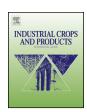
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# Selective fractioning of *Pseudotsuga menziesii* bark and chemical characterization in view of an integrated valorization



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#### ARTICLE INFO

Article history: Received 31 March 2015 Received in revised form 13 May 2015 Accepted 25 May 2015 Available online 2 July 2015

Keywords:
Pseudotsuga menziesii
Bark
Chemical composition
Fractionation
Cork
Phloem

#### ABSTRACT

The outerbark of *Pseudotsuga menziesii* was chemically analyzed after selective fractioning into different particles sizes. Fractionation was selective: after grinding, the coarse fraction (>2 mm) was enriched in cork and was obtained in higher yield (53.9%).

The mean bark chemical composition was, as % o.d. mass: ash 5.9%; total extractives 26.7%; lignin 29.5% and suberin 22.0%. The fine fraction of bark was richer in extractives (31.7%) namely polar compounds soluble in ethanol and water (29.2%). The content in lipophilic extractives was higher in the coarse fraction (5.5%). The polysaccharides contained glucose (65.7% of total neutral monossacharides), mannose (11.8%), xylose (9.0%), arabinose (7.1%) and galactose (6.5%). The ethanol and water extracts contained phenolics, flavonoids, condensed and hydrolysable tannins. The lipophilic extracts were analysed by GC–MS, directly and after saponification, revealing two major compounds:  $\beta$ -sitosterol and tetracosanoic acid. The fine fraction was enriched in extractives and polysaccharides as well as in inorganics, and impoverished in suberin in comparison with coarse fractions.

Milling and fractionation may be applied as pre-treatment for Douglas-fir bark utilization, by separation of cork-rich fractions for cork-based products e.g., composites, and phloem-rich fractions for extraction of polar extractives and further processing of the polysaccharide-lignin matrix under a biorefinery approach.

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#### 1. Introduction

Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) is an important species and one of the world's best timber producers. It is a conifer autochthonous to North America, where it occupies approximately 14.4 million ha in the USA and 4.5 million ha in Canada (Weiskittel et al., 2012). *P. menziesii* arrived in Europe, in 1827, and since then has been widely distributed, more than any other North American conifer (Lavender and Hermann 2014) e.g., 330,000 ha in France (Champs de, 1997), 134,000 ha in Germany (Hapla, 1997), 47,000 ha in the U.K. (Locke, 1987), 30,000 ha in Spain (Vega, 1990). In Portugal, Douglas-fir covers about 10,000 ha and has shown great potential in the central and northern mountains (Goes, 1991; Louro and Cabrita, 1989; Luis, 1989). *P. menziesii* is now the economically most important exotic tree species in European forests (Schmid et al., 2014).

The large stem size and excellent wood properties make Douglas-fir a choice species for providing knot-free sawn timber of great length. Douglas-fir wood is used for structural applications

required to withstand high loads, for plywood and in the construction industry both for interior and exterior uses e.g., its reasonable good durability makes it useful for poles and railway sleepers. Most timber now comes from plantation forests in Europe and North America which are managed to produce fast growing timber with few knots.

Douglas-fir was used traditionally also for other purposes e.g., Indian tribes used different parts of the tree for medicinal purposes (Moerman, 1998) and the antimicrobial and vermicidal activities of its essential oils are well-known (Zou and Cates, 1995, 1997; Jirovetz et al., 2000a,b; Johnston et al., 2001; Tešević et al., 2009).

Bark is the main residue in the wood industry, resulting from the primary processing of logs, and represents an interesting biomass source due to its availability and concentration. The total annual production of bark is well above 20 million tons in the USA and approximately 6–8 million tons in Europe (Ogunwusi, 2013). Since a major cost of processing biomass refers to collection and transportation, the availability of bark at the mill site as a residual side-stream makes it an attractive potential raw material for industrial utilization (Garcia-Perez et al., 2009). Barks' richness in chemicals (e.g., lipophilic extractives, phytosterols, triterpenic acids and other phenolic compounds) (Freire et al., 2002a,b; Pietarinen et al., 2006; Santos et al., 2011) makes them a

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possible raw material for new pharmaceutical and bioactive compounds, green polymers and bio-based materials (Sen et al., 2010; Valentín et al., 2010; Baptista et al., 2013; Miranda et al., 2013). We already know from the literature that some barks from other conifers species such as *Eucalyptus* trees are rich in lipophilic compounds, namely triterpenic acids, with a wide range of biological activities being interesting for phytopharmaceutical applications (Domingues et al., 2010; Domingues et al., 2011a,b; Freire el al, 2002a, Santos et al., 2011; Patinha et al., 2013).

The potential of Douglas-fir bark as a raw-material was recognized early and therefore several studies characterized it, as compiled by Kurth (1950) and Hall (1971). Further chemical and physical characterizations were done more recently e.g. for production of essential oils (Li et al., 2011; Jirovetz et al., 2000a,b) and plant containers (Buamscha et al., 2007) or to assess its impact on bark beetles (Reed et al., 1986).

One of the interesting features of Douglas-fir bark is that it contains a substantial proportion of cork in the rhytidome (Patel, 1975; Krahmer and Wellons, 1973). Cork is an important and economically relevant industrial material with an interesting set of properties and applications, as reviewed by Pereira (2007). It is nowadays obtained from the cork oak (*Quercus suber*) but its presence in other barks has triggered studies on their characterization as potential cork providers e.g., *Quercus variabilis* (Miranda et al., 2013), *Quercus cerris* (Sen et al., 2010) or *Betula pendula* (Miranda et al., 2012; Pinto et al., 2009). The cork from Douglas-fir bark was chemically characterized and found to contain a substantial amount of suberin (Graça and Pereira, 2000).

The idea of valuing the cork component of Douglas-fir bark is not new (Laver and Fang, 1989; Graça and Pereira, 1999). However the complexity of bark structure and chemical composition causes in most of the cases difficulties to usage, especially when specific components are targeted. In the case of Douglas-fir bark, the cork layers are interspersed with phloem regions which make their separation difficult. Mechanical fractioning may contribute to solve this problem since size reduction can allow separating fractions with differentiated compositions (Silva et al., 2011) and its application to fractioning of various barks showed potential for selective enrichment in components (Miranda et al., 2014).

This approach was followed in the present study, aiming at valorizing *P. menziesii* bark residues as a bioresource and targeting towards a fractioning leading to cork enrichment. It was hypothesized that fractioning would result into differing contents of the cork component in the various fractions given the differences in mechanical properties of the tissues contained in the bark, namely between cork and phloem. The bark was triturated and fractions with different particle size were chemically characterized in relation to summative chemical composition, inorganic composition, and extractives analysis. It is the aim to provide information that may sustain an integrated valorization of Douglas-fir bark under a full-resource use concept, mainly through the exploitation of high value low molecular weight compounds from bark.

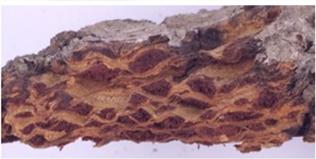
#### 2. Materials and methods

#### 2.1. Samples

The bark sample from *P. menziesii* Mirb. Franco was a composite sample of the outer barks collected from trees with approximately 100 years of age, grown in the central mountain of Serra da Estrela, in Portugal. The barks were stored in indoor conditions with low light and good ventilation.

The bark of *P. menziesii* contains large areas of cork tissue as part of the successive layers of the rhytidome that are clearly visible to the naked eye in the three sections as discontinuous patches





**Fig. 1.** Bark of *Pseudotsuga menziesii* var. *menziesii* showing the successive layers of cork (lighter colored regions) and of phloem (darker colored regions) in the rhytidome in tangential sections (upper figure) and in a transverse section (bottom figure).

interspersed by phloem tissue (Fig. 1). An estimate done by image analysis area measurement in the tangential section of the bark pieces led to an average cork proportion of 58%.

#### 2.2. Fractioning

After air-drying at ambient conditions, the barks were mixed into an homogenized sample and ground in a cutting mill (Retsch SM 2000) using an output sieve with  $10\,\mathrm{mm} \times 10\,\mathrm{mm}$  openings, and sieved with a vibratory sieving apparatus (Retsch AS 200 basic) with standard sieves with the following mesh sizes:  $80\,(0.180\,\mathrm{mm})$ ,  $60\,(0.250\,\mathrm{mm})$ ,  $40\,(0.425\,\mathrm{mm})$ ,  $20\,(0.850\,\mathrm{mm})$ ,  $15\,(1.0\,\mathrm{mm})$  and  $10\,(2.0\,\mathrm{mm})$ . After sieving, the mass retained on each sieve was weighed and the corresponding mass fraction yields were determined. Fractioning of homogenized sample of barks was done in triplicate, and for the yields determination was found the mean value of each.

The different granulometric fractions of bark were macerated in an aqueous solution of  $\rm H_2O_2$  (30% in volume) and  $\rm CH_3COOH$  in a 1:1 (v/v) proportion at 60 °C for 24 h, for cell dissociation, and stained with astra blue. Light microscopic observations were made using Leica DM LA and photomicrographs were taken with a Nikon Microphot-FXA.

#### 2.3. Bark basic density and bulk density of fractions

Bark density  $(\rho_p)$  was determined using oven-dry mass and green saturated volume determined by the water immersion method:

$$\rho_p = m_p/Vp$$

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