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Oil distillation wastewaters from aromatic herbs as new natural source of antioxidant compounds

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Clinopodic Acid P acid (PubChem CID: 57520027)
Homoplantaginin (PubChem CID: 5318083)
Nepitrin (PubChem CID: 120742)
Chicoric acid (PubChem CID: 5281764)
Caftaric acid (PubChem CID: 6440397)
Luteolin-3′-O-glucuronide (PubChem CID: 10253785)
Salvianolic acid K (PubChem CID: 10482829)
Luteolin-7-O-glucuronide (PubChem CID: 5280601)
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ABSTRACT

Distillation wastewaters (DWWs) are generated during the essential oil steam distillation from aromatic herbs. Despite of growing interest on novel source of natural antioxidant compounds as food additives, studies on DWWs are scarse. Herein, the potential of DWWs produced by the distillation of packaged fresh basil, rosemary and sage wastes was evaluated by chemical and antioxidant characterization.

HPLC-DAD-HRMS profiling revealed that DWWs contain water-soluble phenolic compounds, mainly caffeic acid derivatives and flavonoid glycosides, with rosmarinic acid (RA) as predominant components (29–135 mg/100 mL). DWWs demonstrated high levels of total phenolic compounds (TPC, 152–443 mg GAE/100 mL) and strong antioxidant capacities, in ORAC, DPPH and ABTS assays (1101–4720, 635–4244 and 571–3145 μmol TE/100 mL, respectively). Highly significant correlations of TEAC values with TPC and RA contents revealed that phenolic compounds and high RA content were responsible of DWWs antioxidant properties.Thus, DWWs are proposed as a new promising source of natural food additives and/or functional ingredients for cosmetic, nutraceutical and food applications.

1. Introduction

Aromatic herbs are common food adjuncts used as flavoring, seasoning, and coloring agents and sometimes as preservatives. Those mainly belonging to the Lamiaceae family are also a source of secondary metabolites with well recognized pharmacologically activities. Recently they have been exploited as promising ingredients to develop novel products in sectors like pharmaceutical, cosmetic, food and pesticide industries (Trivellini et al., 2016). Particularly, there is a growing interest in the food industry to replace synthetic antioxidants and additives with compounds from natural sources or plant products. One of the most effective approaches employs the extracts of aromatic herbs as an affordable and valuable alternative to the synthetic additives. In fact, numerous studies demonstrate that herbs of Lamiaceae family (mainly rosemary, oregano, sage, basil, mint, and thyme) have food-preserving properties related to the presence of antioxidant and antimicrobial phenolic constituents (Embuscado, 2015; Trivellini et al., 2016). In addition, the consumption of aromatic herbs is growing due to their value as functional foods able to reduce the need for salt and fatty condiments (Viuda-Martos, Ruiz-Navajas, Fernández-López, & Pérez-Alvarez, 2010).

Thus, the use of natural bioactive compounds of aromatic herbs

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represents an attractive novelty for food sector in order to increase the shelf-life and improve the nutraceutical value of the food products.The improved interest of researchers, consumers and the food industry broadened the request and the typology of products based on aromatic plants. For instance, the production of aromatic herbs destined to packaged fresh products for Mass Market Retailers (MMRs) had a sharp increase in recent years. The wastes resulting from processing, packaging and cultivation of packaged fresh herbs may be useful biomasses for the recovery of high-value products, in line with the concept of biorefinery and green extraction (Lin et al., 2014).

A feasible use can be the production of essential oils and aromatic waters, by steam distillation processes, to obtain quality products in a traceable supply chain. However, the essential oil steam distillation generates two main by-products: the residual plant materials and the wastewaters of the oil distillation process (distillation wastewaters, DWWs). The latter are generated by the partial condensation of hot water that passes through the vegetable matrix and is collected in the distillation chamber (Wollinger et al., 2016). After the distillation, the non-volatile compounds of aromatic herbs remain in the distillation by-products and the hydrophilic water-soluble fraction can be dissolved in the DWWs followed to the extraction of plant material with condensed hot water. Valorization of the by-products (vegetal wastes and DWWs) generated from whole chain of production of packaged fresh aromatic herbs, *via* integrated biorefinery schemes, should target the production of high-value products such as essential oils, aromatic waters and natural food additives and/or functional ingredients for cosmetic, nutraceutical and food applications. In this context, the potential of aromatic herb DWWs as source of compounds with antioxidant and antimicrobial activity should be evaluated. DWWs are an unexplored by-product and very limited data are available on their chemical characterization. DWWs from some essential-oil crops have proposed as growth promoter and modifier of the essential oil composition of spearmint (Zheljazkov & Astatkie, 2012). Recently, a chemical study revealed that the rose oil DWW is a rich source of flavonoids with strong anti-tyrosinase activities (Solimine et al., 2016). Also, DWWs of rosemary have been identified as a possible source of the natural antioxidant rosmarinic acid (Wollinger et al., 2016).

Thus, the aim of the present study was to determine the qualitative and quantitative chemical profiles and antioxidant activity of DWWs obtained from the steam distillation of the waste materials generated from chain production of packaged fresh herbs. Particularly, the research was conducted by taking into account three of the most common Lamiaceae species cultivated in Southern Italy, basil (*Ocimum basilicum* L.) type “Genovese”, rosemary (*Rosmarinus officinalis* L.) and sage (*Salvia officinalis* L.), and various waste materials produced during the processing of packaged fresh aromatic herbs. The latter were the fresh leaves of basil (BL), rosemary (RL) and sage (SL) at the vegetative stage, discarded during the packaging, and the plant materials produced by cultivation procedures, as the elimination of basil (BP) plants that have reached the flowering stage, and the pruning of sage (SP) to encourage the rejuvenation of this perennial crop. DWW samples were obtained by the steam distillation applied to these wastes to recovery essential oils and aromatic waters.

To evaluate the potential of aromatic herb DWWs as source of functional compounds, an accurate chemical characterization of DWWs, by HPLC-DAD-HRMS analysis, was firstly carried out. Later, the levels of main constituents (RA and TPC) in DWWs were determined to assess their contribution to DWW antioxidant properties, determined by three *in vitro* assays (DPPH, TEAC and ORAC).

2. Materials and methods

2.1. Chemicals and standards

MS-grade acetonitrile (MeCN) and water were supplied by Romil (Cambridge, UK). Ultrapure water (18 MΩ) was prepared by a Milli-Q purification system (Millipore, Bedford, USA). Analytical-grade methanol and ethanol, MS-grade formic acid (HCOOH), gallic acid (GA), butylhydroxyanisole (BHA), 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox), 2,2-diphenyl-1-picrylhydrazyl radical (DPPH), Folin & Ciocalteu's phenol reagent, 2,2′-azinobis(3-ethylbenzothiazoline-6-sulphonic acid) diammonium salt (ABTS), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AAPH), fluorescein sodium salt, potassium persulfate ($K_2S_2O_8$), caffeic acid (≥ 98% HPLC), hesperidin (≥ 97% HPLC), luteolin-7-O-glucoside (≥ 98% HPLC) and rosmarinic acid (RA) (≥ 98% HPLC) were obtained from Sigma-Aldrich (Milan, Italy).

2.2. Samples

The fresh aromatic herb wastes of *O. basilicum* L. type “Genovese”, *R. officinalis* L. and *S. officinalis* L. were collected at Azienda Agricola Nicola Palma (Capaccio, Salerno, Italy), a farm specialized in the production of packaged fresh herbs for retail chains.

Steam distillations of waste materials were performed with industrial scale essential oil extractor (Tred Technology, Campobasso, Italy) operating to low processing temperatures (75 °C) obtained with an integrated vacuum system. The extractor system was loaded with 6 L of water and 5 kg of each waste material (three independent extractions), homogeneously distributed and compacted on perforated grids to ensure the spreading of steam over the entire load. The steam distillations were carried out for 1 h from the appearance of the first drops of the distillate. The cooled DWW samples (3.4–4.5 L, clear aqueous solutions) were filtrated immediately through 1.0 μm glass fiber filters (circles size 4.7 cm, Millipore, Bedford, USA) to remove residual plant materials, added with ethanol (1%, v/v) and stored at 4 °C until analyses.

2.3. HPLC-DAD-HRMS analysis

Chromatographic analyses were performed using a Platin Blue UHPLC system (Knauer, Labservice Analytica, Bologna, Italy), consisting of two Ultra High-Pressure Pumps, an autosampler, a column temperature manager and a diode array detector, coupled to a LTQ OrbiTrap XL mass spectrometer (ThermoFisher Scientific, Milan, Italy). A Hibar Purospher® STAR, RP-18 endcapped (3 mm × 150 mm, 3 μm; Merck) column was used at a flow rate of 300 $\mu L \cdot min^{-1}$ at 25 °C. Volume of the injection was 5 μL. The mobile phase was a binary gradient of water (A) and MeCN (B), both containing 0.1%, v/v, formic acid. The gradient elution program is as follows: 0–1 min, 5% B; 1–5 min, 5–20% B; 5–6.5 min, 20% B; 6.5–15, 20–24% B; 15–19 min, 24% B; 19–23 min, 24–30% B; 23–26 min, 30% B; 26–38 min, 30–95% B; 38–39 min, 95–98% B; 39–45 min, 98% B; 45–46 min, 98–5% B; 46–52 min, 5% B. UV spectra were acquired in the range of 200–600 nm, and the wavelengths 245, 280, 325 and 350 nm were employed for the detection. The mass spectrometer, equipped with ESI source, was operated in negative mode. High purity nitrogen (N_2) was used as sheath gas (30 arbitrary units) and auxiliary gas (10 arbitrary units). High purity helium (He) was used as collision gas. Mass spectrometer parameters were as follows: source voltage 4.0 kV, capillary voltage − 33 V, tube lens voltage − 41.5 V, capillary temperature 300 °C. MS spectra were acquired by full range acquisition covering 140–1500 *m/z*. For fragmentation study, a data dependent scan was performed and the normalized collision energy of the collision-induced dissociation (CID) cell was set at 30 eV and the isolation width of precursor ions was set at *m/z* 2.0. The resolution was 60,000 and 7500 for the full mass and the data dependant MS scan, respectively. Phenolic compounds were characterized according to the corresponding spectral characteristics: UV and mass spectra, accurate mass, characteristic fragmentation, and retention time. Xcalibur software (version 2.2) was used for instrument control, data acquisition and data analysis.