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CORK: A TRADITIONAL MATERIAL AS SOURCE FOR NEW NATURAL BASED CHEMICALS

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ABSTRACT

Cork powder was submitted to chemical treatments in order to obtain its components. Phenolic rich extracts were obtained upon extraction with water, ethanol and ethanol:water 1:1 mixture. The total phenol content was determined (Folin-Ciocalteau assay) and correlated with the antioxidant capacity (DPPH and FRAP assays). Suberin monomers were obtained through alkaline methanolysis of extractive free cork powder and repolymerized into a new polymeric material.

INTRODUCTION

Cork is the bark of the Oak tree *Quercus suber L.*. Portugal is the major producer and processes *ca* 75% of all the cork, resulting in great economical importance (Gil and Moiteiro 2002). Although variable, the average chemical composition accounts for: suberin (33-50%), lignin (13-29%), polysaccharides (6-25%) and extractives (8-24%) (Conde, Cadahia et al. 1998).
Extractives is a general term designating the non-structural components of cork that are readily obtained through simple solvent extraction. Phenols and other plant metabolites are known to possess important biological activities (J.González, J.M.Cruz et al. 2004).
Cork suberin structure has been proposed to be constituted by a polyester structure of long chain fatty acids, hydroxyl fatty and phenolic acids, linked by ester groups (Bernards 2002). Cork suberin exploitation is of great interest mainly because it can constitute a natural source of α-hydroxyfatty acids and α,ω-dicarboxilyc acids and homologous mid-chain dihydroxy or epoxy derivatives (Gandini 2008).
The antioxidant activities of cork extracts was determined through, DPPH radical scavenging activity and FRAP (ferric reducing antioxidant power). The depolymerization and repolymerization of suberin monomers was performed to prepare new materials.

MATERIALS AND METHODS

Cork powder with particle dimensions of less than 1mm obtained from cork of the best quality was used.
Cork extractives were obtained through extraction on a 50L reactor, with a ratio of 1Kg of material to 12.5L of solvent under reflux conditions for 6h. The final extract was obtained after lyophilization.
Total phenols content was determined by measuring the inhibition of oxidation of Folin-Ciocalteau reagent and comparing to gallic acid standards. DPPH radical scavenging activity was determined by measuring the oxidation inhibition of DPPH produced by the extracts. EC50 is calculated from the plot of scavenging activity against extract concentration. The FRAP value was measured by adding a suitable extract dilution to FRAP solution (25ml of acetate buffer (pH=3.6, 30mM), 2.5ml of 2,4,6-tripyridyzil-5-triazine 10nM and 2,5ml of iron chloride 20mM). Absorbance was measured at 593 and compared to ascorbic acid standards.
Suberin monomers were obtained by treating cork with a 0.5M NaOH MeOH:H_2O 9:1 solution and extracted with chloroform. Suberin repolymerization was performed in bulk adding 0.5% (w/w) of tin oxide as catalyst. The reactor was maintained at 150°C for 3hours, under a constant stream of nitrogen.

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RESULTS AND DISCUSSION

Cork extracts were analyzed for total phenols content, DPPH radical scavenging activity and FRAP. Results are presented in Table 1.

Table 1 – Total phenol and antioxidant tests performed.

Extract	Total Phenols ($mgGA_{eq}/g_{extract}$)	DPPH EC50 µg/ml	FRAP mg AAeq/g ext.
Water	500	2.79	362
Ethanol	391	3.28	276
Ethanol 50%	563	2.13	521

The water and ethanol 50% extracts present the higher phenol content, with special relevance for the latest..
The DPPH EC_{50} and FRAP values are consistent with the total phenols trend. The lower the EC_{50} value, the more effective the extract is as antioxidant. In FRAP assay, the higher the value, the more effective is the antioxidant. Considering the results ethanol 50% and water extracts are the most promising extracts as a potential source for natural antioxidants. Moreover, these results were obtained using crude extracts, as obtained from the extraction process. Fractioning and or isolation of the active molecules in the crude extracts could significantly increase the antioxidant activity.

Suberin monomers have a paste like consistency which becomes liquid at around 60°C. The repolymerization experiments were performed at 150°C under constant stirring and a stream of nitrogen. The reaction product has a rubber like consistency and the FTIR (fourier transformed infra-red) analysis, Figure 1, shows an increase of the ester groups (≈ 1730cm^{-1}), with the corresponding decrease of the carboxylic acid (≈1710cm^{-1}).

Although further work will be necessary, the results obtained so far, show that cork composition chemicals have potential for new non-traditional applications that can result in important valorization for this remarkable material.

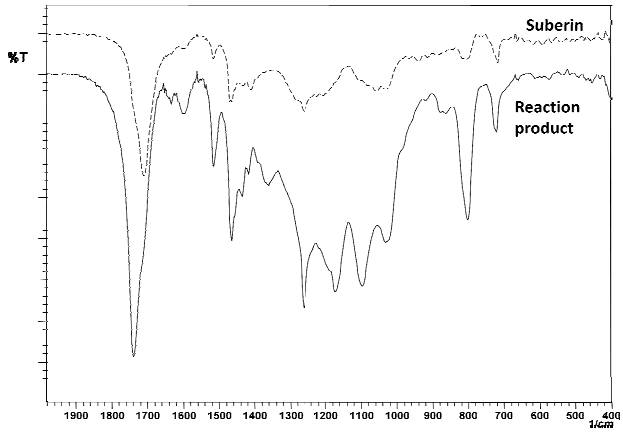

Figure 1 – FTIR analysis of suberin and the esterification reaction product.

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IVO AROSO obtained a degree in chemistry by the Sciences College, University of Oporto in 2003. In 2007 has concluded pos-grad studies in processing and characterization of materials in University of Minho. Since 2008 is conducting research related to cork chemicals in order to obtain its PhD.