Identification of archaeological oak wood by GC-MS analysis

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Introduction

Nowadays, chemical and physical methods are widely used by archaeologists in order to obtain information on ancient artifacts and on the history of the sites where they have been discovered. In particular, analytical methods have been used for assessing the nature and the degree of alteration of archaeological organic materials, as well as the origin of the natural substances used. In this context, buried tree-trunks have been discovered recently on an archaeological site in Gerstheim (Alsace). Based on preliminary investigations, the wood samples seem to originate from oak. The aim of our study was to confirm this hypothesis based on the gas-chromatography-mass spectrometry (GC-MS) analysis of the lipidic extract of one archeological sample. The results were compared with those resulting from the analysis of another archaeological oak wood sample from an old Roman (220-230 AD) bridge of Chalon-sur-Saône (France).

Material and methods

The wood sample was extracted by sonication using a mixture of CH_2Cl_2 and CH_3OH (1:1, v/v). The solvent extract was filtered through a cotton plug and removed under reduced pressure. The extract was first acetylated overnight at room temperature (Ac_2O/Pyridine 1:1 v/v). After removal of the solvent and excess of reagents, the acetylated extract was esterified using an ethereal solution of diazomethane. The extract was further fractionated by liquid chromatography on silica gel eluting with a mixture of CH_2Cl_2/AcOEt (8:2 v/v) and CH_2Cl_2/CH_3OH (1:1 v/v), leading to a moderately polar and a polar fraction (fractions F1 and F2, respectively).
The less polar fraction F1 was analyzed by GC-FID and GC-MS. GC analysis was carried out on an HP 6890 Series gas chromatograph equipped with an "on column" injector, a HP-5 column (30 m, 0.32 mm ID, 0.25 µm film thickness). Hydrogen was used as carrier gas (2.5 ml/min, constant flow). The oven temperature program was as follows: 70°C to 200°C, (10°C/min); 200°C to 300°C (4°C/min) ; isothermal at 300°C. GC-MS analysis was carried out on a TSQ Quantum triple quadrupole mass spectrometer coupled to a TRACE GC ULTRA gas chromatograph (THERMO scientific) equipped with a Tri Plus autosampler, a PTV "simili on column" injector and a HP-5MS column (30 m, 0.25 mm ID, 0.25 µm film thickness). Helium was used as carrier gas and the temperature program was identical to that used for the GC-FID analysis. Mass spectrometer was operated in electron impact mode (EI, 70ev) scanning with a mass range from 50 to 700 m/z.

Results and discussion

GC-MS analysis of our sample shows that four triterpenes (1-4; Fig. 1) predominated the lipid distribution and that five other triterpenes (5-9) were present in lower amounts. Based on the interpretation of mass spectra, it appeared that triterpenes 1-6 were identical to those present in the oak wood sample from the Roman bridge used as a reference material (Fig. 2), although with slight differences regarding their relative proportions. The molecular structure of these triterpenes has been recently identified and is characterized by the uncommon occurrence of an oxygenated functionality exclusively located at the position 2 of the triterpene hydrocarbon skeleton (Le Milbeau et al., 2010). The variations observed in the proportions of these six compounds relative to those in the reference material may be explained, notably, by differences in the burial conditions or preservation/ degradation conditions. However, despite these differences, the rather unusual assemblage of C-2 functionalized triterpenes in the investigated sample shows strong similarities with those of the reference Roman oak wook sample, which strongly suggests that the wood species discovered at the archaelogical site of Gerstheim corresponds to oak.

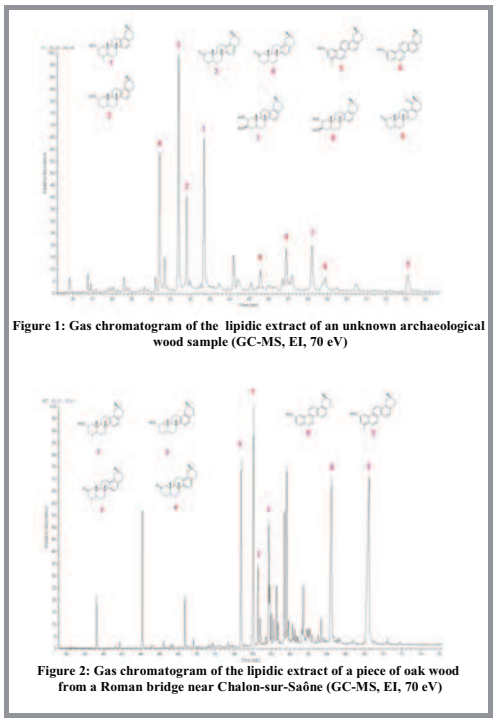

Figure 1: Gas chromatogram of the lipidic extract of an unknown archaeological wood sample (GC-MS, EI, 70 eV)

Figure 2: Gas chromatogram of the lipidic extract of a piece of oak wood from a Roman bridge near Chalon-sur-Saône (GC-MS, EI, 70 eV)

Références

C. Le Milbeau, P. Schaeffer, J. Connan, P. Albrecht, P. Adam (2010) Aromatized C-2 oxygenated triterpenoids as indicators for a new transformation pathway in the environment. Organic Letters, 12, 1504