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1 **Birch bark tar and jewellery: the case study of a necklace from the Iron** 2 **Age (Eckwersheim, NE France)**

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8 **Abstract**

9 Organic residue analysis has been undertaken on an organic material found on a necklace
10 with a pendant unearthed from a necropolis dated to the Early Iron Age (800-475 BC) and
11 located in Eckwersheim (NE France). The molecular composition of the substance, which
12 was investigated using gas chromatography coupled to mass spectrometry, points towards an
13 adhesive used to stick two bronze half-spheres to form a pendant. The predominance of
14 triterpenoids from the lupane series led to the identification of the adhesive as a birch bark tar
15 and constitutes a rare example of the use of such a material in jewellery in the past.

16 **Keywords:** birch bark tar, conifer resin, Early Iron Age, necklace, jewellery, lupane-related
17 triterpenoids.

18 **1. Introduction**

19 Archaeological evidence of birch bark tar, an adhesive substance obtained by dry pyrolysis of
20 birch bark (e.g. Regert et al., 1998; Koller et al., 2001; Rageot et al., 2015), is abundantly
21 documented in the literature. Considered as one of the first man-made organic material, birch
22 bark tar is frequently present among archaeological finds dated from the Neolithic period in
23 Europe and its first use by Neanderthals is dated back to the Palaeolithic (Koller et al.,

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24 2001). This sticky and hydrophobic material has been used for many purposes such as the
25 hafting of lithic or bone tools (e.g. Regert et al., 1998; Koller et al., 2001), the reparation and
26 waterproofing of pottery (e.g. Binder et al., 1990; Charters et al., 1993; Connan et al., 2000;
27 Urem-Kotsou et al., 2002; Rageot et al., 2015), the decoration of ceramics (e.g. Vogt, 1949;
28 Trąbska et al., 2011; Rageot et al., 2015) and, more surprisingly, as chewing-gum (e.g.
29 Aveling and Heron, 1999; van Gijn and Boon, 2006; Karg et al., 2014). The identification of
30 birch bark tar mainly relies on the detection of lupane-related triterpenoids as diagnostic
31 molecular biomarkers. These compounds possess indeed ideal features since lupane-related
32 triterpenoids are abundant in birch tar and their assemblage can be considered as highly
33 specific (Hayek et al., 1989; Schnell et al., 2014). In addition, these compounds are relatively
34 resistant to various alteration processes such as biodegradation which probably accounts for
35 their good preservation even in ancient archaeological samples dating back to the Palaeolithic
36 and Mesolithic Periods (Koller et al., 2001; Aveling and Heron, 1998).

37 We report here the investigation by gas chromatography-mass spectrometry (GC-MS) of the
38 lipid content of a dark organic substance of unknown nature that has served to assemble two
39 bronze half-spheres in order to form the pendant of a necklace (Fig. 1) dating to the Hallstatt
40 D1 period (625-550 BC). Due to the predominance of lupane-related triterpenoids in the lipid
41 extract, their origin (genuine biological compounds *vs.* triterpenes altered by natural or
42 anthropic processes) is discussed in the light of the molecular investigation of reference
43 samples of birch bark and birch bark tars.

44 **2. Materials and method**

45 *2.1. Archaeological sample*

46 Sample A (INRAP - Institut National de Recherches Archéologiques Préventives - reference
47 number: PRL BG 6008-02) corresponds to a dark substance found between two small bronze

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48 half-spheres which were assembled to create the pendant of a necklace (Fig. 1). The jewellery
49 was uncovered among the furniture and artefacts of the tomb 6008 unearthed at Eckwersheim
50 (Alsace, NE France) by an INRAP team led by Dr. Clément Féliu and Dr. Yohann Thomas.
51 The tomb was dated to the Early Iron Age and the necklace between 625 BC and 550 BC
52 (Hallstatt D1 period).

53 2.2. Reference samples

54 The reference samples comprise: (1) the lipid extract of pieces of birch bark (*Betula pendula*)
55 from a trunk in an advanced state of alteration (sample B); (2) the lipid extract of pieces of
56 the same birch bark sample pyrolysed with a heat gun during 10 minutes under N₂
57 atmosphere (sample C); (3) a birch bark tar from *Betula pendula* prepared by descending
58 distillation (sample D, reference number 162/5 20 18 00, Dr. Andreas Kurzweil,
59 Museumsdorf Düppel, Berlin, Germany).

60 2.3. Lipid analysis

61 Samples A - D were extracted by sonication using a mixture of dichloromethane/methanol
62 (CH₂Cl₂/CH₃OH, 1:1, v/v) followed by filtration of the supernatant through celite and
63 removal of the solvent under reduced pressure. An aliquot of the extract in CH₂Cl₂ was
64 acetylated (Ac₂O, *N*-methylimidazole, 30 min, ambient temperature) and, after removal of the
65 solvents and excess reagents, treated with a solution of diazomethane in diethylether to
66 methylate the carboxylic acids. The derivatised crude extract was fractionated on a silica gel
67 column into an apolar fraction eluted with CH₂Cl₂/EtOAc (8:2, v/v) which was analysed by
68 GC-MS and a more polar fraction eluted with CH₂Cl₂/ CH₃OH (1:1, v/v) which was not
69 further investigated.

70 2.4. GC-MS

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71 GC-MS analyses were carried out using a Thermo Trace gas chromatograph (Thermo
72 Scientific) equipped with an autosampler Tri Plus, a programmed temperature vaporizing
73 (PTV) injector and a HP5-MS column (30 m x 0.25 mm i.d. x 0.25 μ m film thickness) using
74 He as carrier gas (constant flow rate at 1.1 ml/min). Temperature program: 70 °C - 200 °C
75 (10 °C/min), 200 °C - 300 °C (4 °C/min), isothermal at 300 °C (40 min). The mass
76 spectrometer was operating in the electron ionization (EI) mode at 70 eV with a scan range of
77 50 to 700 m/z . The data were investigated using Xcalibur Software and mass spectra were
78 compared with the NIST library and literature data.

79 **3. Results and discussion**

80 *3.1. Triterpenoids of the lupane series: birch bark as main ingredient*

81 GC-MS analysis of the organic extract of the substance from the pendant (sample A) led to
82 the identification of specific triterpenoids from the lupane series, indicating a predominant
83 contribution from an angiosperm source. These triterpenoids comprise, notably, lupeol **1**
84 (numbers refer to structures presented in the Appendix), betulin **2**, lupenone **3**, betulone **4**,
85 lupanone **5** and lupan-3,28-diol **6** (Fig. 2) which are important triterpenes of birch bark
86 (Hayek et al., 1990; Krasutsky, 2006; Schnell et al., 2014). The predominance of the same
87 compounds among the lipids of the reference birch bark samples B-D (Fig. 3) was thus not
88 unexpected. Betulin **2**, in particular, largely predominates the gas chromatogram of the lipids
89 from the birch bark sample B, representing ca. 60 % of the apolar lipids. The identification of
90 triterpenoids from the lupane series in the archaeological sample A points thus clearly to
91 birch bark tar which may have been used as an adhesive material. It can be proposed that bark
92 of either *Betula pendula* (silver birch) or *Betula pubescens* (downy birch) served as raw
93 material for the preparation of the adhesive since they are the most common *Betula* species in
94 Europe (Beck et al., 2016).

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95 3.2. Altered triterpenoids as markers for ageing and thermal treatment

96 The distribution of the triterpenoids in the archaeological sample (Fig. 2) is, however,
97 significantly different from that observed with fresh birch bark (Fig. 3). This can likely be
98 explained by the various alteration processes affecting triterpenoids upon the thermal
99 treatment used for the preparation of the substance, in addition to other processes induced by
100 oxidative ageing and/or by diagenetic alteration during burial in the soil.

101 Such processes may notably account for the lower proportion of betulin **2** in the
102 archaeological sample as compared to the large predominance of **2** in fresh birch bark (Fig. 3;
103 Hayek et al., 1989), as well as for the absence of betulonal **7** and betulinic acid **8** - two native
104 triterpenoids from birch bark (cf. sample B; Fig. 3)- in the archaeological material (Fig. 2).

105 In parallel with the absence of some genuine lupane-related triterpenoids from birch bark,
106 three families of triterpenes likely resulting from alteration processes were detected in sample
107 A. They comprise *A-neo*-triterpenoids (e.g., **9**, **10**), Δ^2 triterpenoids (e.g., **12**, **13**), and
108 allobetulane derivatives (e.g., **14-16**). Δ^2 lupane-derivatives **12** and **13** detected in samples A,
109 C and D most likely originate from the thermally-induced dehydration of lupeol **1** and betulin
110 **2** and can be considered as typical pyrolytic compounds. Their formation was observed,
111 notably, during a controlled pyrolysis experiment of birch bark by Regert et al. (2006) and
112 they generally occur in archaeological birch bark tars (e.g. Binder et al., 1990; Charters et al.,
113 1993; Avelling and Heron, 1998; Regert et al., 2003; Rageot et al., 2015).

114 Allobetulane derivatives (**11**, **14-16**; mass spectra in Fig. S1) were also present in samples A,
115 C and D. These compounds are postulated to be formed by an acid-catalysed intramolecular
116 rearrangement of ring *E* (Green et al., 2007; Salvador et al., 2009). Since these compounds
117 exclusively occur in tars (sample D) and not in birch bark (sample B), they are thus
118 considered, like Δ^2 derivatives, to be closely associated to the thermal alteration undergone by

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119 birch bark during tar preparation (cf. Heron et al., 1999; Rageot et al., 2015). The acid
120 catalysis necessary for the intramolecular rearrangement of ring *E* might have been provided
121 by phenols formed by the pyrolytic degradation of lignin (Faix et al., 1990).

122 The *A-neo*-triterpenoids found in sample A (**9** and **10**; MS data shown in Fig. S2 in
123 Supplementary data) and in the reference thermally-treated samples C and D (**9-11**) derive,
124 respectively, from lupeol **1**, betulin **2** and allobetulin **16** by contraction of ring *A*. Their
125 formation most likely involves the acid-catalysed loss of the C-3 alcohol moiety followed by
126 a Wagner-Meerwein rearrangement (Salvador et al., 2009). To our knowledge, these
127 compounds have not been reported from fresh birch bark and might have two distinct origins.
128 They can be formed during the preparation of the tar as shown by Rageot (2015) in the case
129 of birch bark tars prepared in the laboratory, the acid catalysis necessary for their formation
130 being possibly induced, as mentioned above, by phenols formed upon lignin pyrolysis (Faix
131 et al., 1990). In addition, Rageot (2015) has shown that their relative abundance is correlated
132 with the experimental conditions, higher temperatures or longer heating periods likely
133 favoring their formation. Nevertheless, the detection of *A-neo*-triterpenoids, even in small
134 amounts, in the altered birch bark sample B indicates that natural alteration processes may
135 also account to some extent for their formation (ten Haven et al., 1992).

136 *3.3. Input of conifer resin attested by diterpenoids*

137 Besides the predominant lupane-related triterpenoids reported above, GC-MS analysis of the
138 organic extract of the substance from the pendant (sample A) revealed an additional
139 contribution of small amounts of early eluted compounds corresponding to diterpenoids.
140 They comprise di-dehydroabietic acid **17**, dehydroabietic acid **18**, 7-oxodehydroabietic acid
141 **19** along with the related compounds **20** and **21** bearing a hydroxyl function at C-15. All of
142 them derive from abietic acid **22**, a diterpenic acid ubiquitously found in conifer resins (Otto

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143 and Wilde, 2001) and especially abundant in resins from Pinaceae (Otto et al., 2007). The
144 contribution of these diterpenoids revealed thus the presence of conifer material in the
145 archaeological substance which could either correspond to a raw resin or a tar made by dry
146 distillation of conifer wood (e.g. Evershed et al., 1985; Connan and Nissenbaum, 2003;
147 Bailly, 2015). However, in the case of conifer tars, aromatic diterpenoids like retene **23**
148 resulting from the thermal transformation of resinic acids upon pyrolysis are generally
149 abundant. In the present case, such compounds could not be detected, suggesting that the use
150 of a conifer tar can be ruled out. Thus, the ingredient corresponds most likely to a conifer
151 resin. In addition, the identification of oxidized derivatives of **18**, comprising compounds
152 with a ketone at C-7 (**19** and **21**) or a hydroxyl group at C-15 (**20** and **21**), suggests that the
153 resin was severely altered by oxidative processes during the ageing of the adhesive substance
154 (Colombini et al., 2005; Osete-Cortina and Doménech-Carbó, 2005; Bailly, 2015).

155 *3.4. Mode of preparation of the adhesive - Origin of the conifer resin component*

156 The presence of lupane-related biomarkers which have obviously undergone thermal
157 alteration (formation of Δ^2 -triterpenoids and allobetulane derivatives, notably; see above) in
158 sample A clearly indicates that the organic substance corresponds to an adhesive material
159 (birch bark tar) used to assemble the pendant. However, the contribution of small proportions
160 of conifer resin raises the question whether the addition of the latter was intentional or was
161 the result of a “contamination” during birch bark tar preparation. Indeed, a few examples of
162 mixtures of archaeological birch bark tar containing additional substances have been reported
163 by several authors. These substances comprise animal fat, beeswax, plant oil (Dudd and
164 Evershed, 1999; Regert et al., 2003; van Gijn and Boon, 2006; Rageot et al., 2015) and, in
165 some rare cases, conifer resin/tar (Stacey, 2004; Rageot et al., 2015). The input of additional
166 substances can sometimes be intentional in order to improve the properties of the material.

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167 For instance, the addition of beeswax to birch bark tar leads to a substance which is less
168 brittle than pure birch bark tar (Regert et al., 2003; van Gijn and Boon, 2006). It is interesting
169 also to note that Stacey (2004) and Rageot et al. (2015) reported the identification of
170 adhesives very similar in molecular composition to sample A, and which consisted of small
171 amounts of conifer resin mixed with birch bark tar. They were used, respectively, for gluing
172 coral studs on strap unions from harness fittings (Stacey, 2004) and for the reparation of
173 pottery (Rageot et al., 2015). This supports the hypothesis that the admixture of small
174 amounts of conifer resin to birch bark tar might possibly improve its performances as an
175 adhesive and that such mixtures have been prepared on purpose for this specific application.

176 However, based on the relatively small contribution of the conifer resin as compared to the
177 birch bark tar in the case of sample A, it cannot be excluded that the container used for the
178 storage or the production of birch bark tar may have served previously to collect or store a
179 conifer resin and might have thus contaminated the birch bark tar. It should however be
180 mentioned that the relatively low proportion of diterpenes relative to triterpenes observed in
181 sample A does not necessarily reflect the initial proportions of conifer resin and birch bark tar
182 making up the adhesive. Indeed, resinic acids might be significantly more sensitive to
183 oxidative alteration given the presence of reactive benzylic positions on dehydroabietic acid
184 **18** and related structures as illustrated by the detection of several oxidized dehydroabietic
185 acid derivatives (**19-21**) in sample A. The presence of several oxygenated functionalities on
186 these structures might thus be responsible for an enhanced water solubility as compared to
187 lupane-related triterpenoids, thus favouring their progressive removal by leaching, notably
188 after burial.

189 **4. Conclusion**

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190 Identification of triterpenoids from the lupane series in the organic material found on an
191 archaeological necklace pendant clearly indicates that this substance was made
192 predominantly of birch bark tar, together with a small contribution of conifer resin. This
193 material likely corresponds to an adhesive that could have served to fix a decorative item on
194 the pendant. The question remains regarding the role of the conifer resin which could either
195 be part of the ingredients added intentionally to improve the quality of the adhesive material,
196 or correspond to a “contamination” introduced during birch bark tar preparation.

197

198 **Acknowledgement**

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200 traditional techniques (Museumsdorf Düppel, Berlin). The INRAP is thanked for providing
201 the archaeological sample. B.C. thanks the French Ministère de l’Enseignement Supérieur et
202 de la Recherche for a doctoral fellowship.

203 **Appendix**

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298

299 **Figure captions**

300 **Figure 1.** Necklace (a) with a pendant (b) found among the furniture and artefacts of a tomb
301 dated to the Hallstatt D1 period (625-550 BC; Eckwersheim, NE France). Photos and
302 drawing by ©Y. Thomas, INRAP.

303 **Figure 2.** Gas chromatogram of the lipid extract of the adhesive of the necklace pendant
304 (sample A). Bold numbers refer to the structures shown in Appendix. Alcohols are analyzed
305 as acetates and carboxylic acids as methyl esters.

306 **Figure 3.** Gas chromatograms of the organic extract of (a) altered birch bark sample (sample
307 B); (b) altered birch bark sample after pyrolysis (sample C); (c) reference birch bark tar
308 prepared by descending distillation (sample D). Bold numbers refer to the structures shown in
309 Appendix. Alcohols are analyzed as acetates and carboxylic acids as methyl esters.

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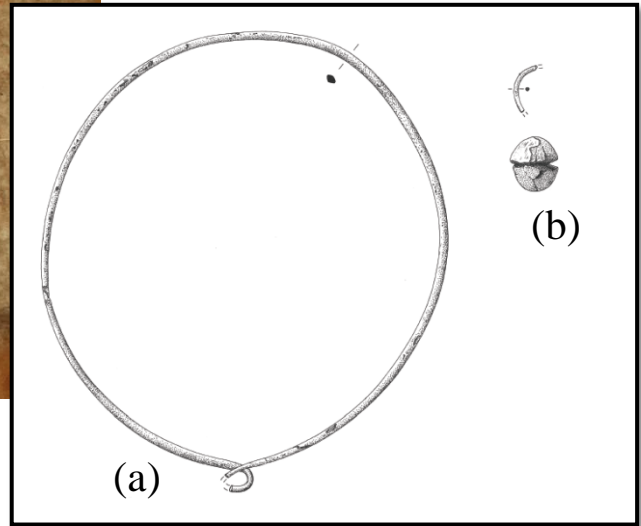


Figure 1

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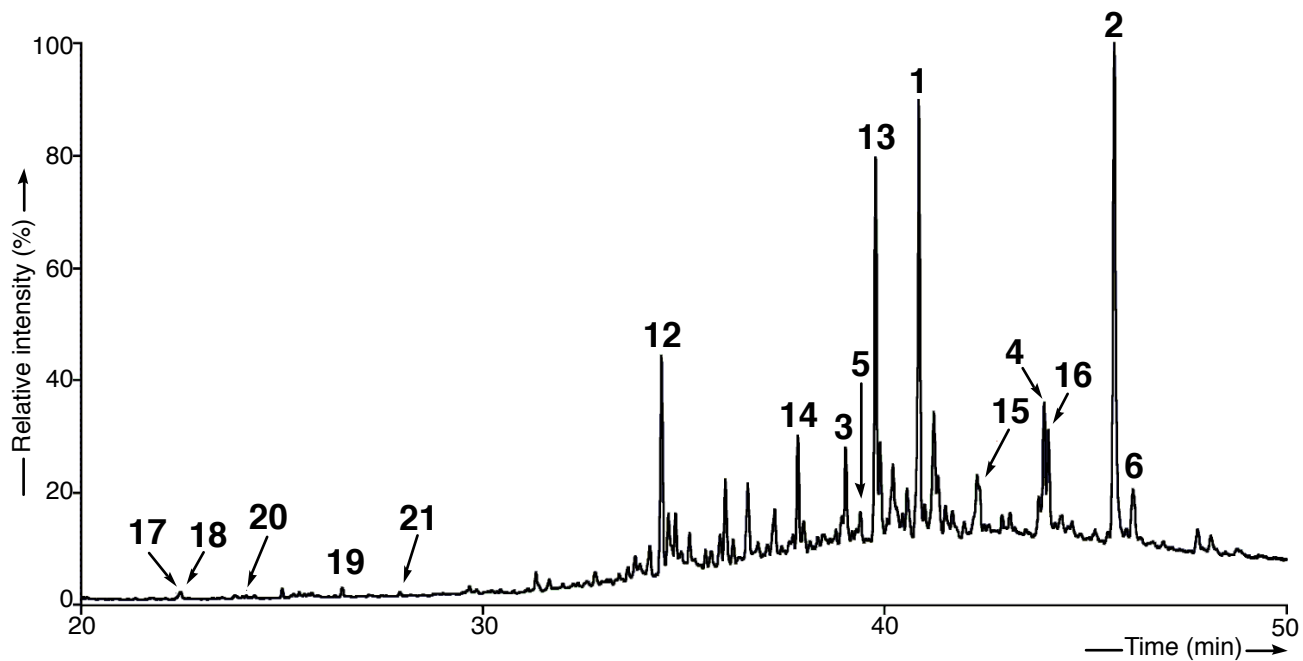


Figure 2

Version avant révision

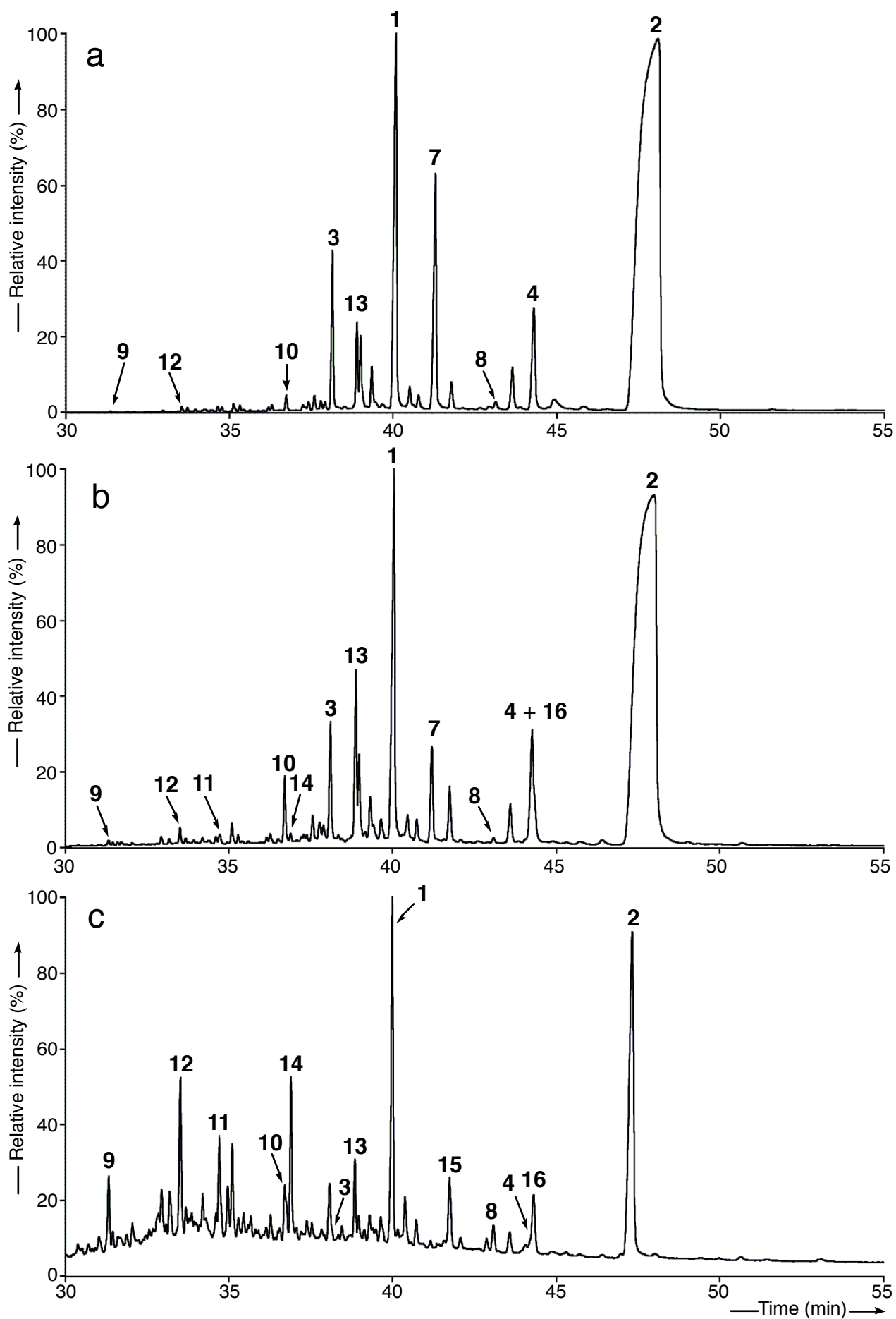
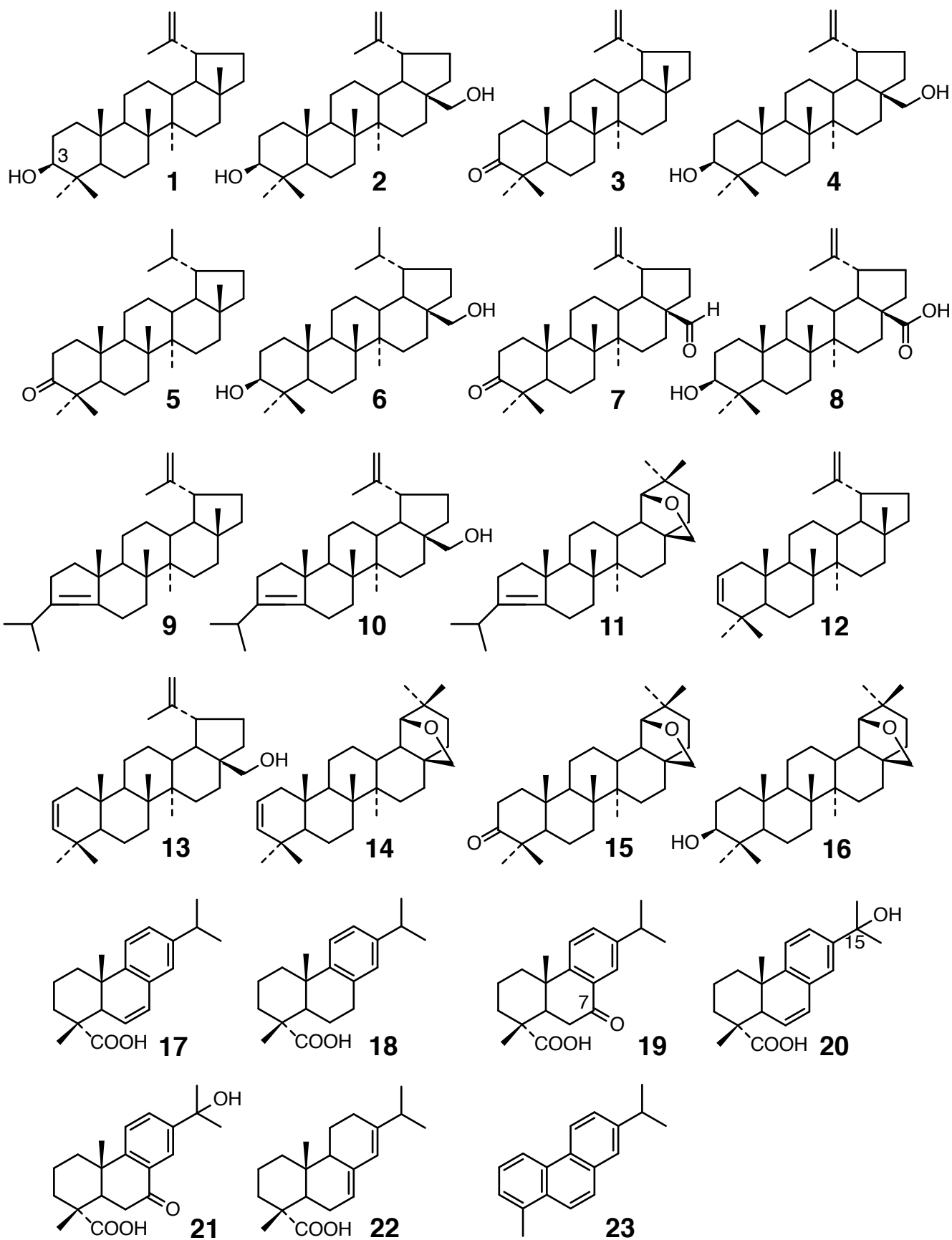


Figure 3

Appendix

Structures cited in the text



Version avant révision

Birch bark tar and jewellery: the case study of a necklace from the Iron Age (Eckwersheim, NE France)

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Supplementary materials

- Figure S1: Mass spectra (EI, 70 eV) of allobetulane derivatives **11**, **14-16**.
- Figure S2: Mass spectra (EI, 70 eV) of *A-neo*-triterpenoids of the lupane series **9** and **10** found in the archaeological sample (sample A) and in the thermally-treated reference samples (samples B and C).

Version avant révision

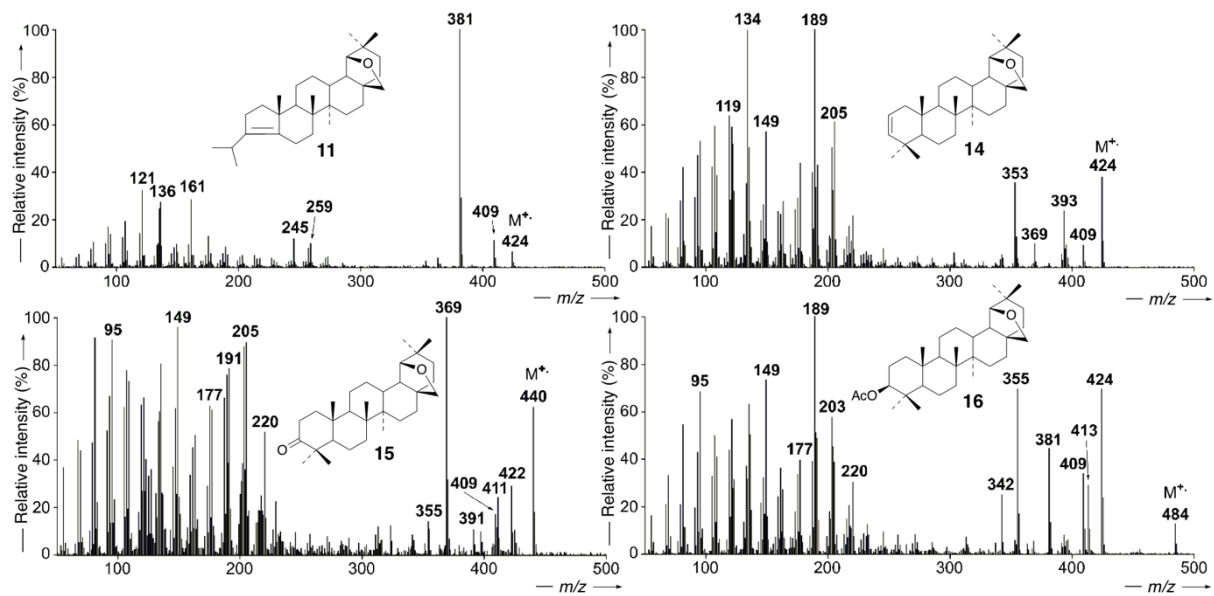


Figure S1: Mass spectra (EI, 70 eV) of allobetulane derivatives **11**, **14-16**. Bold numbers refer to the structures shown in the Appendix.

Version avant révision

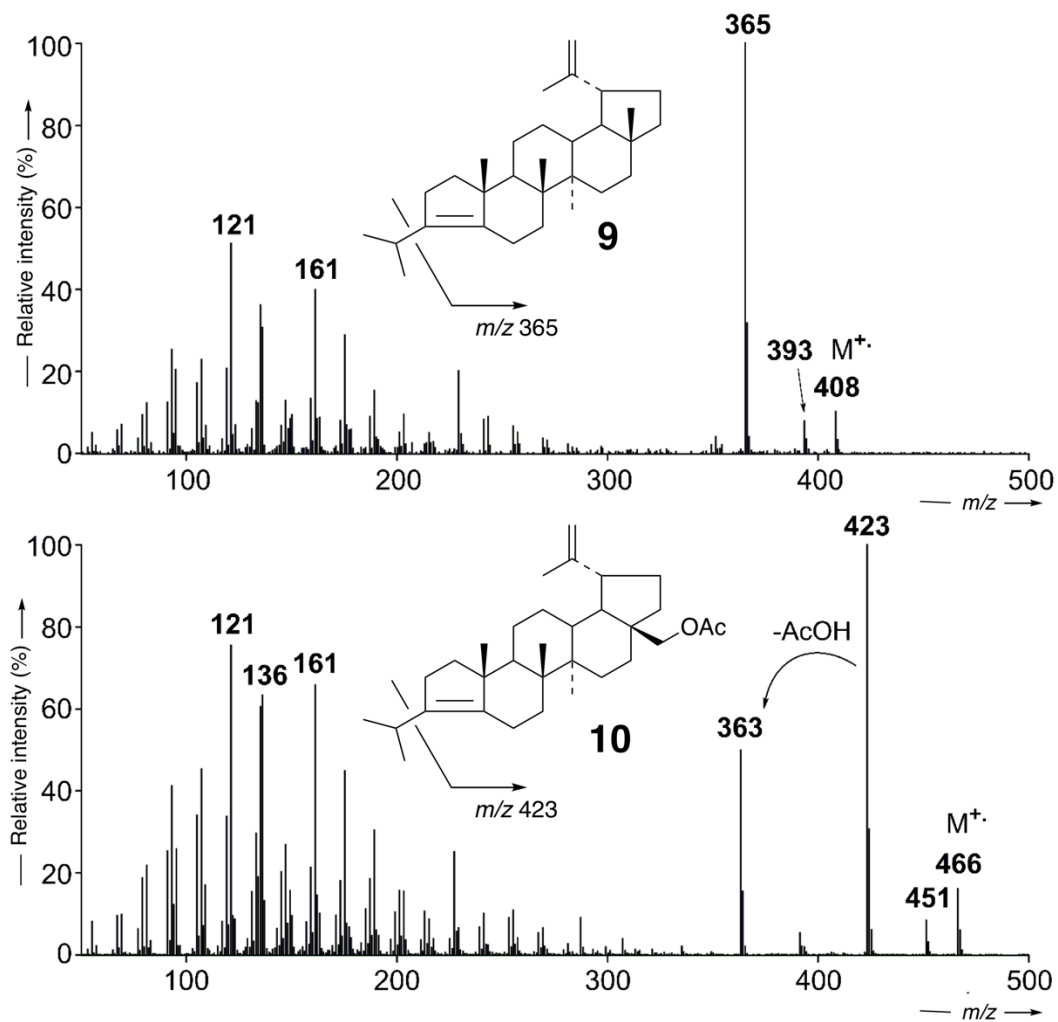


Figure S2: Mass spectra (EI, 70 eV) of *A-neo*-triterpenoids of the lupane series **9** and **10** found in the archaeological sample (sample A) and in the thermally-treated reference samples (samples B and C). Bold numbers refer to the structures shown in the Appendix.