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Novel methodology based on green chemistry for obtaining extracts rich in polyphenols from upcycled cork by-product

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Introduction

Cork is the bark of the cork oak (*Quercus suber* L.), a perennial tree species native and exclusive to Mediterranean forests. The production of cork is possible thanks to the capacity of the cork oak to generate suberous tissue continuously throughout its life.

Cork is a natural material of great value but its industry involves an environmental problem, such as the pollutant load of cork boiling waters [1,2] and the generation of solid waste from the different operations of the industry [1]. However, there is the paradox, that these wastes contain compounds have excellent properties as natural antioxidants and anticarcinogens and, therefore, with applications in the pharmaceutical, cosmetic and food industry [3].
The chemical composition of cork is substantially different from other parts of the tree since cork has some "free" components, not chemically linked to the main structure and, therefore, extractable with solvents [4,5]. One of the most important extractable compounds are phenolic compounds, which are extracted with polar solvents, such as water or methanol, as well as compounds such as phenolic acids, phenolic aldehydes, and coumarins, also include compounds belonging to the chemical families of flavonoids and tannins [3,4].

Phenolic compounds are substances of great interest due to their biological properties, such as antioxidant, antithrombotic, antibacterial, antiallergic, anticancer and anti-inflammatory activity [3,6-8]. Thanks to these properties, they are considered part of the so-called bioactive compounds, i.e., compounds that have a beneficial influence on cellular activity and therefore on health [9]. The interest in natural phenolic compounds have increased considerably in recent years, in addition to their properties, for not presenting adverse effects as often occurs with their synthetic counterparts [10].

Materials & Methods

Raw materials and sample preparation

The cork industry by-products studied were cork boiling water and solid cork residues: 0.5-2.0 mm granulated, high density granulated and cork back (ADT), high density granulated (AD) and mill cork dust (PR).

Samples characterization

- Total phenolic contents (TPC)
- Antioxidant activity (AA) and the half maximal inhibitory concentration (IC50).
- Low molecular weight phenolic compounds.

Phenolic extractions

- *Solid phase extraction for cork boiling waters*
  - The samples of cork boiling water were pre-treated to preconcentrate the phenolic compounds and eliminate interfering compounds. This pre-treatment was performed by solid phase extraction (SPE) with HyperSep C18 cartridges (200mg/3 mL).
- *Traditional methods:* suspension, sonication, Soxhlet.
- *Optimization of extraction processes based on green chemistry*: sonication, maceration, Microwave assisted extraction (MAE), Accelerated solvent extraction (ASE).

Conclusions

The methodology developed in our study follows the guidelines of green chemistry. The cork extracts obtained were rich in phenol compounds with good antioxidant activity. These results, together with the phenolic content values, demonstrate the usage of green chemistry methodology to obtain a cork extract and confirm the potential of these residues as a source of high value compounds.

Results & Discussion

Cork boiling water: In the direct analysis of the ten cork boiling water samples values of 1101 mg gallic acid equivalents (GAE)·L-1 for total phenolic content, 0.52 mmol Trolox·L-1 for antioxidant activity were obtained and eight low molecular weight phenolic compounds were identified. For the cork boiling water pretreated, the increase of phenolic compounds is approximately of 56%.

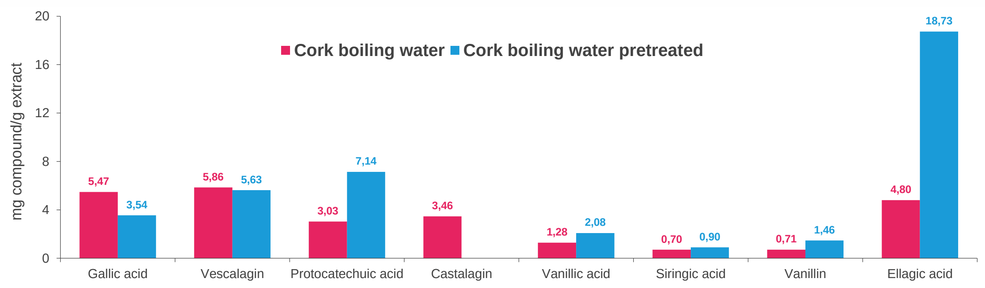

Figure 1. Comparison of low molecular weight phenolic compounds of cork boiling water and the same water pretreated by SPE.

Solid cork residues: ***Traditional methods***

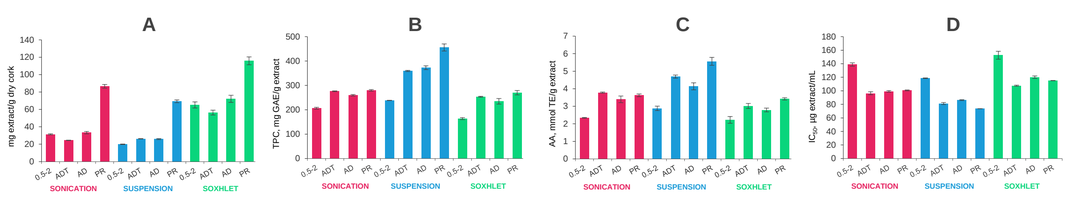

Figure 2. Characterization of extracts obtained by traditional methods: **sonication (pink)**, **suspension (blue)** and **soxhlet (green)**.
A: Yield of the extraction process; **B:** Total phenolic content; **C:** Antioxidant activity; **D:** IC50.

Solid cork residues: ***Green chemistry***

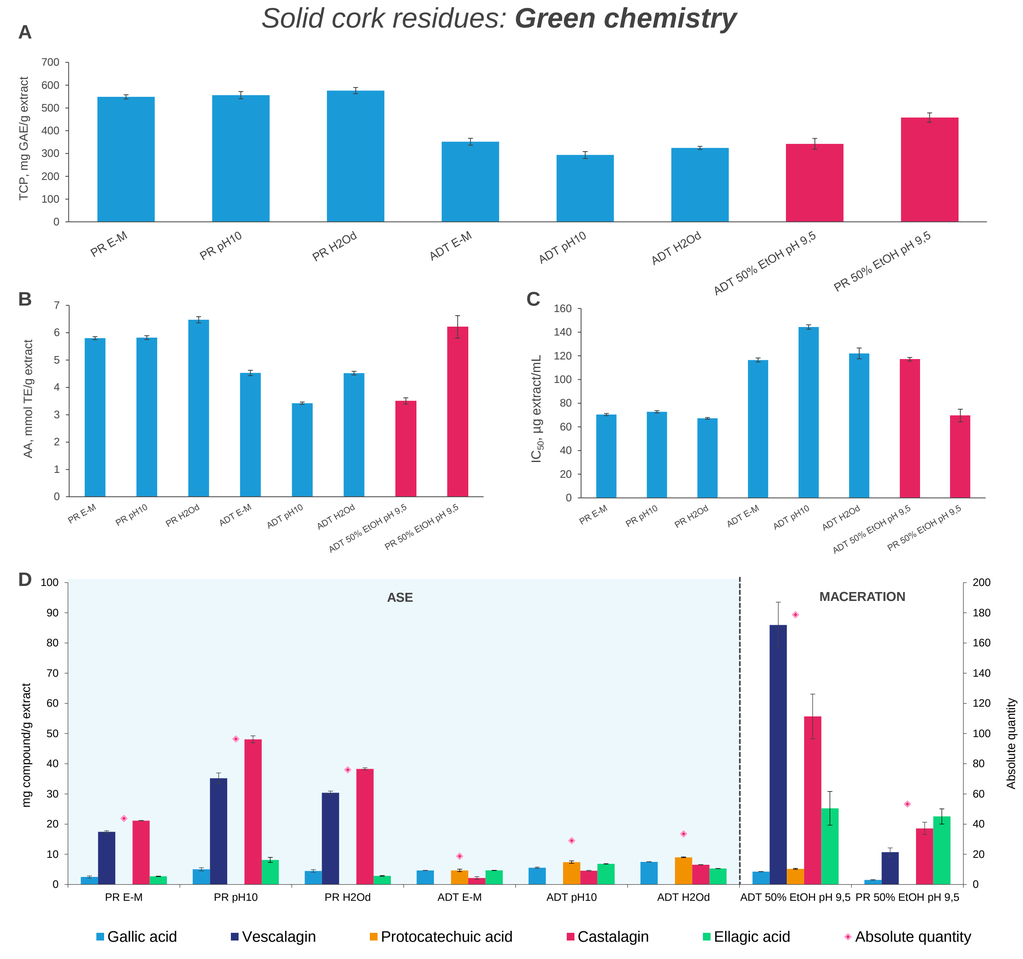

Figure 3. Characterization of extracts obtained by **ASE (blue)** and **Maceration methods (pink).**

A: Total phenol content; **B:** Antioxidant Activity; **C:** $IC_{50;}$ **D:** Low molecular weight phenolic compounds;. Sample coding: PR (mill cork dust); ADT (high density granulated); E-M (ethanol 33%-methanol 0.38%); pH10 (water pH10); H_2Od (distilled water); pH9.5 (alkaline water pH9.5); 50% EtOH pH 9.5 (50% ethanol- alkaline water pH 9.5).

The results of these extraction processes are as following: extraction yields between 22-90mg extract/g dry cork, total phenolic content in the range 293-576mg GAE/g extract, antioxidant activity of 3.3-6.5mmol Trolox/g extract and IC50 between 67-144µg/ml.

Traditional extraction has allowed us to determine that two of the solid cork residues, ADT and PR, have the highest phenolic concentration. These two cork by-products have been used in the optimisation process based on green chemistry and led to the conclusion that the two most efficient extraction methods were maceration and ASE.

Acknowledgements

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