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Oak barks as raw materials for the extraction of polyphenols for the chemical and pharmaceutical sectors: A regional case study

Maxime Dedrie[a], Nicolas Jacquet[b], Pierre-Louis Bombeck[a], Jacques Hébert[a], Aurore Richel[b],*

[a] *Forest Resources Management, Department of Biosytem Engineering, Gembloux Agro-Bio Tech, University of Liège, Passage des Déportés, 2-B-5030 Gembloux, Belgium*
[b] *Unit of Biological and Industrial Chemistry, Gembloux Agro-Bio Tech, University of Liege, Passage des Déportés, 2-B-5030 Gembloux, Belgium*

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ABSTRACT

Despite their potential for chemical recycling, residues from forest harvesting and wood processing are mostly used for industrial applications with low added value (energy, paper pulp, and panels). Bark of both oak species, *Quercus robur* L. 1753, *Quercus petraea* (Matt.) Liebl. 1784 is a by-product from sawmill and pulp mill activities. Bark is mainly used as a fuel for the same wood plants. The aim of this study is to look at the feasibility of enhancing the value of this material through the extraction of bioactive molecules, such as polyphenols (*i.e.* catechin, gallic, and ellagic acids). First, the effect of industrial storage of logs and bark on their polyphenol content was explored. Then, referring to the selection of tan oaks in the past, the question of an optimum harvesting age is addressed in order to maximize the polyphenol content of the barks. In the end, molecular diversity of bark is examined through the identification of molecules of interest, using different chromatographic analyses. The results show an effect of the industrial context and an effect of the raw material age on the chemical properties of the bark. First investigations also highlight molecules of interest and the molecular diversity, which needs to be further explored.

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1. Introduction

Logging and wood processing generate by-products used as raw material for other industries or as an energy source. Bark can be valued as mulch after crushing and sieving or in horticulture after fine grinding and composting phase. However, most often, bark is burned to meet energy needs in the wood processing industries. These activities have a relatively low added value (Rochez et al., 2013; Simon et al., 2014). The bark that protects the tree against external aggression is known to contain many chemicals whose extraction could create new business opportunities. In this context, oak seems to be an interesting species. Already exploited in the past for the production of tannins, oak bark could know a renewed interest in its potential content of high added value molecules.

The oak is found throughout the Northern hemisphere, in Asia, Europe, and North America. This exploratory study examined the oaks present in Belgium only. Belgian forests cover 700,000 ha of which 540,000 ha are located in Wallonia. Oak is present in Wallonia with two species *Quercus robur* L. and *Quercus petraea* (Matt.) Liebl. Oak is the main hardwood species covering 85,000 ha. Standing volume is estimated at 15 million m^3 with an annual increment of 385,000 m^3 and a harvested volume estimated at 245,000 m^3. Globally, Belgium the sixteenth producer of oak in Europe. The production is largely dominated by the Russian Federation, France, and Germany with respective estimated growing stock volumes of oak of respectively 859, 551 and 302 millions m^3 (http://environnement.wallonie.be/dnf/inventaire).

Typically bark represents 10–20% of the log volume and this percentage decreases with the tree growth. The bark proportion tends to increase in the branches with an average value of 20–35%. Bark from *Q. robur* L. is composed of typical lignocellulosic components, mainly cellulose, hemicelluloses, and lignin with an average content of 25% for cellulose, 9% for hemicelluloses, and 38% of lignin. Ashes represent 2% of the total dry weight and extractive components are of about 16% (Dietrichs et al., 1978). These extractives compounds include mainly polyphenols and most especially tannins and phenolic acids (Wegener, 1984). The state of the art describes the presence of some of these polyphenols in oak, either in the log (gallic acid, ellagic acid, vescalagin, castalagin, grandinin, roburin, eugenol, syringaldehyde, coniferaldehyde, and vanillin) or in the bark (catechin, gallocatechin, leucopelargonidin,

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* Corresponding author: Tel.: +32 81 622 633; fax: +32 81 622 231.
E-mail address: a.richel@ulg.ac.be (A. Richel).

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Table 1
Origin and description of the raw materials.

Sample	Longitude	Latitude	Species	Estimated age (year)	C_{130} (cm)[a]
ST1	4°42′38.91″E	50°32′45.24Ň	*Quercus robur* L.	148	179
ST2	4°46′58.62″E	50°36′0.56″N	*Quercus robur* L.	25	31
ST3	4°46′58.62″E	50°36′0.56″N	*Quercus robur* L.	85	103
ST4	4°46′47.71″E	50°35′38.70″N	*Quercus robur* L.	151	183
ST5	4°46′48.33″E	50°35′34.61″N	*Quercus robur* L.	244	295
SY1	5°9′9.20″E	50°4′42.59″N	*Quercus robur* L.	140	200
SY2	5°9′9.20″E	50°4′42.59″N	*Quercus robur* L.	130	205
SY3	5°9′9.20″E	50°4′42.59″N	*Quercus petraea* (Matt.) Liebl.	110	245
SC1	4°44′38.74″E	50°14′9.53″N	/	/	/

[a] C_{130} is the circumference measured at 1.30 m.

leucocyanidin, and leucodelphinidin) (Frederich et al., 2009). The relative abundance of these compounds might depend on growth conditions, tree age, tree components, etc. (Prida and Puech, 2006).

The recovery of such extractive compounds, associated to the valorization of the lignocellulosic fraction, is nowadays of interest in the development of renewable resource-based economy. In this context, this work aims at studying in details the compositional profile of oak bark collected on standing trees (at different growing stages). Moreover, the analyses of oak barks from sawmill industries highlight the impact of the debarking process and the storage conditions on the chemical composition.

In this work, we propose thus to investigate deeply the use of oak barks as suitable raw materials for the extraction of polyphenols. The effect of storage conditions is proposed as well as the impact of the growing stage. The objective is to correlate the effect of these both parameters on the chemical composition of extracts enriched in secondary metabolites obtained from oak barks.

2. Material and methods

2.1. Samples and associated chemical compositions

Oak bark was sampled in Wallonia in February 2014 according the TAPPI T257 cm-12 standard (Table 1). A first batch concern bark collected on standing trees (samples ST1–ST5). A second one originates from a storage yard of a local sawmill (samples SY1–SY3) and the third one comes from a storage container collecting bark residues after the debarking (sample SC1).

After sampling, all raw materials were washed with deionized water to remove impurities. Practically, 1 g of sample was stirred in 5 mL deionized water for 1 min. After filtration, bark samples were dried in an oven at 60 °C for at least 3 h until constant mass, before being conserved at −20 °C. Grinding was performed according to the TAPPI T265 norm into 0.5 mm diameter particles. Storage of the grinded samples was ensured at −20 °C.

Moisture content was evaluated using 1 g of sample held in an oven at 105 °C and weighted regularly until readings stabilized. All values were then expressed on a dry matter basis. Compositional analyses were performed using described protocols (Vanderghem et al., 2011). Fat analysis was ensured using the Soxhlet procedure. A mixture of chloroform and methanol (respectively, in proportion 2:1 v/v) at 65 °C was used according to extract the fat in approximately 5 g of sample, for 5 h. For ash analysis, 3 g of each sample were burned to ash for 12 h in a muffle furnace at 600 °C. Total amounts of extractives were assessed in a Soxhlet apparatus by two successive extractions with water and ethanol (1 g of raw material for 70 mL solvent) (Sluiter et al., 2005). Cellulose and acid soluble lignin contents were measured by the acid-detergent method (ADF) of Van Soest in a Fibertec system (Brussels, Belgium) using cetyltrimethylammonium bromide in 1 M sulphuric acid previously standardized as the acid detergent solution. One gram of each sample was analyzed twice. Acid insoluble lignin also known as Klason lignin was determined by the method described by Sluiter et al. (2008). Total lignin content tallied with the sum of Klason lignin and acid soluble lignin. The amount of total hemicelluloses was estimated as the remainders of the samples after the other substances (fat, ash, cellulose, hemicelluloses, and moisture) were accounted for. Monosaccharides composition (free monosaccharides and non cellulosic carbohydrates) was found out by gas chromatography after hydrolysis and derivatization of monosaccharides in alditol acetates (Blakeney et al., 1983).

2.2. Extraction and characterization of secondary metabolites

Extraction of secondary metabolites was ensured using a solvent-extraction protocol. Water and ethanol extractives were assessed in a Soxhlet apparatus by two successive extractions with water and ethanol (1 g of raw material for 70 mL solvent) (Sluiter et al., 2005). The same protocol was repeated using acetone, ethanol, water, and hexane using an extraction time of 6 h. Extraction yields were estimated gravimetrically by weighing the sample after solvent removal under reduced pressure. The total amount of soluble phenolics was estimated using the Folin–Ciocalteu assay and was determined as miligram equivalents of gallic acid per gram dry matter (GAE), by means of calibration curves with gallic acid standards (Amendola et al., 2010). Catechin, gallic acid and ellagic acid contents were determined using conventional gas chromatography techniques.

2.3. Statistical approach

Each aforementioned experiment was ensured in triplicate. For all collected data, means, and standard deviations were calculated using the Minitab® v.16 software. The Welch's method was used to compare means between samples on each parameter of the same series of data with a level of significant difference defined as $p < 0.05$.

3. Results and discussion

This study was divided into two distinct approaches, willing to highlight, in one hand, the effect of the storage conditions and, in another hand, the impact of the growing age of the oak on the overall chemical compositions and the extractability of secondary metabolites.

ST1 was arbitrary selected as the benchmark. Its chemical composition was compared to samples SC1 and SY1–SY3 in order to assess an effect of the debarking process and storage conditions. The water content was estimated at 43.4 ± 2.4% for ST1, 60.0 ± 2.0% for SY1, 43.6 ± 2.8% for SY2, 56.7 ± 7.8% for SY3, and 49.1 ± 7.6% for SC1. Using the Van Soest's method, cellulose percentages for all samples were found nearly identical with an average content of 23–24% (Fig. 1). Hemicelluloses varied between 12.0 and 16.1%, respectively, for SY2 and ST1, while total lignin contents were

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