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Molecular study of waterproofing agents from the Zambratija wreck

Armelle Charrié

To identify the nature of macro-residues of the protective coating used to waterproof the hull of the Zambratija boat, chemical analyses were undertaken. These analyses combine the techniques conventionally used for this type of organic material, namely infrared spectroscopy and gas chromatography coupled with mass spectrometry (GC-MS). This study was carried out on two samples described herein.

N° sample	Description	Observations
Z1	inner face of the axial element P2	Light brown powder, almost completely soluble in
Z2	inner face of the plank P1	dichloromethane

Methodology

An account of the basic principles of the procedure used to study this type of archaeological material is reported in several publications (Charrié-Duhaut *et al.* 2009a; 2009b). The molecular approach is based on the identification of diagnostic biomarkers derived from naturally occurring organic substances. Biomarkers are compounds that have retained a carbon skeleton specific enough to be related to their biological precursor, thus enabling identification of the natural substances used. In case of alteration, it is possible to rely on specific degradation by-products (Burger *et al.* 2009).

At first, the samples were analysed by attenuated total reflection – Fourier-transform infrared spectroscopy (ATR – FTIR). The powder sample is directly deposited on the crystal. The device used was a Golden Gate spectrometer (Bruker) operating in mono-ATR mode (64 scans recorded).

Then the samples were solubilized ultrasonically with a mixture of dichloromethane/methanol (1:1 v/v). The solution obtained is then silylated using BSTFA + TMSC (99:1). GC-MS analyses were carried out using a Focus Gas chromatograph interfaced with a ISQ mass detector (injector initial temperature: 35°C, HP-5 MS column, 30 m x 0.25 mm i.d., 0.1 µm film thickness, temperature program: 40°C (1 min), 40-100°C (10°C/min), 100-300°C (4°C/min), isothermal 300°C). Helium was used as carrier gas. Mass spectra were produced at 70eV, source 180°C, in full detection mode over 50-700 amu.

Results and discussion

The FTIR spectra of the two samples are similar. The stretching vibrations of the -CH_2 and -CH_3 groups ($2956\text{-}2922\text{-}2869\text{ cm}^{-1}$), as well as their bending bands ($1458\text{-}1384\text{ cm}^{-1}$), account for the hydrocarbon skeleton of the residue. However, the absence of carbonyl groups that are usually expressed by the vibrations of elongations at 1717 and 1701 cm^{-1} and of aromatic rings at 1600 cm^{-1} is noteworthy. The absorbance profiles seem different from that usually observed for a product derived from conifers, more specifically from the family of Pinaceae (Colombini *et al.* 2003; Izzo *et al.* 2013).

The GC-MS profiles of the two samples are again very similar. They are predominantly dominated by diterpenic compounds all derived from abietic and pimaric acid (Fig. 1). These derivatives are diagnostic of coniferous oils, resins, and tars (Bailly *et al.* 2013; Bailly 2015).

The presence of aromatic compounds (retene, tetrahydroretene, 19-norabiétatriene, 18-norabietatriene for the main) indicates a product having undergone heating, and therefore probably pitch, tar obtained by heating coniferous wood (Fig. 2). Heating, however, remained moderate since the proportion of polyaromatic hydrocarbons remains low compared to acids. The predominance of dehydroabietic acid, the presence in significant amounts of abietic, pimaric, isopimaric acid indicates a low degree of alteration.

Bailly *et al.* (2016) described a series of alkyl guaiacyl dehydroabietates as novel markers of pitch. Such mixed esters between dehydroabietic acid and alkylmethoxyphenols were identified in the two samples. They are characterized by the fragments m/z 173 and 255 (characteristic of the “dehydroabietate” part) and a molecular mass of 436 u.m.a.

Conclusion

The molecular data clearly show that the two samples correspond to pitch, characterized by the identification of diterpenic structures related to abietic / pimaric acid and alkyl guaiacyl dehydroabietates.

Captions and figures

Fig. 1: Examples of diagnostic compounds of pitch.

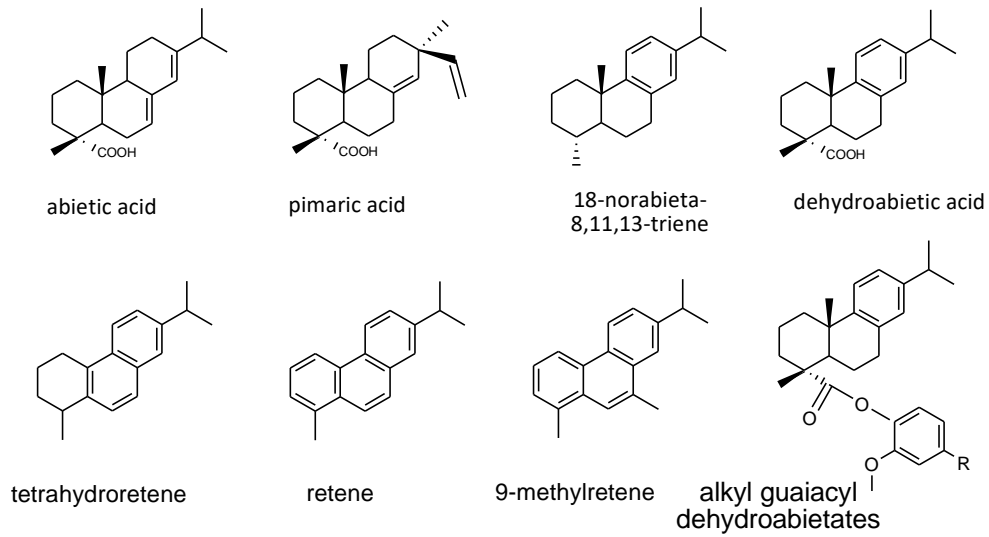


Fig. 2: GC-MS profiles of samples Z1/8 and Z2

