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CO_2-supercritical extraction, hydrodistillation and steam distillation of essential oil of rosemary (*Rosmarinus officinalis*)

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ABSTRACT

Essential oil of rosemary was obtained by supercritical CO_2-extraction (SCE), hydrodistillation (HYDRO), and steam distillation (SD). Quantity of oil, antioxidant activity, and chemical composition (gas chromatography-mass spectrometry, GC-MS) of the essential oils were evaluated. For SCE, oil was obtained at two temperatures (40 and 50 °C) and two pressures (10.34 and 17.24 MPa) using a rosemary particle size of 600 ± 50 μm. The yield was between 1.41 and 2.53 g essential oil (EO) 100 g^{-1} of dry rosemary (% w/w). The antioxidant activity values were in the range 29.67–37.55 mg equivalent of Trolox (ET) g^{-1} of EO or 22.66–30.81 mg ascorbic acid (AA) g^{-1} of EO. Yields of essential oil were between 0.35 and 2.35%. The antioxidant activity was found in the range 1.73–2.60 mg ET g^{-1} of EO or 1.50–2.20 mg AA g^{-1} of EO. Camphor, eucalyptol, β-caryophyllene, and borneol acetate were the main chemicals detected by GC-MS in EO.

1. Introduction

The possibility of replacing the extraction of natural products using organic solvents by supercritical fluid extraction was proposed by Djarmati et al. (1991) and Nguyen et al. (1991). The extraction of antioxidants from plant sources using organic solvents has the disadvantage of causing oxidative transformations during solvent removal (Sebastian et al., 1998). It has been reported that the supercritical fluid extraction may render extracts with higher antioxidant activity than those obtained by using organic solvents. Wenqiang et al. (2007) reported 19.6, 10.1, and 11.5% of essential oil from clove buds using the SCE (50 °C, 10 MPa), SD, HYDRO methods, respectively. Goretti et al. (2004), on the other hand, reported 54.0, 34.6, and 73.1% of eugenol in essential oil obtained by the SD, MO (microwave oven distillation), and SCE methods, respectively.

The supercritical fluid extraction technology meets some desirable properties for the production of natural products and/or functional ingredients. According to Rizvi et al. (1994), when a gas is compressed isothermally at pressures beyond its critical pressure, the gas performs as a solvent at its critical temperature; such fluids are called supercritical fluids. A supercritical fluid behaves very well above its triple point. Products of biological origin, such as natural food preservatives or functional ingredients, are sometimes heat labile and easily oxidized; consequently they need to be processed at low temperatures and, if possible, using oxygen-free atmospheres. Carbon dioxide is not oxidant and has a critical temperature of 31.1 °C, making it suitable for the extraction of natural sensitive products from parts of plants. The use of supercritical carbon dioxide, for obtaining extracts from plants, is a technique used for recovering of high value-added ingredients (Pourmortazavi and Hajimirsadeghi, 2007; Reverchon and De Marco, 2006; Babovic et al., 2010; Herrero et al., 2010).

Today, due to the consumer's demands and the increasing legal restrictions for delivering healthy foods to consumers, the supercritical CO_2-extraction could be the alternative to the solvents extraction of heat labile components. Thus, high quality products, free from solvents could be obtained (Reglero et al., 2005). Despite the above information, the reason for the limited use of the supercritical fluid extraction technology is the high cost of investment

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compared to the solvent extraction technology (Reglero et al., 2005). Nevertheless, in an experimental way, the supercritical technique has been used widely for extracting essential oils of a number of different parts of plants such as seeds of pomegranate (Abbasi et al., 2008), mint leaves (Aghel et al., 2004), lime (Atti-Santos et al., 2005), patchouli (Donelian et al., 2009), ocimum leaves (Goretti et al., 2004), just to mention some.

Rosemary is an aromatic plant belonging to the Lamiaceae family. Rosemary has been cultivated since ancient times and recognized as one of the plants with the highest content of antioxidants. Substances in *R. officinalis*, associated with such activity, are carnosol, rosmanol, isorosmanol, rosmadiol, carnosic acid, rosmarinic acid, and methyl carnosate (Ibañez et al., 2003). Traditionally, rosemary oil is extracted by steam distillation. The extraction with supercritical CO_2, as an alternative method for solvents extraction, may retain the essential oil components without any change or degradation; in addition, this solvent may also remove other groups of compounds. It has already been obtained the rosemary essential oil by the supercritical extraction process. Researchers have investigated effects of particle size, flow rate of the solvent, pressure, temperature, and the addition of ethanol to the tested material (Bensebia et al., 2009). Carvalho et al. (2005) have already investigated the effect of the CO_2 supercritical fluid extraction of essential oil of rosemary on the kinetics, performance, composition, and antioxidant activity of the oil. However, the extraction conditions may vary according to a number of variables that can change (biological material) or can be changed (type of equipment, working variables). Regarding biological materials, plants may differ in composition depending on the season, growing conditions, variety, pre-treatments such as dying or blanching. In the case of working variables, equipments, depending if they are of a commercial brand or constructed in place, can have different instrumentation for controlling variables such as pressure (pressure gauges), temperature (temperature gauges), flow of gases, among others, that may restrict the use of the equipment. In any case, the working conditions should be optimized for each biomaterial and fluids used for the extraction.

Usually, essential oils are complex mixtures of up to 100 components, these can be low molecular weight aliphatic compounds (alkanes, alcohols, aldehydes, ketones, esters, and acids), monoterpenes, sesquiterpenes, and phenylpropanes. There are a number of essential oils which components, such as carvacrol, cinnamaldehyde, citral, *p*-cymene, eugenol, limonene, menthol, and thymol, have been considered by the FDA as GRAS substances and are registered by the European Commission as food flavorings (Pérez, 2006).

The aim of this study was to characterize the antioxidant activity and chemical composition of the essential oil of rosemary grown in Mexico obtained by the supercritical CO_2-extraction, hydrodistillation, and steam distillation methods.

2. Materials and methods

2.1. Materials

Fresh rosemary (*Rosmarinus officinalis* L.) was purchased in the local market of the city of Cholula, Puebla, Mexico.

2.2. Sample preparation

Rosemary branches were dried in a foods tray dryer (Excallibur, Pennsylvania, and USA) at a temperature of 35 °C for 24 h. Leaves were removed from the branches for obtaining the essential oil. Whole and pulverized, in a mortar, dried rosemary leaves were used for the oil extraction. The pulverized sample was sieved using a kit Keck Sieve Shaker (Cole Parmer, Vernon Hills, IL, USA). Dried samples were packed into plastic bags, sealed under vacuum, protected from light and stored at room temperature until use.

2.3. Supercritical CO_2-extraction system

The supercritical fluid-extraction equipment was assembled and starting to work at the University of the Americas Puebla. The extraction system is a modification based on a system found in the Laboratory of Thermodynamics of the Thermophysics Research Area on solubility (Eustaquio-Rincón and Trejo, 2001) and recovery (Avila-Chávez et al., 2007) of hydrocarbons at the Instituto Mexicano del Petróleo (IMP) in Mexico City. The supercritical fluid-extraction equipment consists of three main sections: the inlet or feeding section, the extraction section and the outlet section.

2.3.1. Inlet section

This section provides the solvent (CO_2) and allows to reach the required pressure conditions for entering into the extraction section. The system of this section is made up of one tank of CO_2 (99% purity), one compressor, one pressure gauge, one thermo compressor, one Supercritical Fluid Pump model SFT-10 by Supercritical Fluid Technologies Inc. (Newark, DE, USA), and serpentine flow tubing for driving CO_2 to the recollection cell.

2.3.2. Extraction section

In this section, the extraction process takes place at the working temperature and pressure conditions. It consists of the following parts: an equilibrium cell for extraction made of 316 stainless steel (6.1 cm in diameter, 18 cm in height, and 0.526 L in volume), a pressure gauge attached to the extraction cell, a heating system made up of light bulbs and fans, and a Cole Parmer Digi-Sense temperature controller R/S (Vernon Hills, IL, USA) attached to a gauge sensor (ASL F200 Precision Thermometers), (Instrumart, Carlsbad, CA, USA).

2.3.3. Outlet section

In this section, the extract is separated from the solvent by changing the supercritical conditions at room atmospheric conditions. It consists of the following parts: glass recollection cell for recovering of product, a heating bath and a flowmeter for measuring volumetric flow rate.

2.3.4. Oil extraction

25 g of dried ground rosemary, with a particle size of 600 ± 50 μm, were placed in the equilibrium extraction cell. Extractions were performed at temperatures of 40 and 50 °C and pressures of 10.34 and 17.24 MPa. The CO_2 volumetric flow rate was 126.24 ± 20.83 mL min^{-1}. The recollection cell was immersed in a water bath at 8 ± 0.5 °C for condensing all extracted vapors. All tests were performed twice.

2.4. Hydrodistillation and steam distillation

The process, for obtaining the essential oil by the SD and HYDRO methods, was conducted in a Clevenger type distillation apparatus. The apparatus is made up of a heat source, a 2 L pear-shaped glass (PSG) container for creating steam by boiling water, a 2 L spherical glass container (SGC) with upper and bottom entrances, a straight glass condenser, and a glass collector for separating and recovering the essential oil; oil appears on top of water in the collector. *Steam distillation* (SD): sample is placed in the SGC flask and water in the PSG container. Water is then heated and the crated vapor passes though the sample in the SGC container. Consequently, vapor drag the essential oil and is condensed and recovered in the glass