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Chemical characterization of the lipophilic fraction of giant reed (*Arundo donax*) fibres used for pulp and paper manufacturing

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Abstract

The chemical composition of lipophilic extractives from *Arundo donax* stems (including nodes and internodes), used for pulp and papermaking, was studied. The lipid fraction was extracted with acetone and redissolved in chloroform, and then fractionated by solid-phase extraction (SPE) on aminopropyl-phase cartridges into four different fractions of increasing polarity. The total lipid extract and the resulting fractions were analysed by gas chromatography and gas chromatography/mass spectrometry, using short- and medium-length high-temperature capillary columns, respectively. The main compounds identified in the fibres included series of long-chain *n*-fatty acids, *n*-alkanes, *n*-aldehydes, *n*-alcohols, monoglycerides, free and esterified sterols and triterpenols, steryl glucosides, steroid hydrocarbons and steroid and triterpenoid ketones. Minor amounts of other compounds such as diglycerides, waxes and tocopherols were also identified among the lipids of *A. donax*.

Keywords: *Arundo donax*; Lipophilic extractives; Pitch; Fatty acids; Sterols; Steryl glucosides; GC; GC/MS

1. Introduction

In the last decades, fast growing plants have received particular attention as alternative sources of cellulose fibres (van Dam et al., 1994; Moore, 1996). These non-wood plants are the common fibre source for paper pulp production in developing countries where wood fibres are not available. In the developed world, although wood is still by far the main raw material for pulp and paper manufacture, a market exists for high-value-added papers from these fibres. *Arundo donax* L. (giant reed) is a widely distributed naturally growing perennial rhizomatous grass with a segmented tubular structure like bamboo (Seca et al., 2000), which has been considered as one of the promising non-wood plants for pulp and paper industry (Shatalov and Pereira, 2002). The easy adaptability to different ecological conditions, the annual harvesting period and the high biomass productivity (32–37 t (year ha)$^{-1}$ of dry biomass) reached by intensive cultivation (Vecchiet et al., 1996), combined with appropriate chemical composition (Shatalov et al., 2001), make *A. donax* very attractive as an alternative source of fibres (Shatalov and Pereira, 2005).

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To improve the utilisation of *A. donax* fibres, it is necessary to broaden the knowledge of structural features of its components. Previous chemical research on *A. donax* includes chemical composition, general features of macromolecular components (Pascoal Neto et al., 1997) and structures of isolated hemicelluloses (Driss et al., 1973; Joseleau and Barnoud, 1974, 1975, 1976). A few studies on the lignin composition (Joseleau and Barnoud, 1976; Joseleau et al., 1976; Faix et al., 1989) showed that it is composed of guaiacyl- and syringyl-propane units with minor amounts of *p*-hydroxyphenylpropane units (Faix et al., 1989) and associated with phenolic acids (Tai et al., 1987). However, until now no studies about the composition of *A. donax* lipophilic fraction have been performed.

The amount and composition of lipophilic extractives is an important parameter in wood processing for pulp and paper production and it is dependent on factors such as the plant species, age, and growth location. The different lipid classes have different chemical behaviour during pulping and bleaching (Gutiérrez and del Río, 2003; Freire et al., 2005). The lipophilic extractives are also responsible for the formation of sticky deposits on the machinery, giving rise to dark spots in bleached pulp and paper, the so-called pitch, both with negative economic impact on pulp and paper industry (del Río et al., 1998, 2000; Gutiérrez et al., 2004; Gutiérrez and del Río, 2005; Silvestre et al., 1999). The accumulation of lipophilic compounds leads also to higher chemicals consumption during pulping and bleaching and therefore increasing production costs. On the other hand, extractives or their derivatives, might contribute to the toxicity of paper pulp effluents and products (McCubbin and Folke, 1995; Rigol et al., 2003). The detailed identification of such lipophilic components is therefore an important step in the study of the behaviour and fate of extractives during pulp and paper production and consequently in the search for new solutions to control pitch deposition as well as to decrease effluent toxicity.

In the present paper, the chemical composition of the lipophilic extractives from *A. donax* fibres was studied. Gas chromatography (GC) and GC/mass spectrometry (GC/MS) using, respectively, short- and medium-length high-temperature capillary columns with thin films, that enable elution and separation of high-molecular-mass lipids such as waxes, steryl esters and triglycerides, are employed. For a more detailed characterization of the different homologous series and other minor compounds, the extract was fractionated by a simple solid-phase extraction (SPE) method using aminopropyl phase cartridges, as described previously (Gutiérrez et al., 1998, 2004).

2. Experimental

2.1. Samples

Samples of *A. donax* L. reed stems (including nodes and internodes) were supplied by the University of Huelva, Spain. The samples were air-dried and milled using a knife mill (Janke and Kunkel, Analysenmühle). For the isolation of lipids, the milled samples were Soxhlet extracted with acetone for 8 h. The lipophilic extractives were obtained by redissolving the dried acetone extract in chloroform and evaporated to dryness under nitrogen.

2.2. Solid phase extraction (SPE) fractionation

The chloroform extracts (5–20 mg) were fractionated by a SPE procedure in aminopropyl phase cartridges (500 mg) from Waters (Division of Millipore, Milford, MA, USA), as already described (Gutiérrez et al., 1998, 2004). Briefly, the dried extract was taken up in a minimal volume (<0.5 mL) of hexane:chloroform (4:1) and loaded into the cartridge column previously conditioned with hexane (4 mL). The cartridge was loaded and eluted by gravity. The column was first eluted with 8 mL of hexane and subsequently with 6 mL of hexane:chloroform (5:1), then with 10 mL of chloroform and finally with 10 mL of diethyl ether:acetic acid (98:2). Each isolated fraction was dried under nitrogen.

2.3. GC and GC/MS analyses

For identification and quantification, the total extracts and the SPE fractions were analysed by GC and GC/MS. For GC analysis, a Hewlett-Packard HP 5890 gas chromatograph equipped with split–splitless injector and a flame ionization detector (FID) system was used (Hewlett-Packard, Hoofddorp, Netherlands). The injector and detector temperatures were set at 300 and 350 °C, respectively. Duplicate samples (1 μL) were injected in the splitless mode. Helium was used as the carrier gas. The capillary column used was a 5 m × 0.25 mm i.d., 0.1 μm film thickness, high-temperature, polyimide-coated fused silica tubing DB-5HT from J&W Scientific (Folsom, CA), especially processed for use at 400 °C. The oven was temperature programmed from 100 °C (1 min) to 350 °C (3 min) at 15 °C min^{-1}. Peaks were quantified by area and a mixture of standards (tetracosane, hexadecanoic acid, β-sitosterol, cholesteryl oleate and triheptadecanoin) was used for quantitation. The data from the two replicates was averaged.