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Chemical composition and cellular structure of ponytail palm (*Beaucarnea recurvata*) cork

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ABSTRACT

Ponytail palm (*Beaucarnea recurvata* Lemaire) is a succulent plant indigenous to Mexico frequently used as an ornamental plant throughout the world. The mature trees develop a thick corky outer bark that was studied here for the first time and compared with cork of *Quercus suber* Linnaeus (cork oak) and other species. The anatomical structure of ponytail palm cork showed a typical honeycomb structure in the tangential section and a brick-wall layer in the transverse section. The cells were larger and had thicker cell walls than those of *Q. suber* cork. Ponytail palm cork had a distinct growth ring pattern but the cell wall undulation lacked the regular wave pattern as in *Q. suber* cork. Fiber-like cellular structures were present protuberating from the lenticular channels. Ponytail palm cork chemically differs from *Q. suber* and other corks by a much lower content of suberin and enhancement of the lignocellulosic nature (18.2% extractives, 11.8% suberin, 29.7% lignin and 39.0% polysaccharides). Although in general similar to that of *Q. suber* cork, suberin composition of ponytail palm cork has specific features namely regarding the ratio of α,ω-diacids and ω-substituted hydroxyacids and presence of higher amounts of alkanoic acids. The lignin of ponytail palm cork is a HGS-type of lignin (1:12:5) with a S/G ratio of 0.4. These results add to data showing that monomeric composition of suberin and lignin of corks are species' specific. The lipophilic extractives included mainly saturated alkanoic acids and sterols while the polar extractives showed overall low amount of phenolics and unremarkable antioxidant properties.

1. Introduction

Ponytail palm (also known as elephant's foot), is a succulent plant indigenous to Mexico (García-Mendoza and Galván, 1995; Eggli, 2002, Walker, 2015). It is a monocot angiosperm of the *Asparagaceae* family and one of the 12 species of the genus *Beaucarnea* (Rojas-Piña et al., 2014).

Ponytail palm is an evergreen perennial that at maturity grows a stem that expands at the base up to 3 m in diameter with several erect branches forming a tree up to 9 m (Fig. 1). Each branch ends in a tuft of long strap-shaped, recurved leathery leaves, and the mature plants flower with panicles of small white flowers. The bark of older plants is rough and fissured and has a corky appearance (Fig. 1). In its regions of origin, most populations of this species are in danger because of habitat destruction due to urban expansion and increase in agriculture (Contreras et al., 2008). However, the plant is easily raised from seed and available through the commercial nursery trade. Its distinctive architecture has made it a valued ornamental that is found now throughout the world as mature trees in gardens and outdoor spaces as well as potted plants in indoor conditions.

The species is well adapted to hot and dry climates, and the swollen stem base is regarded as a water storage adaptation. The cork bark may also contribute to plant protection since cork is an insulator and rather impermeable to fluids (Pereira, 2015). This has triggered our research interest in line with the on-going studies on cork-containing barks (Leite and Pereira, 2017). To our knowledge, no information is available on the structure and chemical composition of ponytail palm bark, namely on its cork layer.

Cork is a cellular material that constitutes the outer layer of the periderm that surrounds stem and branches and is chemically out singled from other lignocellulosic materials by the presence of suberin as a cell wall structural component. Cork has an interesting set of properties and is an industrial raw material that is processed into different products, the most well-known being the wine cork stoppers (Pereira, 2007). Although the main source for cork is the cork oak, other species are potential cork providers (Leite and Pereira, 2017). The different corks show in general similar structure with some biometric differences while most specific features regard their chemical composition namely the content and composition of suberin (Pereira, 1988a, 1988b, 2013; Şen et al., 2010; Ferreira et al., 2016a, 2016b; Mota et al., 2016;

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Fig. 1. Ponytail palm tree and the surface and cross-sectional features of its stem cork bark.

Cardoso et al., 2017).

In the current study, the chemical and anatomical features of the cork of ponytail palm were investigated. The overall objective is to contribute to the state-of-the-art of the knowledge on non-conventional corks leading to a better understanding of the species-related chemical characteristics as well as to a potential valorization of these sources for cork production. Comparison of the data obtained with results from corks of other species, namely with *Q. suber* cork, was made to better outline the existing differences.

2. Materials and methods

2.1. Samples

The ponytail palm bark samples were collected from mature plants growing as ornamentals in the campus of Instituto Superior de Agronomia, Lisbon, Portugal (Fig. 1). Several stems were cut and air-dried under well ventilated in-door conditions. The outer region of the bark with a cork appearance and deeply fissured (Fig. 1) was clearly out singled and manually separated. The cork samples were combined, triturated with a Retsch cutting mill and sieved. The 40–60 mesh (0.29–0.42 mm) fraction was taken, oven-dried at 60 °C overnight and used for the subsequent chemical analyses.

Cork samples were also taken and cut in small cubes for microscopic observations.

2.2. Chemical summative composition

Chemical summative composition analyses comprised determinations of inorganic material (ash), extractives, suberin, klason and acid-soluble lignin, and polysaccharides. The analytical procedures were previously described (Şen et al., 2010) and are here only briefly detailed.

Ash was determined after incineration at 500 °C overnight and the residue weighed. Extractives content was determined by successive Soxhlet extractions of ponytail palm cork with dichloromethane, ethanol and water during 6 h, 18 h and 18 h extraction time for each solvent respectively.

Suberin content was determined in the extractive-free cork using methanolysis for depolymerisation (Graça and Pereira, 2000a). The suberin content (that corresponds to the fatty acid derivatives resulting from suberin depolymerization) is quantified as percent of dry cork mass.

Klason and acid-soluble lignin, and carbohydrates contents were determined on the pre-extracted and desuberinised material using total hydrolysis with sulphuric acid.

The polysaccharides content was determined by the neutral monosaccharide monomers released by the total acid hydrolysis used for lignin determination. The sugar monomers were determined using a high performance anion exchange chromatography (HPAEC). The separation was performed with Aminotrap plus CarboPac SA10 anion-exchange columns. The polysaccharide content was calculated by the sum of the individual sugar masses. The detailed methodology can be found elsewhere (Sartori et al., 2018).

2.3. FTIR-ATR

The cork sample was oven-dried and ground with a MM200 mixer mill (Retsch GmbH, Haan, Germany). Spectra were acquired with a Bruker FT-IR spectrometer. The cork powder was placed on the diamond (ATR-FTIR) and the reflectance spectra were collected in the range of 4000–400 cm^{-1} with a spectral resolution of 4 cm^{-1}.

2.4. Composition of suberin

The monomeric composition of suberin was determined in aliquots from the methanolic extracts obtained during suberin depolimerization. The samples were evaporated, derivatized by trimethylsilylation and immediately analyzed by GC–MS. Samples were derivatized prior to analysis in 120 µL of pyridine and the compounds with hydroxyl and carboxyl groups were trimethylsilylated into trimethylsilyl (TMS) ethers and esters, respectively, by adding 80 µl of bis(trimethylsily)-trifluoroacetamide (BSTFA). The reaction mixture was heated at 60 °C for 30 min in an oven. The derivatized extracts were immediately analyzed by injection in a GC–MS Agilent 5973 MSD with the following GC conditions: Zebron 7HG-G015-02 column (30 m, 0.25 mm; ID, 0.1 µm film thickness), flow 1 ml min^{-1}, injector 380 °C, oven temperature program, 50 °C (1 min), rate of 10 °C min^{-1} up to 150 °C, rate of 4 °C min^{-1} up to 300 °C, rate of 5 °C min^{-1} up to 370 °C, rate of 8 °C min^{-1} up to 380 °C (5 min). The MS source was kept at 220 °C and the electron impact mass spectra (EIMS) taken at 70 eV of energy.

The area of peaks in the total ion chromatograms of the GC–MS analysis was integrated and their relative proportions expressed as percentage for semi-quantitative analysis. Compounds were identified