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

Ivo Aroso, João F. Mano and Rui L. Reis
Department of Polymer Engineering
E-mail: ivo.aroso@dep.uminho.pt

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ABSTRACT

Cork material was submitted to chemical treatments in order to break its structure and to obtain its components. The individual fractions obtained comprise individual fractions obtained with dichloromethane, ethanol and water. The extractive fractions total phenol content was determined (Folin-Ciocalteau assay) and correlated with the antioxidant capacity (DPPH and FRAP assays). It was found that the higher the phenolic content the higher the antioxidant capacity is. These procedures envision the valorization of cork as a potential natural source for new chemicals.

INTRODUCTION

Cork is the bark of the Oak tree *Quercus suber L.* which is periodically harvested every 9–12 years, depending on the regions. The cork Oak is a slow growing, evergreen tree that flourishes only in specific regions of the Western Mediterranean (Portugal, Spain, Southern France, Italy and North Africa) and China. Europe holds *ca* 60% of the total production area (cork forests) and produces more than 80% of the World's cork. Portugal is the major producer and processes *ca* 75% of all the cork(Gil and Moiteiro 2002).

The cork chemical composition is affected by different factors, such as, geographical origin, climate or age of the trees. Overall the average chemical structure of cork is based on: 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. This fraction is composed by compounds involved in the methabolic process and artifacts that have suffered further modifications. Because these molecules are not covalently linked to the cell wall, they are readily obtained through simple solvent extraction procedures given that appropriate solvents are used. Plant methabolites, in particular, phenolic rich compounds have been found to possess important biological effects. Flavonoids and other polyphenols were shown to possess anti-tumoral, anti-allergic, anti-platelet and anti-imflammatory activities among others. This study concentrates in the fractionated extraction of the extractives fraction and its further valorization as a possible antioxidant molecules source(J.González, J.M.Cruz et al. 2004; Silva, Sabino et al. 2005).

Procedures for obtaining the complete extractives fraction of cork have been developed and are based in the sequential extraction with the solvents dichloromethane, ethanol and water. The antioxidant capacity is determined following long established and nowadays universal procedures for DPPH radical scavenging activity.

In the present study we envisage the valorization of suberin as a starting material for new polyester materials and of the cork extractives as a new natural source of antioxidant molecules.

MATERIALS AND METHODS

Cork material used in the form of powder with particle dimensions less than 1mm and obtained from boiled natural cork of the best quality.

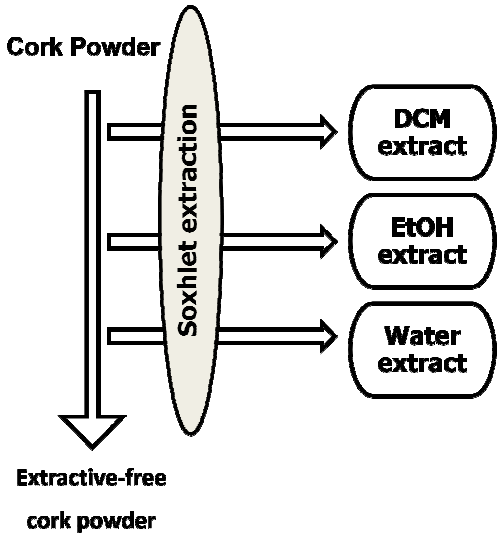
Cork extractives were obtained through soxhlet extractions. Each extraction procedure is carried for 6h after which the solvent is removed by evaporation under reduced pressure, suspended in water and lyophilized.

Total phenols content (Folin-Ciocalteau) was determined as described elsewhere(Santos, Pinto et al.). Briefly, 2.5mL of diluted (1:10) Folin-Ciocalteu reagent and 2mL of 20% sodium carbonate are added to 0.5mL of accurately weighed extract. Suitable gallic acid solutions are used for standards, and total phenols content is calculated from the Absorbance value at 760nm and expressed as gallic acid equivalents.

DPPH radical scavenging activity was determined as described elsewhere (Santos, Pinto et al.). Briefly 0.25mL of DPPH 0.8mM in MeOH was added to accurately weighed aliquots of the extracts. The absorbance of the mixture was measured after 30min at 517nm. EC50 is calculated from the plot of scavenging activity against extract concentration and represent the amount of extract necessary to decrease the initial DPPH concentration by 50%.

RESULTS AND DISCUSSION

The cork extractives fraction was obtained following the extraction procedure depicted in Scheme **1**. After lyophilized, the extracts were recovered as powder solids and were used as such in the total phenols content and DPPH scavenging activity.



Scheme 1 – Extraction procedure scheme for cork extractives with solvents: DCM (dichloromethane); EtOH (Ethanol) and water

In **Table 1** are presented the values for total phenols and DPPH EC50 radical scavenging activity.

Table 1 – Total Phenols and DPPH EC_{50} value

Extract	Total Phenols ($mgGA_{eq}/g_{extract}$)	DPPH EC_{50} ($g_{extract}/g_{DPPH}$)
DCM	2,7	1,33
H_2O	471	0,24
EtOH	587	0,13

The extracts obtained with water and ethanol presents the higher values for the total phenols content, with special relevance for the latest which presents the highest value. The extract obtained with dichloromethane presents a residual value and it can be considered that phenolic molecules are absent.

The DPPH EC_{50} value and trend are consistent with the total phenols trend. As lower the EC_{50} value, the more effective the extract is in quenching the radicals, therefore, less quantity is required for the same effect. The ethanol extract presents the higher scavenging activity followed by the water extract. The dichloromethane extract doesn´t seem to have radical scavenging activity.

Considering the results presented ethanol and water extracts are the most promising as a potential source for natural antioxidants. Moreover, the present results were obtained using crude extracts, as obtained. A proceeding work in identification and isolation of the active molecules or fractioning could substantially increase the extract activity.

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AUTHOR BIOGRAPHY

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.