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Flowers of *Ulex europaeus* L. — Comparing two extraction techniques (MHG and distillation)

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ABSTRACT

Microwave hydrodiffusion and gravity (MHG) extraction of *Ulex europaeus* was proposed for the production of extracts. The extraction time and yield and the antioxidant and sensorial properties of the extracts were significantly affected by the irradiation power. MHG treatment at 100 W during 76 min provided optimum yields and the extracts showed the highest reducing power and antiradical activity. The extraction time could be reduced in relationship to that needed with steam distillation (153 min) to reach comparable extraction yields and retaining the antioxidant properties. The flower extracts from the two tested technologies showed similar color (colorless) and olfactometric characteristics (floral and ripe fruity aroma).

1. Introduction

Gorse (*Ulex Europaeus*, Linn.) is an evergreen shrub of the Leguminosae family, having spiny branches and bright yellow flowers with a strong and characteristic scent. The medicinal and insecticidal applications have been limited, and mainly restricted to the seeds, which contain alkaloids, studied by different authors [1,2]. Terpenoids and glycosides are the main constituents of flowers [3], and the phenolic content in the flowers is higher than that in other parts of the plant [4]. Volatile organic compound emission was higher for flowering branches than for other plant parts, and isoprene represented 90% of the total. Trans-ocimene and alpha-pinene are the main monoterpenes, accounting for 48% and 37% of the total monoterpenes, and other minor monoterpenes are camphene, sabinene, beta-pinene, myrcene, limonene and gamma-terpinene [5].

The aroma, antioxidant properties and color of the flowers could facilitate their utilization in cosmetics or perfume industry, either as a whole or as extracts. Compounds responsible for these attributes have been also widely employed as ingredients, additives or food flavors or in packaging materials [6]. Extraction of natural products can be carried out by several methods, from the use of different organic solvents (acetone, methanol, ethanol, hexane, etc.) to conventional methodologies, such as steam distillation, hydrodistillation and hydrodiffusion. In order to minimize the use of organic solvents, green chemistry was applied to the extraction of essential oils and antioxidants, by using supercritical fluid extraction (principally with carbon dioxide), subcritical water, ionic liquids, etc.

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[7,8]. Recently, microwave-assisted techniques have been successfully applied to the extraction of natural compounds.

The microwave-assisted extraction has also been useful to recover phenolic compounds from flowers with ethanol, i.e. the extraction of chlorogenic acid from flowers of *Lonicera japonica* Thunb, in shorter time and with higher yields than with conventional heat-reflux extraction [9]. But this technique shows additional advantages for the extraction of essential oils, offering energy and time savings, clean processes, higher product yields and better sensory, antimicrobial and antioxidant properties of the extracts [10,11]. Microwave-assisted techniques were successfully proposed for the isolation and concentration of volatile compounds and essential oils from flowers of fresh mango [12], Damasc rose [13], lavandin [14] and chamomille [15], without adversely influencing the composition of the essential oils and the extracts showed DPPH radical scavenging activity and reducing power.

Among the variety of microwave aided processes available, one method which can offer good results is microwave hydrodiffusion and gravity (MHG) [14]. In addition, it can be applied to the green extraction of natural products according to the biorefinery concept, offering operational advantages derived from the reduction of solvent, energy, wastes… [16]. The extraction and recovery are performed in a single stage involving the application of microwave irradiation and earth gravity [17,18]. The hydrodiffusion allows the extract to diffuse outside the plant material and the extract is dropped on a spiral condenser outside the microwave cavity; water and essential oil are collected and can be separated by density. MHG was successfully applied to the extraction of volatile compounds from fresh plant materials with a minimum 60% of initial moisture [17–19]. To avoid chemical modifications caused by temperature and prolonged extraction time on the aromatic and volatile molecule components, solvent free microwave extraction was proposed [20]. This technique can offer products with enhanced aromatic and antioxidant properties due to the higher content in oxygenated monoterpenes. MHG has also been proposed for the extraction of water soluble fractions with antioxidant properties from different sources, including brown algae [21] and mushrooms [22]. In addition, many natural colors also display antioxidant activity and solvent free microwave extraction techniques can overcome the limitations of other conventional techniques used for their extraction [16,20].

The present study is aimed at selecting the conditions during microwave hydrogravity to maximize the extraction yield from *Ulex europaeus* flowers, and to compare the antioxidant and aromatic properties of the extracts with those produced by steam distillation.

2. Materials and methods

2.1. Materials

The flowers of *U. europaeus* L. were manually collected in April and May 2013 from San Xoán de Río (Ourense, NW Spain). Flowers were separated from leaves and stems and stored at −18 °C.

All standards and reagents were of analytical grade and were purchased from suppliers, such as Merck, Sigma–Aldrich, Panreac and Fluka. Stock solutions were prepared and stored in a freezer at 4 °C and the working standard solution or reagents were prepared by dissolving a required amount of specific reagent in double-distilled water.

2.2. Extraction

The flower samples used for the study were extracted at least three times with two different extraction techniques.

2.2.1. Steam distillation (SD)

The traditional steam distillation without a cohobation system was applied to 50 g of fresh flowers treated with 250 mL of deionized water. Steam was passed through the sample kept in a bag. The distillation process lasted 160 min, including the time required by water to reach the boiling point in a 1 L glass vessel. For comparative experiments, fractions of 30 mL were collected and the last fraction was discarded.

2.2.2. Microwave hydrogravity extraction (MHG)

The MHG procedure for the extraction of flowers was carried out in an open vessel NEOS-GR (Milestone Srl, Italy) microwave extractor with a 1.5 L Pyrex extraction vessel. During experiments at selected irradiation power, time and temperature were recorded. The temperature was measured by using a fiber optic temperature sensor inserted in the microwave cavity. Fresh samples (100 g) were placed in the microwave cavity and subjected to several irradiation powers (25, 50, 100, 150 and 200 W) and fractions of 5 mL were collected, cooled down and analyzed.

The drained liquid phase was analyzed for total solubles, total phenolics, *in vitro* antioxidant properties, color and olfactory characteristics. Analysis was performed in triplicate and the mean values were reported.

2.3. Analytical methods

The extraction yield was gravimetrically determined. The total phenolic content was determined by the Folin-Ciocalteu assay [23] and expressed as gallic acid equivalents (GAE).

The ability to reduce the ferric 2,4,6-tripyridyl-s-triazine (TPTZ) complex under acidic conditions was determined by the FRAP assay [24]. The FRAP reagent was prepared with 25 mL of 300 mmol/L acetate buffer (pH 3.6) and 2.5 mL of a 10 mmol TPTZ/L solution in 40 mmol/L HCl and 20 mmol/L $FeCl_3 \cdot 6\ H_2O$ in distilled water. A volume of 100 μL samples was mixed with 3 mL of the reagent, and the absorbance was monitored at 593 nm. Ascorbic acid was used as the standard.

The scavenging capacity against the ABTS radical (2,2′-azinobis-(3-ethyl-benzothiazoline-6-sulfonate)) was used [25]. The radical cation was produced by reacting 7 mM ABTS stock solution with 2.45 mM potassium persulfate.