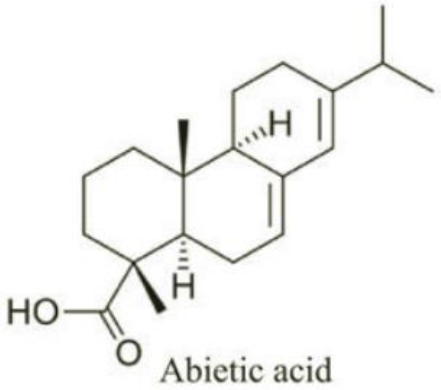
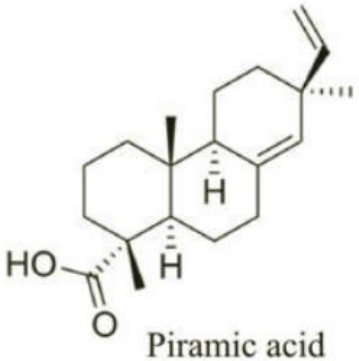
Journal of Applied Spectroscopy, Vol. 82, No. 2, May, 2015 221-227

the composition of resin residues found in 22 amphorae from Apollonia Pontika (SE Bulgaria). In particular this analysis of the resin residues was aimed at discovering the content of the amphorae and to verify the hypothesis on the transport of wine, named "Retsina". Additionally this hypothesis has been confirmed by a similar analysis of the modern resin sample from Aleppo pine (Pinus Halepensis) growing in the Attica region (Greece).



Abietic acid



Piramic acid

TABLE 2. Results from ^{1}H NMR Spectroscopy

Alkanes (R-CH_3)	1–0.5
Diterpenoid acids	3–0.5
Alcohols	4.5–3.5
Aliphatic carbohydrates to aromatic structure	4.9–6
Aromatic	8.3–6

pimaric acid (5.293 ppm), dehydroabietic (7.255, 7.166, 6.989 ppm), and abietic acid (5.78 ppm).

modern resin samples, collected from pine trees (Pinus Halepsensis) grown in the Attica region (Greece, near Athens), shows a similarity between the ancient and modern resin samples.

the content of the amphorae has been wine, probably Retsina, the object of trade connections between the Greek colony in Apollonia Pontika and Greece.

Identification of archaeological triterpenic resins by the non-separative techniques FTIR and ^{13}C NMR: The case of *Pistacia* resin (mastic) in comparison with frankincense

Silvia Bruni *, Vittoria Guglielmi Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 121 (2014) 613–622

^{13}C NMR measurements were performed with a Bruker AC 300 spectrometer and the spectra were obtained as result of 7000 scans. The J-modulating spin-echo sequence (J-mod) was used, providing spectra in which the quaternary and methylene signals (negative in our spectra) have opposite phase to those of methine and methyl resonances.

ΡΗΤΙΝΕΣ ΚΩΝΟΦΟΡΩΝ:
Sandarac (Β. Αφρική)
ΜΑΣΤΙΧΑ (Χίος)
Dammar (από τροπικά δένδρα)
Elemi (Φιλιππίνες)
Frankincense (Αίγυπτος)
Myrth (Αιθιοπία, Σομαλία)
Larch (Ευρώπη)
Black pine (Ευρώπη)

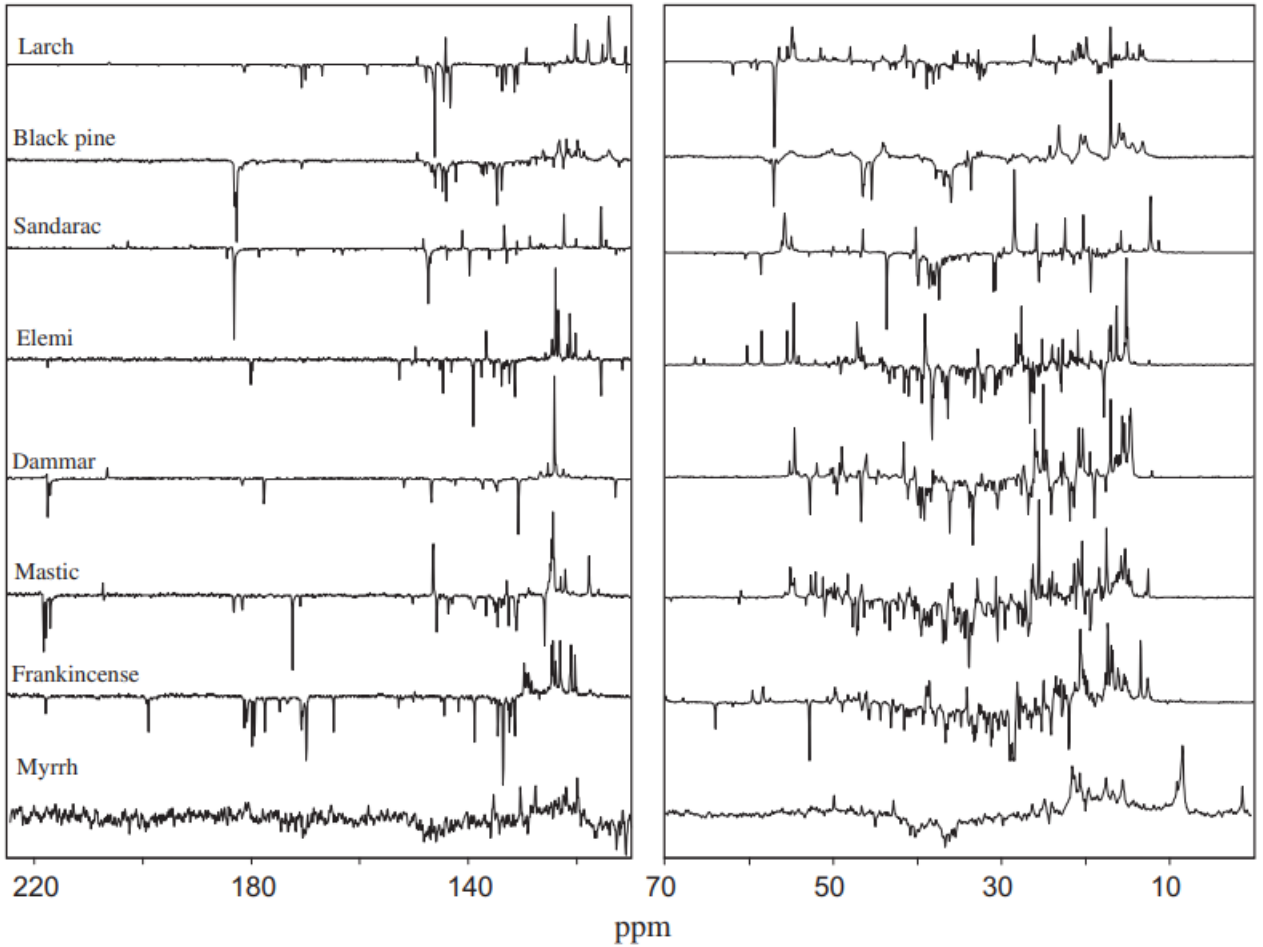


Fig. 3. ^{13}C NMR spectra of fresh reference resins and gum-resins.

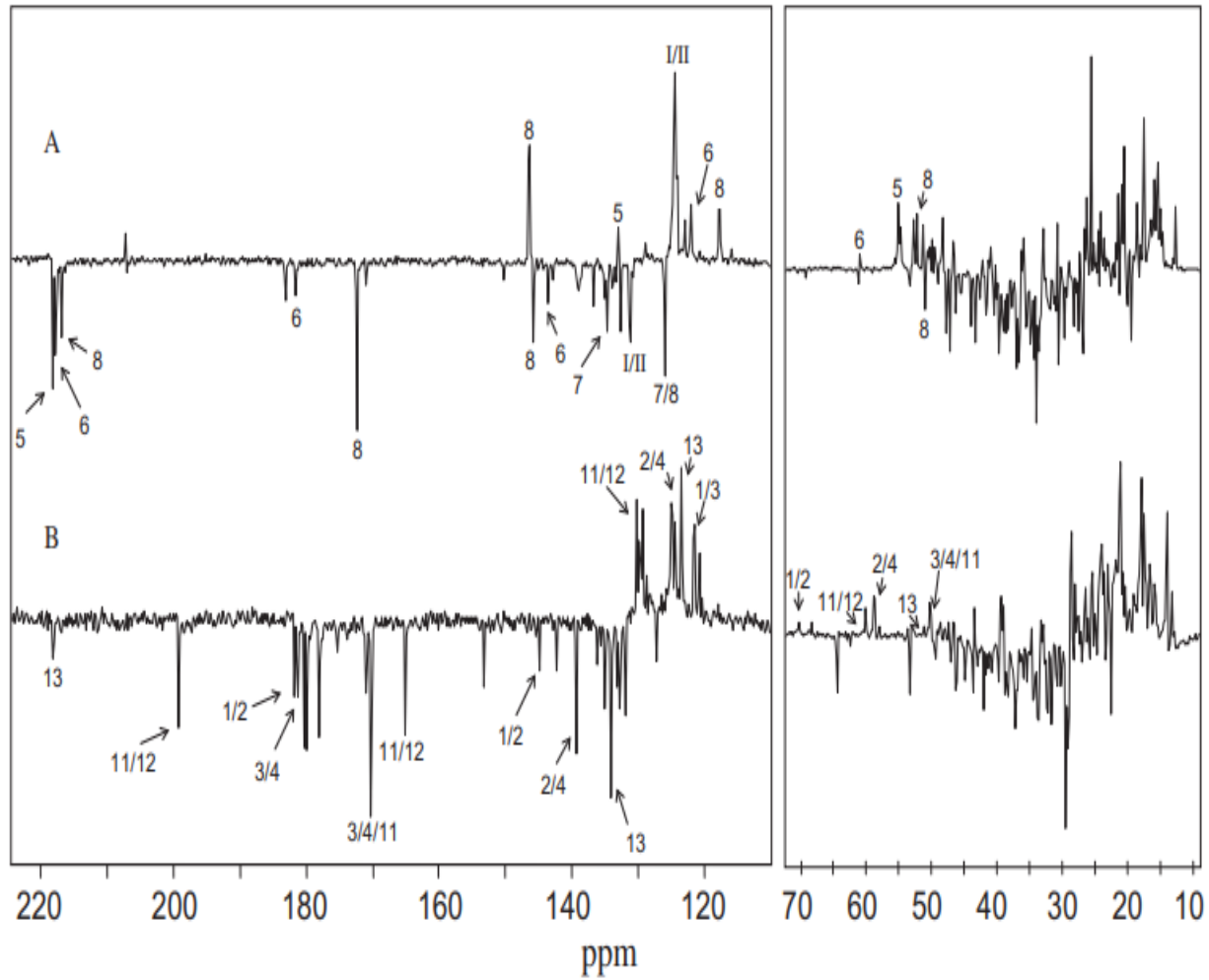


Fig. 4. ^{13}C NMR spectra of extracts from: (A) mastic resin; (B) frankincense. The numbers 1–10 correspond to the structures shown in Fig. 8; 11 = 11-keto-boswellic acid, 12 = 3-O-acetyl-11-keto-boswellic acid, 13 = 3-oxo-tirucallic acid; for I and II see text.

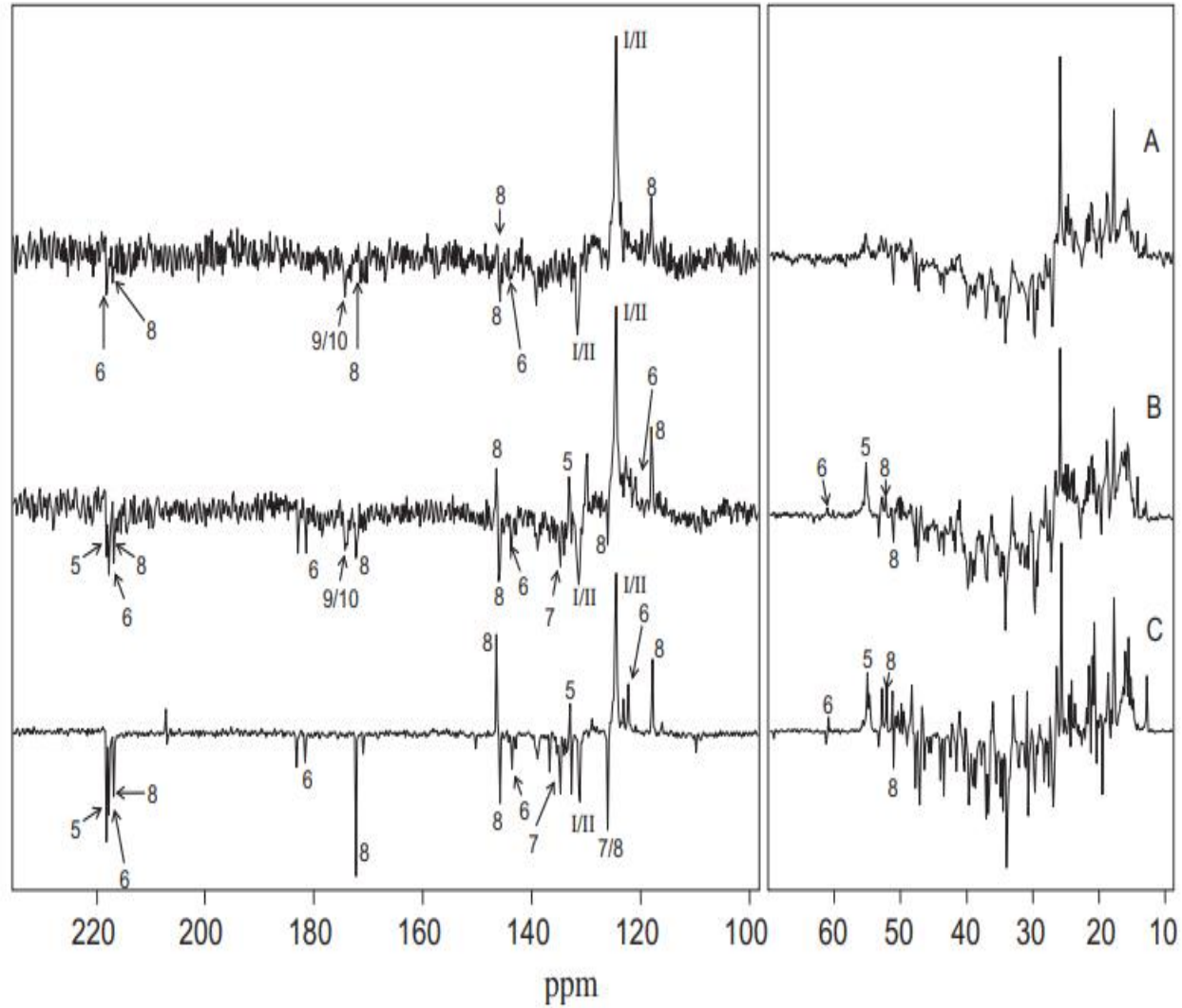


Fig. 6. ^{13}C NMR spectra of extracts from: (A) organic component of the sample from the urn of the Saints Gervasio and Protasio; (B) sample from the "sarcophagus of the Lady"; (C) fresh mastic resin. For numbering of the peaks see Fig. 8 and text.

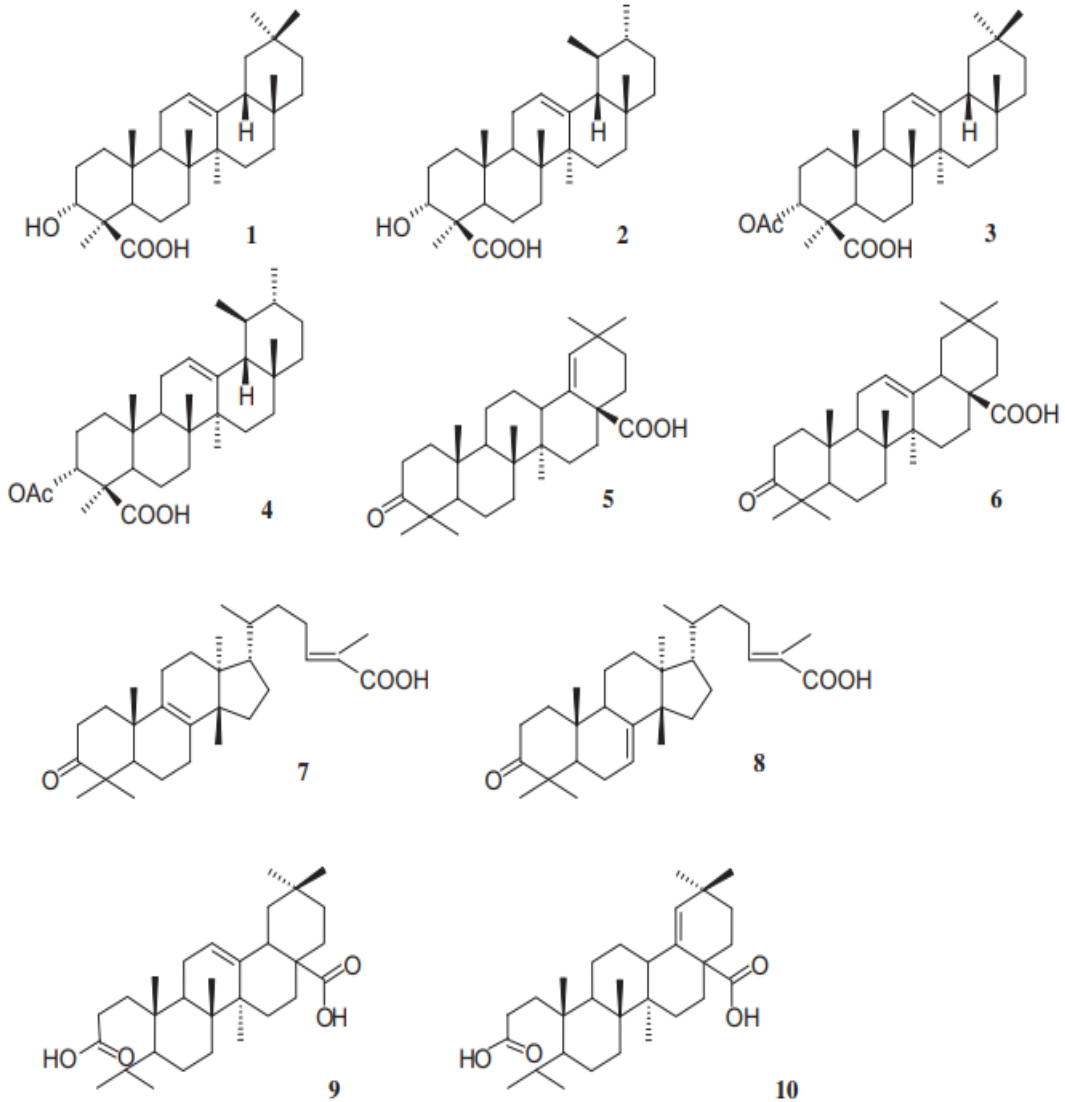


Fig. 8. Molecular structures of: α-boswellic acid (1), β-boswellic acid (2), 3-O-acetyl-α-boswellic acid (3), 3-O-acetyl-β-boswellic acid (4), moronic acid (5), oleanonic acid (6), isomasticadienonic acid (7), masticadienonic acid (8), 3,4-seco-olean-12-en-3,28-dioic acid (9), 3,4-seco-olean-18-en-3,28-dioic acid (10).

Table 2
Main terpenoid compounds identified in fresh reference resins with chemical shift values (ppm) of the corresponding ^{13}C NMR peaks. Literature references for the assignments are listed in the last column.

Resin type	Compounds	Chemical shifts (ppm)	Ref.
Pinaceae	Dehydroabietic acid	146.7, 145.6, 126.8, 124.0, 123.7	
	Isopimaric acid	150.1, 135.4, 120.9, 109.2	[26–30]
	Abietic acid	145.0, 122.2, 120.4	
Larch	Larixol	145.5, 145.2, 108.4, 71.6, 56.4	
	Larixyl acetate	170.1, 144.3, 56.4	[31]
Sandarac	Trans-communic acid	183.0, 147.9, 141.6, 133.9, 133.5, 109.9, 107.7, 56.5, 56.3, 44.2, 39.3, 38.5, 38.0, 29.0, 25.9, 23.3, 19.9, 12.9, 11.8	[32]
Mastic	Moronic acid	218.2, 183.3, 132.8, 55.2	
	Oleanonic acid	217.7, 181.6, 143.5, 122.1, 61.0	
	Masticadienonic acid	216.9, 172.3, 146.4, 145.7, 132.5, 125.9, 117.6, 52.2, 51.0	[33–38]
	Isomasticadienonic acid	218.2, 134.5, 132.5, 125.9	
	Polypodatriene	131.0, 124.3	
Elemi	α-Amyrin	139.6, 124.5, 59.2, 47.8, 39.6, 38.9, 28.8, 28.2, 27.3, 23.4, 21.4, 18.4, 16.9, 15.6, 17.5	
	β-Amyrin	145.1, 121.8, 78.9, 55.3, 47.7, 38.8, 37.0, 28.2, 18.4, 16.9, 15.6	[39]
Dammar	Hydroxydammarenone	218.2, 131.7, 124.6, 55.1, 25.7, 17.6	[39,40]
Frankincense	α-Boswellic acid	181.8, 144.7, 121.4, 73.3	
	β-Boswellic acid	181.8, 139.3, 124.8, 73.3, 58.9	
	3-O-acetyl-α-Boswellic acid	181.3, 170.3, 144.7, 121.4, 75.15, 50.3	
	3-O-acetyl-β-Boswellic acid	181.3, 170.3, 139.3, 124.8, 75.15, 58.9, 50.3	[41–43]
	11-Ketoboswellic acid	199.3, 170.3, 165.1, 130, 60.0	
	3-O-acetyl-11-ketoboswellic acid	199.3, 165.1, 130, 60.0	
	3-Oxo-tirucallic acid	218, 181.3, 134.9, 133.9, 132.8, 131.8, 123.4, 51.2	
Myrrh	Furanoeudesma-1,3-diene	135.6, 122.1, 120.1, 119.4, 116.7, 42.9, 36.7, 35.3, 20.4, 19.8, 15.4, 8.2,	[44]

Table 3
Chemcal shifts (ppm) of peaks in ^{13}C NMR spectra of fresh *Pistacia* resin and archaeological samples. Superscripts in bold character indicate the assignment to specific components of the resin (for numbering see Fig. 8 and text).

Mastic	Sample from the "sarcophagus of the Lady"	Sample from the urn of the Saints Gervasio and Protasio
Chemical shift (ppm)		
$^{5/7}$218.2	$^{5/7}$218.1	–
^{6}217.7	^{6}217.8	^{6}217.8
^{8}216.9	^{8}216.9	^{8}216.6
^{5}183.3/183.1	^{5}183.3	–
^{6}181.6	^{6}181.4	^{6}181.2
–	$^{9/10}$174.1	$^{9/10}$174.1
$^{7/8}$172.3	$^{7/8}$172.2	$^{7/8}$172.2
^{8}146.4	^{8}146.5	^{8}146.7
^{8}145.7/9	^{8}145.9	^{8}145.7
^{6}143.5	^{6}143.6	–
^{7}134.5/6	^{7}134.7	–
^{5}132.8	^{5}133.0	–
$^{7/8}$132.5/6	$^{7/8}$132.6	$^{7/8}$132.6
$^{I/II}$131.0	$^{I/II}$131.1	$^{I/II}$131.2
$^{7/8}$125.9	$^{7/8}$125.8	$^{7/8}$125.6
$^{I/II}$124.3	$^{I/II}$124.3	$^{I/II}$124.3
^{6}122.1/3	^{6}122.05	^{6}122.3
^{8}117.6	^{8}117.7	^{8}117.5
^{6}61.0	^{6}61.1	–
^{5}55.2	^{5}55.2	–
^{8}52.2	^{8}52.3	–
^{8}51.0	^{8}51.1	–

ΧΡΗΣΗ ΤΗΣ ΜΑΣΤΙΧΑΣ ΤΗΣ ΧΙΟΥ ΤΗ ΡΩΜΑΙΚΗ ΠΕΡΙΟΔΟ