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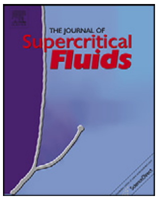

Supercritical fluid extraction of Spanish sage essential oil: Optimization of the process parameters and modelling

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ABSTRACT

The objective of the work was to optimize the extraction of Spanish sage essential oil by supercritical fluid (SFE) and to obtain extract useful for medical applications, such as, the case of Alzheimer disease. Different extraction conditions were tested and the evolution of the extracted oil composition was monitored by GC-MS analysis for the different fractions recovered at fixed time intervals. A comparison with an extract obtained by conventional hydrodistillation (HD) was also proposed for comparison. Particularly, different pressure and temperature values (90 bar–40 °C, corresponding to a density of 0.48 g/ml, and 100 bar–50 °C, corresponding to a density of 0.38 g/ml), three flow rates (1.32 kg/h, 1.02 kg/h and 0.72 kg/h) and three particle sizes of the vegetable material (0.8 mm, 0.5 mm and 0.3 mm) were studied. The major compounds found in the extracts were camphor (45%), 1,8-cineole (15%), camphene (4%), borneol (4%), myrcene (3%) and α-pinene (2%). A mathematical model was successfully applied to correlate the experimental data.

1. Introduction

Spanish sage essential oils (*Salvia lavandulifolia* Vahl.) and its individual monoterpenoid constituents are considered by the European Herbal Encyclopaedias enhancing/anti-dementia drugs because of their help in body cholinergic activity by inhibiting cholinesterase. This activity, coupled to antioxidant, anti-inflammatory, estrogenic and CNS depressant (sedative) properties [1], is relevant to the treatment of Alzheimer's disease, since the anti-cholinesterase are currently the only drugs available for this treatment [2,3].

The supercritical fluid extraction (SFE) of the sage essential oil should improve the oil quality avoiding any thermal stress to the terpenes component. However, SFE conditions (mainly pressure and temperature which are responsible for the supercritical fluid solvent power) must be optimized since these variables are directly responsible for the extract composition, and, therefore, for its functional properties [4,5]. However, other factors such as the bed geometry, the number of extraction and separation vessels, and the solvent flow rate can influence the process performance [6].

Supercritical extraction of the Spanish sage volatile oil has not been studied yet. However other authors studied the supercritical extraction oil from other varieties of sage. For example, Reverchon et al. [7] in 1995 and, some years later, Aleksovski et al. in 2007 [8] obtained the oil from *Salvia officinalis* L. with supercritical CO_2. In both works the working conditions to extract volatile oils were supercritical pressures between 8 MPa and 13 MPa, supercritical temperatures between 40 °C and 60 °C and flow rates between 0.3 kg/h and 2 kg/h approximately. The main difference between both works was that Reverchon et al. carried out the condensation of the extracts in two separation vessels and Aleksovski just in one, which meant the absence of waxes in the volatile extract collected by Reverchon et al.

The aim of this work was to evaluate the extracting capability of the supercritical fluid over the Spanish sage to get a potentially good extract for medical applications. Particularly, two pairs of pressure and temperature values (90 bar–40 °C, corresponding to a density of 0.48 g/ml, and 100 bar–50 °C, corresponding to a density of 0.38 g/ml), three flow rates (1.32 kg/h, 1.02 kg/h and 0.72 kg/h) and three particle sizes of vegetable material (0.8 mm, 0.5 mm and 0.3 mm) were tested. The evolution of the oil composition during all the extraction experiments was monitored by GC-MS analysis at fixed time intervals and a comparison with the essential oil obtained by hydrodistillation was also proposed.

For possible industrial application of the SFE process, it is very important to have extensive knowledge of the models which

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Nomenclature

ε	$(1-\rho_b/\rho_s)$ bed porosity
γ	$(\rho_f\varepsilon/(\rho_s(1-\varepsilon)))$ solvent-to-matrix ratio in the bed (kg of solvent/kg of insoluble solid)
ρ_b	bed density (g/ml)
ρ_s	solid density (g/ml)
ρ_f	fluid density (g/ml)
a_0	specific surface area per unit volume of extraction bed (1/m)
c_u	$(x_u/(1+x_u))$ solute content in the untreated solid (kg(solute)/kg(solid))
C_1	fitting parameter
C_2	fitting parameter
e_{exp}	experimental extraction yield (kg(extract)/kg(insoluble solid))
e_{cal}	calculated extraction yield (kg(extract)/kg(insoluble solid))
E	amount of extract (kg)
k_f	fluid phase mass transfer coefficient (1/s)
K	$(=y_0/x_{1,0})$ partition coefficient
KI	Kovats index
M	solid charge in the extractor (kg)
N	number of separated fractions in the SFE curves
N_m	$(=(1-c_u)M)$ charge of insoluble solid (kg)
q	relative amount of the passed solvent (kg(solvent)/kg(insoluble solid))
q_c	relative amount of the passed solvent when all the solute in broken cells has been extracted (kg(solvent)/kg(insoluble solid))
Q	solvent flow rate (kg/s)
r	grinding efficiency (fraction of broken cells)
Re	proportion of each compound in the global extract (kg(compound n) 100/kg(extract))
RSMD	root squared mean deviation
t	extraction time (s)
x_u	concentration in the untreated solid (kg(solute)/kg(insoluble solid))
$x_{1,0}$	initial concentration in broken cells (kg(solute)/kg(insoluble solid))
y_0	initial fluid phase concentration (kg(solute)/kg(solvent))
Y_e	global yield of the process (kg (solute) 100/kg(dried plant))
Y_{fj}	cumulative yield of the family (kg (family j) 100/kg(fraction))

allows us to correlate and extrapolate the experimental data. The model used in this work was the one proposed by Sovová [9] that should be the most appropriate to describe the experimental data collected.

2. Materials, apparatus and methods

2.1. Raw material characterization and preparation

Sage used for the experiments was cultivated under controlled conditions by the CITA (Centro de Investigación y Tecnología Agroalimentaria de Aragón, Spain) in Villarroya de la Sierra (Zaragoza, Spain), a dry land at a height of 732 m in the north-east of the Iberian Peninsula. CITA supplied stalks with leaves and flowers with a water content below 10% (w/w).

Leaves and flowers were grounded in batch of 0.2 kg each for about 50 s using an electric grinder. During the milling, the vegetable material was cooled with liquid nitrogen to avoid the loss of volatile compounds. The selection of particle size was made by a vibratory sieve shaker. The mean particle diameters of the three selected vegetable sets were 0.8 mm, 0.5 mm and 0.3 mm. Grounded samples were stored at −15 °C.

2.2. SFE and hydrodistillation apparatus

The SFE plant is illustrated in Fig. 1 and constructed following the layout reported by Reis-Vasco et al. [10]. The main constituents were a pump (CP, model Dosapro Milton Roy), with a filter (F), an extraction vessel of 1 L (R) and two separators, one for the recovery of waxes [7,11] and another one for the recovery of essential oil (SP1 and SP2, I.V. 180 mL). Temperatures in the extraction vessel and separators SP1 and SP2 were maintained with the aid of jackets for circulating liquids from thermostated baths. Other important elements were a refrigerator cylinder of 0.5 L (S1, Hoke), a heat exchanger (S2), a back pressure regulator (BP, Tescom Corporation) and a flowmeter plus a totalizer of CO_2 (GM, model GFM371S, Aalborg). Several valves (V1–V7, model 10-11AF4, HiP and V8–V9, model 1300, HOKE) connected the different sections of the pilot plant. Pressure and temperature were measured and/or controlled with manometers (M1, M3 and M4, model EN-837-1, WIKA), a pressure transducer (M2, model PX-425, Omega), thermocouples (T1–T6, model Junior TTC, Kosmos), and temperature controllers (model E5CN, Omron).

The experimental procedure adopted is the following: first, about 90 g of triturated sage were introduced into the extraction vessel which was filled, in a symmetrical disposition, with several porous inert materials (glass spheres, nickel sponge and glass frit), with the vegetable material placed in the middle. The porous elements were used to avoid any material packing in the extractor. After the extraction vessel and separators reach the working temperature, the pump is started up to the desired flow rate and the valves set at the desired pressure. The CO_2 stream to the second separator is manipulated by opening valves V8 and V9 at fixed time intervals in order to collect and weigh the recovered oil and to obtain samples for GC-MS analysis. All the experiments ended when the slope in the asymptotic region was lower than 7% of the maximum slope (in the initial steps of the experiments).

The hydrodistiller was of Clevenger type, made in the Faculty of Sciences, Zaragoza, Spain. An amount of about 40 g of vegetable material was used for each hydrodistillation. The samples were hydrodistilled for 4 h.

2.3. Analysis of the extracts

The analysis of the volatile extracts was determined using, first, a Trace GC 2000 Series Termo Quest with a flame ionization detector (FID) and a split injector equipped with a capillary column of fused silica (DB-5, 30 m × 0.25 mm × 0.25 μm). The carrier gas was helium (3.0, Abelló Linde) at a flow rate of 1.3 ml/min. The injector and detector temperatures were 310 °C. The temperature programming was 70 °C (1 min), then 70–310 °C at 5 °C/min. Samples of 0.1 μL were injected with a split ratio of 1:50. The identification of some compounds was done by comparison with the retention times of authentic standards. The proportion of each compound in the oil was made through its area percentage in the chromatogram. A quadrupole mass spectrometer Shimadzu QP2010 was also used to complete the composition determination. The injection temperature was 275 °C. Helium was the carrier gas at 1.0 mL/min. The sample (0.1 μL) was injected, with a split ratio of 20.0. The MS conditions were as follows: ionization energy 70 eV, electronic impact ion source temperature 200 °C, quadrupole temperature 100 °C, scan rate 1.5 scan/s, mass range (42–300) u.