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Pyrolysis–gas chromatography/mass spectrometry of *Quercus* sp. wood Application to structural elucidation of macromolecules and aromatic profiles of different species

M.F. Nonier [a,*], N. Vivas [a], N. Vivas de Gaulejac [a], C. Absalon [b], Ph. Soulié [b], E. Fouquet [b]

[a] *Tonnellerie Demptos seconded to the CESAMO (Centre d'Etude Structurale et d'Analyse des Molécules Organiques), Université Bordeaux I, 351 Cours de la Libération, F-33405 Talence, France*
[b] *CESAMO, Université Bordeaux I, Talence, France*

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Abstract

Analytical pyrolysis was applied to oak wood to provide useful information concerning the structure of oak wood components and the corresponding extractable polymers (lignins, polysaccharides). We have established the aromatic profile of the formed products during heating and also the chemotaxonomy of different oak wood species, focusing on the qualitative and quantitative aspects.

Keywords: Oak wood; Pyrolysis; GC/MS; Polysaccharides; Lignins; Flavours

1. Introduction

Traditionally, various oak wood species have been used in cooperage for barrel making. During ageing in barrels, only some extractive compounds are solubilized and can affect the composition and the quality of the products [1,2]. As a rule, barrels are made with oak heartwood (*Quercus robur*, *Q. petraea*) and occasionally with other species (*Q. alba*, *Q. accutissima*, *Q. garryana*) [3]. The largest extractable fractions are polymerized ellagitannins, lignins and lignans [4,5] and polysaccharides [6]. The overall composition of oak heartwood is similar: 40% cellulose, 20% hemicellulose, 25% lignins, 10% tannins.

The study of wood constituents is often carried out once they have been extracted and purified. However, an in situ study would also appear to be an interesting approach to analysis. The method generally used is based on the combination of pyrolysis with mass spectrometry [7–9]. This technique is relatively recent and has proven to be of interest when studying macromolecules which tend to undergo marked structural modification during extraction [10] due to partial depolymerization which is indispensable if they are to be isolated.

Pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) is an analytical technique which is able to provide useful information concerning the structure of oak wood components, assuming that pyrolysis products represent, to a greater or lesser degree, the structural units forming the macromolecule. Py–GC/MS is based on depolymerization of the macromolecules by heat followed by identification of the fragments by mass spectrometry. For the polymer subunits which are not, or are only slightly volatile, the increase in temperature leads to their thermal degradation and then to the identification of the products formed [11]. Nevertheless, the information obtained by this technique is dependent on the selected pyrolysis temperature. A low temperature will cause evaporation of some adsorbed compounds from the macromolecular network that are not primary constituents of the macromolecule [12,13]. On the other hand, a high pyrolysis temperature will produce extensive fragmentation of the sample, yielding molecular fragments of low molecular weight and producing secondary reactions [13–15].

* Corresponding author. Tel.: +33 5 40 00 25 78; fax: +33 5 40 00 26 23.
E-mail address: n.vivas@cesamo.u-bordeaux1.fr (M.F. Nonier).

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The study of pyrolysis temperature selection for both lignin and polysaccharides, identified as products in pyrolysates of oak wood, could be of importance in determining the most appropriate temperature for the pyrolysis of oak wood substances, or at least for studying components of the oak wood macromolecule. Pyrolysis temperature is usually chosen without having accomplished a detailed study on the effects of pyrolysis temperature on the oak wood macromolecules. Our objective was to seek the most appropriate pyrolysis temperature for selected materials in order to acquire the greatest possible information concerning the chemical structure of oak wood and its macromolecules. This work initially allowed us to study composition of oak wood and their corresponding extractable polymers (lignins, polysaccharides), then to establish the aromatic profile of the formed products during the heating and the chemotaxonomy of different oak wood species.

2. Experimental

2.1. Plant material

The oak samples were made up of heartwood from approximately 120-year-old trees, from homogeneous and appropriately maintained forest compartments. Four different oak wood species were studied: *Q. petraea* from the center of France, *Q. accutissima* from the north-east of China, *Q. garryana* from Oregon (USA), *Q. alba* from Missoury (USA). Only the first quarter of the trunk, the cooperage grade timber, was used for the study. The wood was chopped or sawed and then naturally dried for 24 months. The different samples were planed and then crushed to sawdust in liquid nitrogen, before being strained so as to keep only particles smaller than a 60 mesh size. The samples were freeze-dried, stored and analyzed within a period of 2 months.

2.2. Sample preparation

Selective precipitation of polymerized or combined molecules with high molecular mass has been described in order to fractionate red wine tannins. Utilizing the same principle, we have developed a method of fractionation by selective precipitation of the main groups of oak heartwood macromolecules [16]. Our protocol is composed of three stages: precipitation of the insoluble fraction in water (lignins); followed by the precipitation of the insoluble fraction in ethanol/water (9:1, v:v) (polysaccharides); finally, isolation of the soluble fraction in both water and aqueous ethanol (ellagitannins). Methods of characterization are IR spectroscopy associated with techniques specific for each group.

Preparation of oak extracts: sawdust (*Q. petraea*) (60 mesh) was extracted with acetone/water (7:3; v:v) at room temperature during 12 h. The extract was filtered, acetone and water were removed under reduced pressure (see Fig. 1).

2.3. Analytical pyrolysis

A ''PYROJECTOR SGE II'' (Fig. 2) was used as pyrolyzer, in conjunction with a Varian™ 3400 CX model gas chromatography apparatus equipped with a Varian™ Saturn 4D ion trap detector. Samples (approximately 0.1–0.2 mg) were placed in the pyrolyzer and triplicate pyrolysis experiments were carried out at different temperatures: 300, 400, 450, 500, 600 °C. General profiles for pyrolyzates were obtained using EI-MS. Separation of the pyrolysis products was achieved using a fused-silica capillary column: RTX-20 WCOT™ (30 m × 0.25 mm i.d. × 1 μm phase thickness, 80% dimethyl and 20% diphenylpolysiloxane). Helium was used as the carrier gas at a nominal flow-rate of 1 ml/min. The inlet mode was splitless. The gas chromatography oven was operated using the following programme: isothermal for 10 min at 50 °C, then raised from 50 to 280 °C at 6 °C/min. The mass spectrometer was set at 70 eV. Spectra were produced using a ChemStation software package. Identification was achieved by mass fragmentometry, by comparison of their mass spectra and relative retention times with those of compounds reported in the literature and the National Institute of Standards library (NIST). When possible, the identifications were accomplished by comparison with authentic standards.

Quantification was based on peak areas (total integral of identified compounds equals 100). The syringyl/guaiacyl

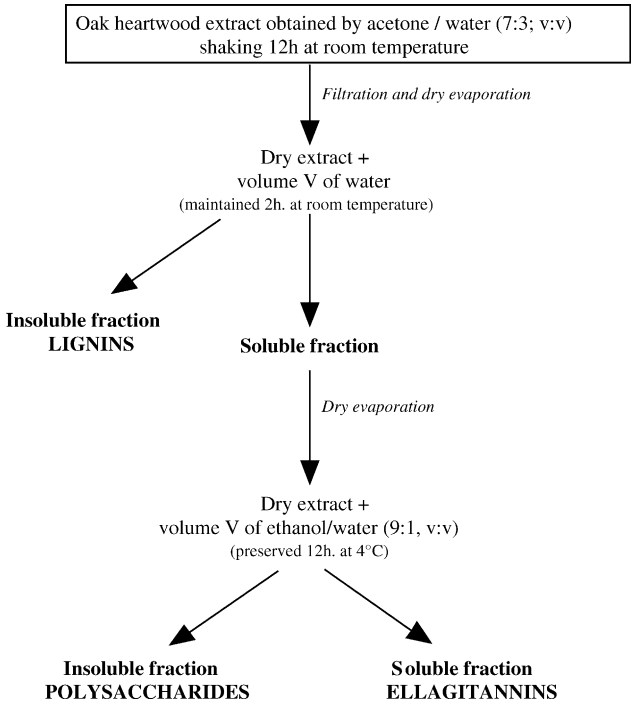

Fig. 1. Fractionation protocol by selective precipitations of oak heartwood macromolecules [16].