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Polyphenol composition and antioxidant and metal chelating activities of the solid residues from the essential oil industry

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ABSTRACT

Essential oils of aromatic plants have numerous applications in fields like medicine, cosmetic and food industry. Nevertheless, the average yield of essential oil distilled from aromatic plants is below 5% (w/w) and consequently a considerable amount of solid residues is generated. These residues are especially rich in polyphenols that can be exploited as health-promoting compounds in food and feed or as anti-aging ingredients in cosmetic products, and thus to enhance the overall profitability of the aromatic plants. In this work, we have tentatively identified the polyphenols present in solid residues from the steam distillation of *Cistus ladanifer*, *Lavandula* × *intermedia*, *Santolina rosmarinifolia* and *Thymus mastichina*, and evaluated their antioxidant and chelating activities by means of several *in vitro* methods, such as the β-carotene/linoleate model system, reducing power, DPPH radical scavenging, and iron and copper ion chelation. A *Soxhlet* extraction and an ultrasound-assisted extraction have been used in terms of comparison. Most of the extracts whether they were obtained by *Soxhlet* system or by ultrasonic method showed good antioxidant activities. *Soxhlet* ethanolic extract of *T. mastichina* showed an antioxidant activity comparable to the standard red grape pomace. The influence of the total polyphenol content on the chelating activities was not as important as on the antioxidant activities and the predominant role of certain polyphenols and/or the presence in the extracts of other compounds with a favourable chemical structure to metal complexation can be assumed. This was the case of the ultrasound ethanolic extract of *C. ladanifer*, which was the most effective in iron chelating activity despite its medium-to-low content of total polyphenols. All these data point to profit from these aromatic plant solid residues as a valuable source of bioactive compounds.

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1. Introduction

Aromatic plants have been widely used from ancient times in medicine, cosmetics and for preserving and improving the flavour of foods. Their beneficial properties have been mainly attributed to the presence of essential oils, which are complex mixtures of compounds belonging to diverse chemical families including terpenes, alcohols, aldehydes, phenolic compounds, esters, ethers and/or ketones. These compounds are well characterized in most of the aromatic plants and numerous publications have been devoted to their antioxidant, antimicrobial, antitumor and bioplaguicide properties (Gould, 1997; Miguel, 2010; Santana et al., 2012).

Essential oils are usually obtained from raw plant materials (flowers, buds, seeds, leaves, twigs, bark, herbs, wood, fruits and roots) by distillation with water and/or steam. The average yield of essential oil distilled from aromatic plants is below 5% (w/w) and consequently a considerable amount of both liquid and solid residues is generated during the industrial processing (Santana-Méridas et al., 2012). These residues may result in environmental concerns if they are not properly managed, but they are also a significant source of bioactive compounds that can increase the overall profitability of the aromatic plants improving the rational utilization of natural resources.

Residues from distillation are especially rich in polyphenols that can be exploited as health-promoting compounds, as antioxidants in food and feed or as anti-aging ingredients in cosmetic products (Navarrete et al., 2011; Torras-Claveria et al., 2007). However, the

Abbreviations: A.U., absorbance units; DPPH, 2,2-diphenyl-1-picrylhydrazyl; IC_{50}, 50% inhibition concentration; PV, pyrocatechol violet; ROS, reactive oxygen species; SXEE, *Soxhlet* ethanolic extract; USAEE, ultrasound-assisted ethanolic extract.

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literature concerning chemical and biological characterization of these residues is scarce especially in the case of solid residues. Torras-Claveria et al. (2007) have detected flavonoids and hydroxycinnamoylquinic acid derivatives with antioxidant activities in lavandin (*Lavandula* × *intermedia* Emeric ex Loiseleur) waste and Parejo et al. (2004) have reported the separation and characterization of phenolic compounds in the remaining material after distillation of fennel (*Foeniculum vulgare* Mill.). More recently, phenolic compounds with antioxidant, antiradical and antiacetylcholinestarase activities have been described in spent flowers and green leaves of oil-bearing rose (Göktürk and Baydar, 2013) and in decoction waters of some aromatics plants (Albano et al., 2012).

Since much of phenolic compounds are not volatile, are not degraded with thermal treatments and remain in the aromatic plants wastes after distillation of raw plant materials (Torras-Claveria et al., 2007). Aerial parts of *Cistus ladanifer* L. show abundance of hydrolysable tannins derived from gallic and ellagic acids, and flavonoids like quercetin, kaempferol and apigenin derivatives (Barrajón-Catalán et al., 2011; Barros et al., 2013; Chaves et al., 1998; Fernández-Arroyo et al., 2010), whereas *Lavandula* × *intermedia* is characterized by the presence of phenolic acids and procyanidins (Blažeković et al., 2010). To our knowledge, the polyphenol composition of aerial parts of *Santolina rosmarinifolia* L. and *Thymus mastichina* L. has not been yet investigated. However, *Thymus* species have been reported as sources of a large variety of phenolic acids and flavonoids, which play important role as antioxidants (Roby et al., 2013) and as taxonomic markers providing distinction of species (Boros et al., 2010; Corticchiato et al., 1995; Marin et al., 2003). Literature on the polyphenol composition of the genus *Santolina* is very scarce although some flavonoids like apigenin, luteolin and quercetin have been described as components of *Santolina oblongifolia* Boiss. with anti-inflammatory activity (Silván et al., 1996).

In this work, we have identified the major polyphenols present in solid residues after the steam distillation of *C. ladanifer*, *Lavandula* × *intermedia*, *S. rosmarinifolia* and *T. mastichina*, and evaluated their antioxidant and chelating activities by means of several *in vitro* methods, such as the β-carotene/linoleate model system, reducing power, DPPH radical scavenging, and iron and copper ion chelation. Two methods of extraction have been used: *Soxhlet* extraction and ultrasound-assisted extraction. The objective is to investigate the potential of such residues as source of antioxidant compounds in order to improve the added value of these aromatic plants.

2. Materials and methods

2.1. Standards and reagents

Gallic acid, Folin–Ciocalteu's phenol reagent, linoleic acid, β-carotene, Tween 20, potassium ferricyanide (III), iron (III) chloride, iron (II) chloride tetrahydrate, 2,2-diphenyl-1-picrylhydrazyl (DPPH), ferrozine, pyrocatechol violet (PV) were purchased to Sigma–Aldrich (St. Louis, MO, USA). The phenolic compounds standards, rosmarinic acid, luteolin, catechin and syringic acid were from Fluka-Sigma–Aldrich® (St. Louis, MO, USA), and luteolin-O-glucoside, quercetin, kaempferol, apigenin-7-O-glucoside from Extrasynthese® (Genay, France). All other chemicals were of analytical grade.

2.2. Plant material

Solid residues from steam distillation at industrial scale of Lavandin cv. Super (*Lavandula* × *intermedia* Emeric ex Loiseleur), rock rose (*C. ladanifer* L.), green lavender cotton (*S. rosmarinifolia* L.) and white thyme (*T. mastichina* L.) under ecological cultivation, were obtained from *Peñarrubia del Alto Guadiana* S.L. distillery (Albacete, Spain, http://www.guadianaecologico.com/). Red grape pomace was from a local winery.

2.3. Sample preparation and extraction

The plant material was dried at room temperature in the shade and ground prior to extraction. Approximately 50 g of dried plant material was thoroughly extracted with ethanol in a *Soxhlet* apparatus during 48 h. The crude extracts were subsequently filtered under vacuum and evaporated in a rotary evaporator to obtain the *Soxhlet* ethanolic extract (SXEE). Likewise, 1 g of dried plant material was mixed in 10 mL of ethanol and subjected to the ultrasound-assisted extraction in a Sonorex Super RK 255H type, 50–60 Hz, 360 W (300 mm × 150 mm × 150 mm internal dimensions) ultrasonic bath (Bandelin Electronic, Berlin, Germany) during 15 min. The crude extracts were then filtered (Whatman grade 1) and evaporated under nitrogen flow to obtain the ultrasound-assisted ethanolic extract (USAEE). Red grape pomace was extracted by *Soxhlet* and used as natural antioxidant standard. All samples were kept in sealed tubes at 4 °C until analysis.

2.4. Total polyphenol content of SXEEs and USAEEs

The content of total polyphenols was determined by the Folin–Ciocalteu method as described in Slinkard and Singleton (1977). Gallic acid was used as standard and total polyphenol content was expressed as milligrams equivalent of gallic acid per gram of dry extract.

2.5. Phenolic compounds identification and quantification

The compounds present in the samples were tentatively identified according to their UV and mass spectra and retention times compared with those of standards (when available), with data reported in the literature and/or with positively identified compounds in other reference plant samples.

2.5.1. LC–MS system

The qualitative chemical profile of both SXEEs and USAEEs was achieved using the LC–MS (ESI) technique in a Shimadzu LC/MS-2010A equipped with a LC-10ADvp binary pump, a DGU-14A degasser, a SIL-10ADvp autosampler, and a SPD-M10Avp Photo Diode Array Detector.

2.5.2. LC–MS method for extracts of C. ladanifer solid residues

Method was adapted from Fernández-Arroyo et al. (2010). SXEEs and USAEEs were dissolved in methanol (10 mg/mL) and injected in a 250 mm × 4.6 mm, 5 μm particle size Discovery HS-C18 column (Supelco, Bellefonte, PA, USA) at a flow rate of 1 mL/min at 27 °C. The following gradient of mobile phase A (0.1% formic acid in water at pH 3.2) and mobile phase B (acetonitrile) for the separation of polyphenols was used: Initial 95% (A), 5% (B); 20 min 85% (A), 15% (B); 25 min 85% (A), 15% (B); 35 min 75% (A), 25% (B); 43 min 75% (A), 25% (B); 53 min 100% (B). The injection volume was 20 μL and the UV detection was performed in the 200–700 nm range. Negative ion mass spectra [ESI-SCAN(−)] were recorded in the range of 100–1300 *m*/*z*. The interface conditions were as follows: capillary voltage −3.50 kV, CDL voltage −20.0 V, CDL temperature 250 °C and detector voltage 1.48 kV. The nebulizing gas flow rate was 1.5 L/min and the Heat Block temperature in the mass analyzer was 300 °C.

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