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Isolation of Rock Rose Essential Oil Using Supercritical CO_2 Extraction

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ABSTRACT

Supercritical carbon dioxide has been used as a solvent for the extraction of rock rose leaf (*Cistus ladanifer L.*). The aim of this work was to identify the best processing conditions to obtain rock rose essential oil. The operating variables were selected so that the only extracted compounds were essential oils and waxes (8–10 MPa and 30–60°C), avoiding the coextraction of high-molecular-weight compounds that do not contribute to fragance formation. Moreover, a two-stage separation procedure was used to separate the waxes from the essential oil. The supercritical extracts were characterized by gas chromatography (GC) to assess the presence of undesirable compounds and to obtain the detailed oil composition. The best oil was produced by extraction at 9 MPa and 40°C and fractionation of the product in two separators in series operating at $P = 7$ MPa, $T = -10$°C and at $P = 2$ MPa, T = –10°C, respectively. Organoleptic analysis confirmed the high quality of the product.

Key Words. Rock rose; Essential oil; Liquid CO_2 extraction; Supercritical CO_2 extraction

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INTRODUCTION

Rock rose shrubs are one of the most common characteristic plants of the Mediterranean regions. In Spain, large mountainous regions, probably more than 10,000 km^2, are covered by these bushes. Although rock rose leaves and branches are usually employed as firewood, an extract from this plant, known as labdanum, is commercialized in Spain and, to a lesser extent, in Portugal, Morocco, and Greece.

Labdanum is a raw material from which the perfume industry obtains odoriferous compounds. In the conventional extraction process, labdanum is obtained by steam distillation of the ground plant. However, because of the high energy costs associated with this method, alternative new technologies that may compete advantageously with the industrially established method should be investigated.

Among these alternative processes, extraction with supercritical CO_2 (SCE) seems to be promising. The method has been successfully applied for the extraction of essential oils and other related products from numerous vegetable substrates, as reviewed by Stahl (1), Kerrola (2), and Reverchon (3). Furthermore, in the field of aromatic materials, the procedure was usually found to be superior to classical techniques, such as steam distillation or extraction with liquid solvents, because it prevents thermal degradation and solvent pollution of the extracts (1). In addition, because most of the substances involved are highly soluble even at modest gas pressures (approximately 10 MPa), they can be isolated with a comparative minimum of effort.

The SCE of essential oil from plants is not easy to accomplish, because apart from oil, the vegetable matter contains many different families of lipophilic solutes (usually fatty acids, waxes, pigments, resins, etc.) that show a high affinity with supercritical CO_2. Conversely, because these compounds do not contribute to fragance formation, they are undesirable in the supercritical extract.

Fortunately, except for waxes, the content of unwanted compounds can be controlled by the choice of appropriate extraction conditions (1, 3). However, because the paraffins that typically constitute waxes are rather soluble in supercritical CO_2 and located in a favorable position with respect to extraction (4), the coextraction of waxes is almost inavoidable (2).

Nevertheless, it is possible to obtain pure essential oils by inducing the selective precipitation of the extract in two or more separators operated in series at appropriate pressure and temperature conditions. By means of this technique, the complete separation of cuticular waxes from essential oil has been achieved for various vegetable matter (5–8).

In this paper, we report the results obtained in the supercritical fluid extraction of rock rose leaves using CO_2 as supercritical solvent. The aim of the work was to produce accurate experimental data on the SCE of rock rose leaf in order to identify the best processing conditions to obtain its essential oil. With this objective in mind, experiments have been performed at conditions that prevent coextraction of all undesired compounds but cuticular waxes. Moreover, to separate essential oil from waxes, a selective precipitation of the extracts in two separators operated in series was attempted. The method induced the fractional separation of the extracts by selective supersaturation and precipitation of the undesired compounds (waxes) in the first separator. Thus, pure essential oil was recovered in the second separator. At optimum operating conditions, the components that constitute the essential oil and the waxes were identified.

MATERIALS AND METHODS

Materials

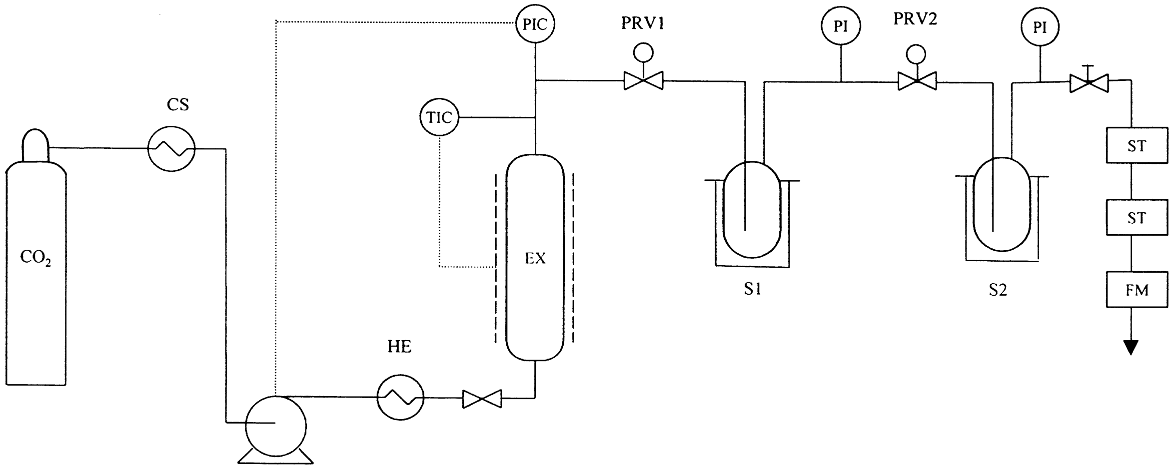
Liquid CO_2 (purity 99.5%) was supplied by Carburos Metálicos, S. A. (Madrid, Spain). Rock rose leaves were collected in July in the county of Ciudad Real (Spain). This mountainous site is 620 m above sea level, with an average annual rainfall of 350 mm. The rainy months are October, November, March, and April. Annual average minimum and maximum temperatures are –4 and 45°C, respectively.

In the extraction experiments only mature leaves, i.e., those nascent in the spring and exuding high levels of labdanum during the summer, were used. The essential oil content of the vegetable matter was 5 mg of essential oil/g dry plant, as determined by steam distillation (8).

Prior to the extraction, the fresh plants were allowed to dry until the moisture content was 7% by weight on a dry basis. Then, the plants were ground and sieved in two consecutive steps in order to prevent overheating of the samples. In the first step, three size fractions with average particle diameters of 0.46, 0.65, and 0.94 mm were separated. Next, part of the fraction of 0.46 mm was stored in a freezer for 5 hr and then ground and sieved again to obtain two more fractions with average particle diameter of 0.30 and 0.175 mm.

Apparatus and Extraction Procedure

The schematic diagram of the supercritical apparatus used is shown in Fig. 1. Liquid CO_2 was provided from a steel cylinder and, after being cooled in a cold bath (about 0°C), it was compressed by a membrane dosage pump (model GH 140/1H, Lewa, Leonberg, Germany). Then, prior to being fed to a 2-L ($H/D = 15$) stainless steel cylinder which held the sample to be extracted, the CO_2 was heated to the desired operating conditions in a tubular heat exchanger. After leaving the extractor, the CO_2 loaded with the extracted com-



CO_2: CO_2 cylinder
CS: Cooling system
HS: Heat exchanger
EX: Extractor
PRV: Pressure regulating valve
FM: Flow meter
S: Separator
ST: Sorbent trap

FIG. 1 Flow schematic of the supercritical extraction system.

pounds (essential oil and waxes) flowed through separator 1, where waxes were precipitated. Then, the oil-laden CO_2 passed through separator 2, in which the essential oil was collected. The depressurized CO_2 vented through two solid sorbent traps (activated carbon) and, when they were rinsed post-extraction, no detectable amounts of essential oil components were found. The gas flow leaving the system was measured by a flow metering system (Fisher-Rosemount, Veenendaal, Netherlands) comprising a sensor (model DL65) and a signal processing transmitter (model RTF9739E) connected to a communicator (model HART 275). At the end of each run, the extractor and separators were cleaned manually and the pipes after the extractor were washed with a volatile solvent (acetone).

In all experiments about 500 g of rock rose leaf was extracted. The yields of rock rose essential oil and waxes were determined by gravimetric quantification of the extracts collected in the second and first separator, respectively.

Temperature and pressure in the extractor and in the separators were measured using Fe-Const thermocouples and differential manometers, respectively (Duragauge, Autoclave Engineers Inc., Erie, PA).

Temperature was controlled in the extractor using a digital controller (model 808, Euritherm Corp., Reston, VA) that regulated the electric current through a resistor that surrounded the extractor cylinder. A pressure control system, comprising a pressure sensor–transmitter (model 060E3020, Danfoss, Madrid, Spain) and a frequency converter (model VLT 5006, Danfoss) that regulated the pump piston stroke length and frequency, was used to regulate the extractor pressure.

Separator pressures were controlled using appropriate pressure-reducing regulators (model 44-2262-242/241, Tescom, Elk River, MN). Temperatures in both separators were controlled by immersing them in cooled baths (model Frigiterm 10-6000382, Selecta, Barcelona, Spain).

GC Analysis of Essential Oil and Waxes

The essential oil and waxes were analyzed by gas chromatography (GC) on a model 6890 gas chromatograph (Hewlett-Packard, Avondale, PA) equipped with a split/splitless injector and a flame ionization detector connected to a ChemStation (Hewlett-Packard). The column for oil separation was an HP-5, 50 m × 0.32 mm i.d., film thickness of 0.17 μm. GC conditions were as follows: injector temperature, 200°C; detector temperature, 250°C; oven temperature program, held at 60°C for 10 min, heated to 180°C at 2°C/min, and held at 180°C for 30 min; carrier gas velocity (N_2): 2 mL/min; injection volume, 2 μL; split ratio, 1/20.

The column used for wax identification was an HP-1, 25 m × 0.20 mm i.d., film thickness of 0.33 μm. GC conditions for wax separation were as follows: injector temperature, 320°C; detector temperature, 330°C; oven temperature program, held at 120°C for 5 min, heated to 300°C at 5°C/min, and held at 300°C for 10 min; carrier gas velocity (N_2), 2 mL/min; injection volume, 1 μL; split ratio, 1/10.

The compounds were identified by comparison with the retention time of standards, and in case of doubt, the standard addition method was employed for peak verification. Reference oils and pure compounds used were supplied by Análisis Vínicos Inc. (C. Real, Spain).

The percentage composition of the essential oil and the wax compounds was computed from GC peak areas without using correction factors.

RESULTS AND DISCUSSION

Natural fragrances contained in rock rose leaf were extracted with supercritical carbon dioxide. Use of this solvent does not contaminate the extracted products and, at the low temperatures (30–60°C) and pressures (8–10 MPa) used, it is unlikely that decomposition reactions would occur during the extraction process.

Preliminary tests were performed with the aim of identifying the best separation conditions, i.e., those pressure and temperature settings in separator 1 which ensure that the waxes do not contaminate essential oil collected in separator 2, and that oil does not pollute the waxes recovered in separator 1. Moreover, to prevent volatile oil loss, separator 2 was set at 2 MPa and–10°C.

To assess the effectiveness of the separation process, the composition of the product precipitated in separator 2 was studied. Various operating conditions in separator 1 were tested, beginning with a base case (8 MPa and 20°C) in which about 0.33 mg/mg of product collected in separator 2 was attributed to waxes. Results are summarized in Table 1. The optimum results were obtained when separator 1 was operated at 7 MPa and –10 or –20°C. At both conditions, a nearly complete precipitation of the waxes was achieved in the first separator (where essentially pure waxes were collected) and a colorless oil with a strong rock rose odor was collected in the second separator. Because a temperature reduction from –10 to –20°C did not improve the separation efficiency, 7 MPa and –10°C were the operating conditions selected for separator 1 in subsequent experiments.

The accuracy of the experimental data was determined by comparing the essential oil yields obtained from five independent runs carried out under identical conditions ($P = 9$ MPa, $T = 60$°C, $F = 0.7$ kg/hr, $d_p = 0.46$ mm, and $t = 3$ hours). In these experiments the oil yields were very similar (5.0, 4.7, 4.8, 4.7, and 4.8 mg of essential oil/g dry plant), indicating that reproducibility of the data was good. Nevertheless, in order to minimize the experimental error, duplicate runs were performed at all conditions; the experimental data reported in this paper represent the average of the results obtained in two independent runs.

Effect of Operating Variables on the Extraction Yields

The extraction pressure, extraction temperature, particle size of the vegetable matrix, and contacting time between solvent and solute were identified as the parameters that mainly contribute to process optimization, and therefore, their effect on the yield of essential oil has been studied in detail. With

TABLE 1
Approximate Contribution of Essential Oil and Waxes to the Composition of the Extract Collected in Separator 2 at Various Operating Conditions of Separator 1

Separation conditions	Essential oil (mg/mg extract)	Waxes (mg/mg extract)
8 MPa and 20°C	0.67	0.33
7 MPa and 20°C	0.87	0.13
7 MPa and 0°C	0.92	0.08
7 MPa and –10°C	0.98	0.02
7 MPa and –20°C	0.98	0.02

Extraction conditions: $P = 9$ MPa, $T = 60$°C, $F = 0.7$ kg/hr, $d_p = 0.46$ mm.

TABLE 2
Extraction of Rock Rose Leaves: Operating Variables

Experiment number	Pressure (MPa)	Temperature (°C)	Flow (kg/hr)	Particle size (mm)	Extraction time (min)
E-1 (A to E)	8	30	0.7	0.46	15, 30, 60, 90, 180
E-2 (A to E)	8	40	0.7	0.46	15, 30, 60, 90, 180
E-3 (A to E)	8	50	0.7	0.46	15, 30, 60, 90, 180
E-4 (A to E)	8	60	0.7	0.46	15, 30, 60, 90, 180
E-5 (A to E)	10	30	0.7	0.46	15, 30, 60, 90, 180
E-6 (A to E)	10	40	0.7	0.46	15, 30, 60, 90, 180
E-7 (A to E)	10	50	0.7	0.46	15, 30, 60, 90, 180
E-8 (A to E)	10	60	0.7	0.46	15, 30, 60, 90, 180
E-9 (A to E)	9	40	0.7	0.46	15, 30, 60, 90, 180
E-10 (A to E)	9	40	0.4	0.46	15, 30, 60, 90, 180
E-11 (A to E)	9	40	1.0	0.46	15, 30, 60, 90, 180
E-12 (A to E)	9	40	1.3	0.46	15, 30, 60, 90, 180
E-13 (A to E)	9	40	0.7	0.94	15, 30, 60, 90, 180
E-14 (A to E)	9	40	0.7	0.65	15, 30, 60, 90, 180
E-15 (A to E)	9	40	0.7	0.30	15, 30, 60, 90, 180
E-16 (A to E)	9	40	0.7	0.175	15, 30, 60, 90, 180

this objective in mind, a series of experiments was planned with the operational variables as listed in Table 2.

The pressure and temperature experimental ranges analyzed were selected so that the CO_2 density at supercritical conditions was about 0.6 g/cm^3 or less. According to the literature (1, 3), the extraction of essential oils under such conditions avoids the coextraction of many undesired high-molecular-weight compounds that do not contribute to aroma. This statement is supported by solubility data and experimental data on the extraction of many vegetable materials (5–9). Nevertheless, to confirm this, two experiments (E-1 and E-5) were performed using liquid CO_2 as solvent.

The influence of temperature and pressure (experiments E-1 to E-9) on the yields of essential oil is shown in Figs. 2 and 3, respectively. Regarding the effect of temperature, Fig. 2 illustrates that, at a fixed pressure (8 MPa), an increase of the operating temperature from 40 to 60°C produces lower extraction yields; the results are almost independent of this variable in the temperature range from 30 to 40°C. Similar results were obtained when operating at 10 MPa. These results show, on the one hand, that essential oil yields obtained with liquid CO_2 (those performed at 30°C, the lowest temperature tested) are not higher than those obtained with supercritical CO_2, probably because of the lower selectivity of liquid CO_2, as we will discuss later. On the other hand, the increasing yields obtained with decreasing temperature when operating at su-

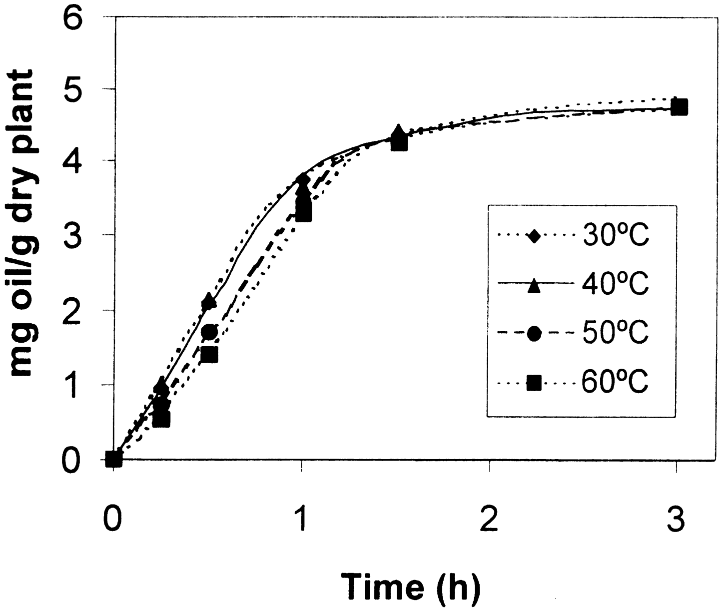


FIG. 2 Effect of temperature on the extraction yield of rock rose essential oil.

percritical conditions may be explained because, in the experimental range analyzed, an increase in temperature produces a reduction of the supercritical CO_2 density (and consequently of its solvent power) that it is not counterbalanced by the increase in vapor pressure of the essential oil constituents. This result agrees with that obtained by Reverchon (10), who studied the supercrit-

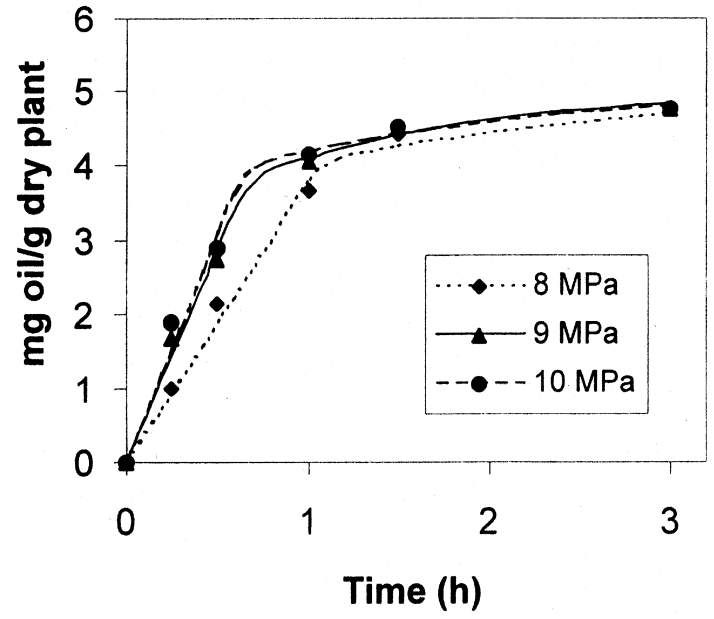


FIG. 3 Effect of pressure on the extraction yield of rock rose essential oil.

ical desorption of limonene and linalool from silica gel. Thus, taking into account these experimental findings, a temperature of 40°C was selected as the optimum temperature value for performing the extraction of rock rose leaves.

With respect to the influence of pressure, Fig. 3 shows that, at a fixed temperature (40°C), the oil extraction yields increase with increasing pressure, i.e., with supercritical CO_2 density. These results conform to the general principles of supercritical CO_2 extraction (1) and other studies on the extraction of natural products (2, 3, 11, 12). However, although from 8 to 9 MPa a significant increase in the oil extraction rate was observed, from 9 to 10 MPa such the increase was considerably smaller. At 30, 50, and 60°C, the experimental data showed a similar pattern. Consequently, a pressure of 9 MPa was selected as optimum for the SCE of rock rose oil. In this way, the energy costs associated with the extraction could be reduced.

As stated, another important parameter that contributes to process optimization is the contacting time between the supercritical fluid and solute. This parameter is related to the fluid dynamics of the extraction process and gives information about its influence on the overall mass transfer mechanisms. The effect of contacting time on the extraction rate has been evaluated by varying the CO_2 flow rate between 0.4 and 1.3 kg/hr (experiments E-9 to E-12). These extractions yielded curves that substantially overlapped when expressed against extraction time for fluid flows from 0.7 to 1.3 kg/hr (see Fig. 4). However, at 0.4 kg/hr, the extraction yields were substantially smaller. It may be assessed that contacting time affects oil yield only in the range from 0.4 to 0.7

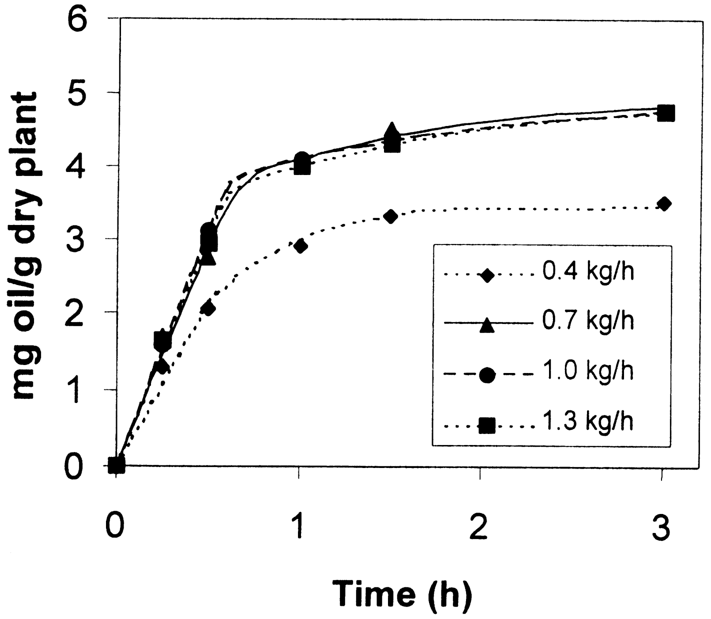


FIG. 4 Effect of fluid flow on the extraction yield of rock rose essential oil.

kg/hr and, therefore, that the controlling step in extraction is not external diffusion in the range from 0.7 to 1.3 kg/hr.

On the other hand, in Fig. 5 we show the mass of oil extracted (m_{oil}) per mass of solvent (m_{s}) as a function of extraction time. Note that this quantity increases with decreasing flow rates, and is approximately similar at 0.4 and 0.7 kg/hr. These results suggest that CO_2 efficiency to extract oil is higher and approximately similar at the two smallest flow rates. A solvent flow of 0.7 kg/hr was selected to perform the SCE of the plant material. At this flow rate, a given degree of extraction could be accomplished in the shortest time, using the minimum amount of solvent.

These results suggest that diffusion inside the vegetable matrix could be the limiting stage in the extraction process at 0.7 kg/hr. This hypothesis was tested by performing supercritical extractions at different average particle diameters (0.175, 0.30, 0.46, 0.65, and 0.94 mm) of the vegetable matrix (experiments E-9 and E-13 to E-16). In the extraction range from 0.30 to 0.94 mm, the extraction yields increased with decreasing particle diameter (see Fig. 6), supporting the hypothesis that internal diffusion is the limiting stage of the mass transfer mechanism. However, almost similar results were found in experiments performed with the two smallest particle sizes, 0.30 and 0.175 mm, probably because essential oil losses occurred during the comminution process. Other authors have also observed this almost unavoidable phenomenon (7, 13). Accordingly the fraction of particles with average diameter of 0.30 mm was selected as optimal for conducting the SCE of rock rose leaves.

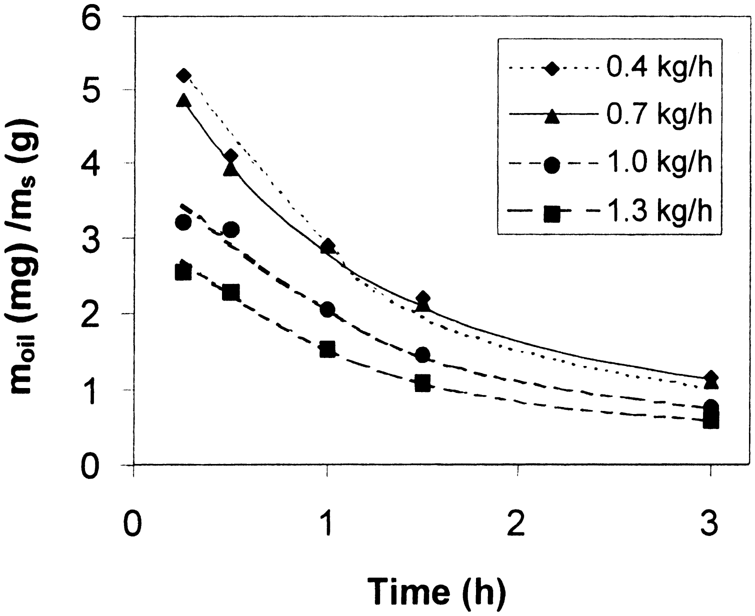


FIG. 5 Evolution with time of the $m_{\mathrm{oil}}/m_{\mathrm{s}}$ ratio at different flow rates.

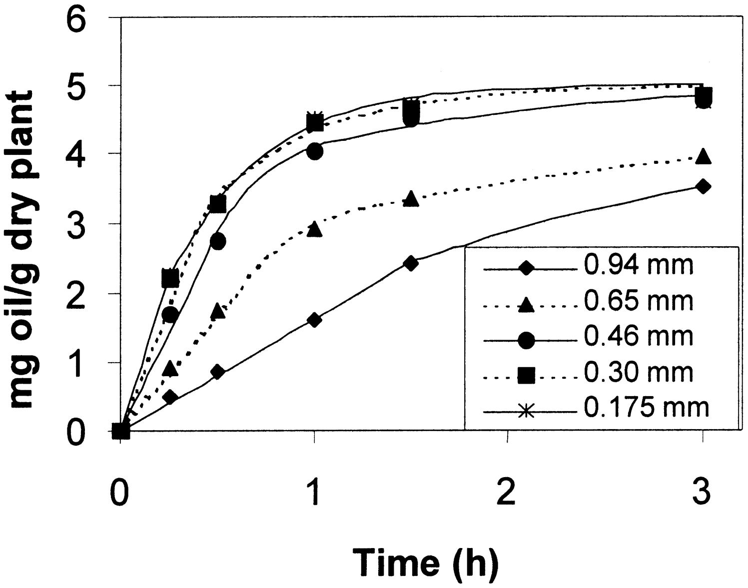


FIG. 6 Effect of particle diameter on the extraction yield of rock rose essential oil.

Once the optimum conditions for the extraction of essential oil were identified, we checked if separation conditions selected in preliminary experiments were also valid at optimal conditions. Results obtained in these experiments showed that, effectively, they were valid.

Effect of Operating Variables on the Essential Oil Percentage in the Supercritical Extracts

Results presented in Figs. 2 and 3 show that, even though the extraction rates depend on temperature and pressure conditions, the maximum essential oil yields (asymptotic yields) were about the same in all cases. However, the yield of waxes that accompanied the oil was strongly affected by extraction pressure. In Fig. 7, where the relative percentage of essential oil in the supercritical extracts is reported for the extraction conditions of experiments E-2, E-6, and E-9, it can be observed that, at a fixed temperature, the extract obtained at 8 MPa contained a lower quantity of undesirable compounds than the extract produced at higher pressures (Fig. 7). Similar results were found at the other pressure levels considered, and a similar finding was also reported by Poiana et al. (14) in their study on the SCE of bergamot oil. These authors found that the oil percentage in the extracts obtained at 12 MPa was approximately twice the oil percentage in the extracts produced at 30 MPa.

Regarding temperature, the experimental data showed that the oil percentage obtained with liquid CO_2 was always much less than the oil percentage ob-

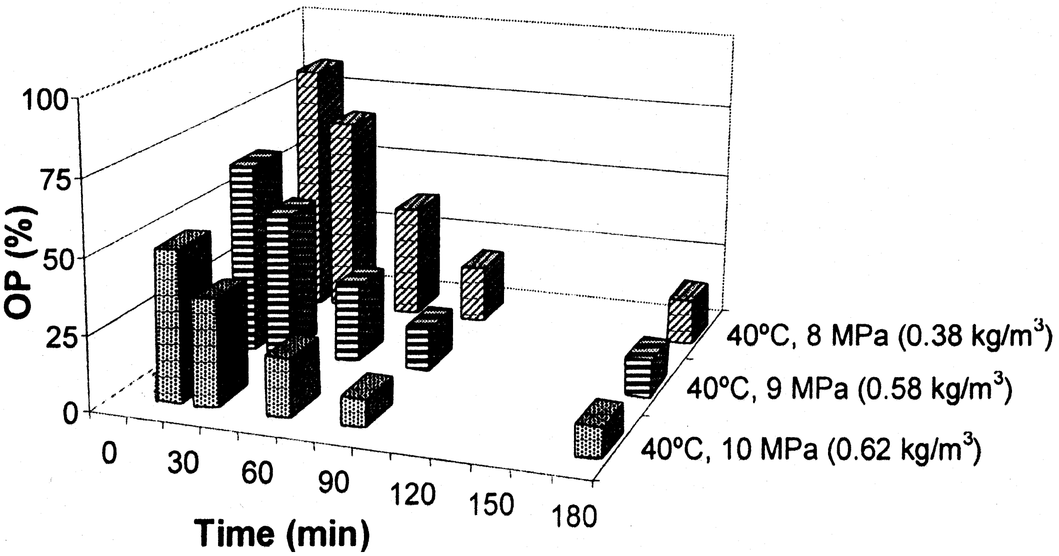


FIG. 7 Essential oil percentage in the supercritical extracts obtained at 40°C and different pressures.

tained at supercritical conditions (Figs. 8 and 9). This result was somewhat expected because liquid CO_2 has a larger solvent power and, consequently, a lesser selectivity than that of supercritical CO_2.

Figs. 8 and 9 also show that, at supercritical conditions, the effect of the variable depended on the pressure level considered. At 10 MPa (Fig. 8) the es-

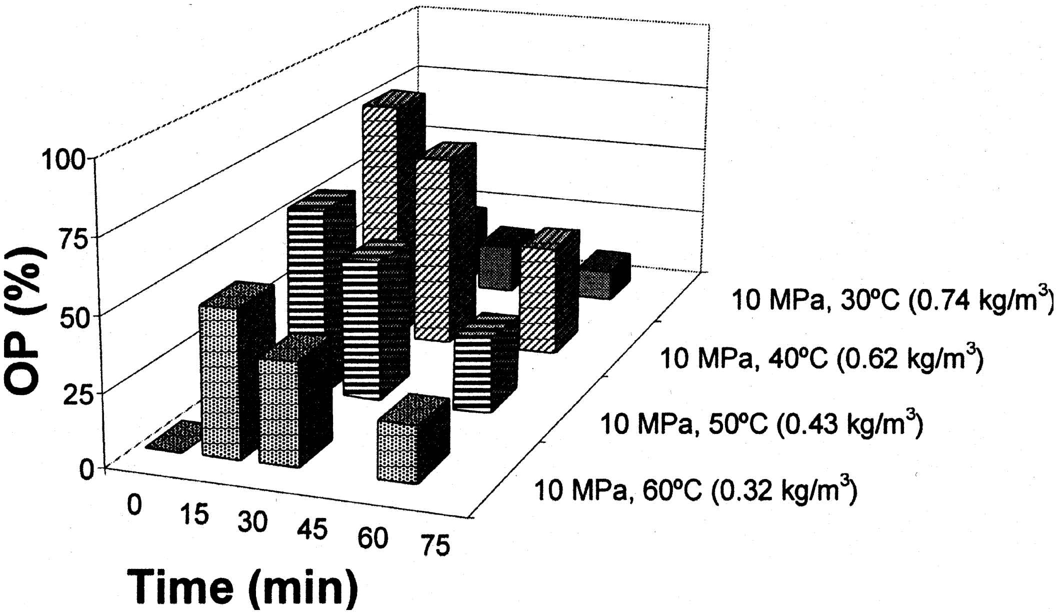


FIG. 8 Essential oil percentage in the supercritical extracts obtained at 10 MPa and different temperatures.

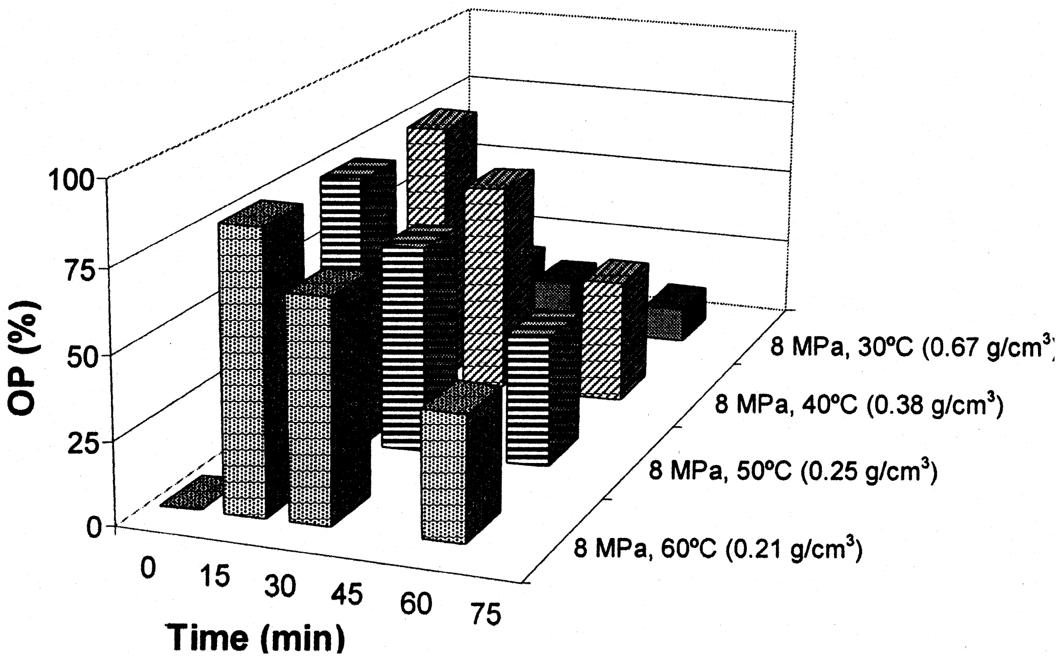


FIG. 9 Essential oil percentage in the supercritical extracts obtained at 8 MPa and different temperatures.

sential oil percentage increased with decreasing temperature, whereas at 8 MPa (Fig. 9) this percentage was almost independent of temperature. These results seem to depend, exclusively, on supercritical CO_2 density (i.e., on fluid solvent power). Thus, for supercritical experiments in Figs. 7 and 8, where the fluid density changes from approximately 0.3 to 0.6 g/cm^3, the influence of the variables on the essential oil percentage can be clearly appreciated. However, for experiments in Fig. 9, where CO_2 density changes from approximately 0.2 to 0.35 g/cm^3, no significant effect can be observed.

The influence of fluid flow and particle size on the percentage of essential oil in the supercritical extracts was also analyzed, but no effect was found.

Composition of the Supercritical Extract at Optimum Extraction Conditions

The composition of the oil obtained under optimum conditions ($P = 9$ MPa, $T = 40$°C, $F = 0.7$ kg/hr, and $d_p = 0.30$ mm) is shown in Table 3. These results roughly agree with those reported in the literature on the composition of the essential oil obtained by steam distillation (8, 15). Note that the oil composition varies with time, probably due to the different diffusion times of the various families of compounds constituting the oil (3, 16). For example, examining the evolution of the two main oil components, α-pinene and camphor,

TABLE 3
Percentage Composition in Rock Rose Leaf Essential Oil Isolated by Supercritical CO_2 at Optimum Extraction Conditions

	Extraction time (min)				
Compound	15	30	60	90	180
α-Thujene	1.18	1.14	1.14	1.13	1.15
α-Pinene	20.35	19.80	19.51	19.50	19.46
Camphene	4.58	4.22	4.19	4.20	4.19
Sabinene	0.09	0.06	0.11	0.06	0.08
β-Pinene	0.63	0.65	0.64	0.64	0.66
β-Myrcene	0.16	0.15	0.17	0.15	0.15
α-Phelandrene	0.46	0.49	0.48	0.48	0.48
1,4-Cineole	4.31	4.18	4.05	3.95	3.92
p-Cymene	4.22	4.06	3.99	3.99	3.98
Limonene	1.73	1.69	1.66	1.66	1.66
1,8-Cineole	3.74	3.38	3.30	3.26	3.29
Bencyl alcohol	1.25	1.20	1.12	1.12	1.12
Acetyl pyrrol	0.60	0.54	0.54	0.54	0.54
γ-terpinene	4.36	4.18	4.11	4.11	4.10
Terpinolene	0.41	0.45	0.44	0.44	0.44
Linalool	1.23	1.25	1.08	1.10	1.10
α-Thujone	1.53	1.59	1.37	1.37	1.38
β-Thujone	1.33	1.30	1.22	1.19	1.19
Camphor	24.68	23.48	22.34	22.00	22.06
Pinanone	0.60	0.59	0.56	0.56	0.55
Isoborneol	0.10	0.10	0.08	0.12	0.10
Borneol	4.90	4.76	4.52	4.43	4.40
Menthol	0.05	0.05	0.06	0.06	0.06
γ-Terpineol	5.12	4.81	4.69	4.61	4.61
α-Terpineol	1.15	1.04	1.03	0.99	0.99
Verbenone	0.88	0.90	0.81	0.81	0.81
Nerol	1.00	0.90	0.91	0.91	0.91
Neral	1.23	1.16	1.13	1.11	1.11
Lynalyl acetate	1.00	0.94	0.91	0.90	0.92
Bornyl acetate	1.36	1.26	1.24	1.22	1.20
Thymol	4.64	4.38	4.23	4.16	4.16
β-Cariophylene	0.21	1.04	1.48	1.60	1.61
α-Santalene	–	–	Trace	Trace	Trace
β-Gurjunene	0.05	0.36	0.42	0.49	0.47
Humulene	0.31	1.01	1.47	1.62	1.65
Aromandrene	0.06	0.10	0.36	0.40	0.41
β-Selinene	0.23	1.30	2.04	2.18	2.18
α-Selinene	0.26	1.08	1.74	1.92	1.93
β-Bisabolene	0.09	0.21	0.45	0.48	0.47
γ-Cadinene	0.08	0.20	0.46	0.52	0.53
α-Cadinene	–	–	Trace	–	Trace

TABLE 4
Variation with Extraction Time of the Rock Rose Oil Percentage Composition Isolated by Supercritical CO_2 at Optimum Extraction Conditions

	Extraction time (min)				
Compound families	15	30	60	90	180
Monoterpenes	38.00	36.90	36.40	36.37	36.35
Oxigenated monoterpenes	60.70	57.80	55.20	54.40	54.40
Sesquiterpenes	1.30	5.30	8.35	9.20	9.20

it was found that the percentage of α-pinene (a monoterpene hydrocarbon) and camphor (an oxygenated monoterpene) slightly decreased with time. The rest of the monoterpenes and oxygenated monoterpenes showed similar trends. The percentage of sesquiterpenes increased with time in all cases. These results for the behavior of the different families of essential oil constituents are summarized in Table 4 and roughly agree with those reported in the literature for other plant materials (3).

The composition of the waxes obtained at optimum extraction conditions was also analyzed. Table 5 shows the relative percentage of the different compounds constituting this undesired fraction that is inevitably coextracted with essential oil. In contrast to the behavior exhibited by the essential oil fraction, the percentage composition of waxes was not dependent on extraction time.

TABLE 5
Percentage Composition in the Waxy Fraction Isolated by Supercritical CO_2 at Optimum Extraction Conditions

Compound	Percentage composition
Nonadecene	4.3
Methyl-octadecene	4.3
Methyl-eicosane	7.1
Tricosane	11.6
Pentacosane	8.9
Hexacosane	4.8
Heptacosane	13.9
Octacosane	4.0
Methyl-heptacosane	4.0
Nonacosane	21.0
Triacontane	5.6
Entriacontane	6.5
Tritriacontane	4.0

The different behavior exhibited by these two families of compounds may be explained by considering their different locations along the vegetable structure. Because waxes are located on the leaf epidermis (4), it may be hypothesized that they are mainly solubilized by leaching (which allows equilibrium conditions to be reached). This would explain why the composition of the waxy fraction was constant as long as waxy compounds were present in the vegetable matrix. In contrast, essential oil compounds are inside the vegetable structure, in cell organelles called vacuoles (4) and, therefore, it is usually supposed that their extraction is dependent on complex diffusion phenomena; essential oil compounds with shorter diffusion times would be extracted first (3). This would explain why the essential oil composition changed with time.

Finally, organoleptic analysis of the oil extracted at optimum conditions was performed using the standard panel testing (17). Fifteen panelists were used and tests were replicated twice. The product showed an odor not distinguisable from that of the starting vegetable matter. Essential rock rose oil obtained by steam distillation was also tested. Testers evaluated its odor as slightly sweeter than that of rock rose plants.

Data Modeling

Mathematical modeling of the relevant features of the SCE process is required to generalize the experimental results that can be applied to new process conditions. Furthermore, modeling is useful in the development of scale-up procedures from laboratory to pilot and industrial scale.

Three different types of models have been proposed for the modeling of the SCE of essential oils: empirical, that based on heat transfer analogy, and that based on differential mass balance integration (3). In this work, we analyzed the extraction data using three models based on the last approach (13, 18, and 19). All of the models have been frequently applied to the SCE of natural products (3, 12, 20, 21) and may describe the SCE of milled plant material in a cylindrical extractor when solvent flows axially through the bed. The models suppose that the solvent is solute-free at the entrance of the extractor and that the solid bed is homogeneous with respect to particle shape and size. The models differ, however, in the particle shape assumed for the solid matrix and in the initial distribution of solute within the particles at the beginning of the extraction. Thus, models 1 (18) and 2 (13) consider solute to be uniformly distributed within the particles, but model 1 assumes the particles to be spherical, and model 2 considers particles to be flat. On the other hand, model 3 (19) assumes that spherical particles are composed of crushed and uncrushed cells, offering different resistance to extraction, i.e., it considers a nonhomogeneous distribution of solute within the particles.

The fitting of the data to these models showed that the most sophisticated, model 3, was the best to fit the experimental data, and that the ability of model

1 and model 2 (which basically only differ on the particle shape assumed) to predict the data was practically similar. Standard deviations for model 1–3 were, respectively, 0.020, 0.021, and 0.015 mg oil/g dry plant.

When these results are taken into account, the resulting model curves are shown in Figs. 2–6 for the optimum values of the fitting parameters of model 3: $k_f a$ and $k_s a$, the fluid-phase and solid-phase mass transfer coefficients, respectively, and r, the grinding efficiency (parameter that represents the percentage of oil offering less resistance to extraction). The mean values of these parameters ($k_f a = 3.93 \times 10^{-4}$ sec^{-1}, $k_s a = 5.47 \times 10^{-5}$ sec^{-1}, and $r = 75\%$) are similar to those observed by other authors (19–21) in the SCE of oil compounds at pressure and temperature ranges similar to those adopted in this work. As shown in these figures, a quite satisfactory fit was obtained and, therefore, the model may be used to give a first estimate of the solid-phase and fluid-phase mass transfer coefficients of essential oil.

CONCLUSIONS

The SCE of essential oil from rock rose leaves was studied experimentally. The extraction yields do not depend on fluid flow rate but increase with increasing pressure, decreasing temperature, and particle size. The pressure effect has been attributed to the increasing CO_2 density, and therefore to the increasing solubility power of the fluid with increasing pressure. At supercritical conditions, the influence of temperature was explained by considering the combined effect of solute vapor pressure and fluid density on the essential oil solubility. Finally, from the effects of fluid flow and particle diameter on the oil yields, it could be assessed that internal diffusion inside the vegetable matrix is the controlling step of the extraction process. From these experimental results, the optimum conditions for performing the SCE of rock rose leaves were determined: $P = 9$ MPa, $T = 40°\mathrm{C}$, $F = 0.7$ kg/hr, and $d_p = 0.30$ mm.

The effect of the operating variables on the essential oil/wax ratio in the supercritical extract was also studied. No effect of fluid flow and particle diameter on this ratio was observed. Considering this fact and that the percentage of essential oil in the products obtained at higher density was smaller than in the extracts produced at lower densities, it could be stated that fluid density was the most important factor affecting the essential oil/wax ratio in the extracted material.

The percentage composition of the supercritical extract obtained under optimum conditions was analyzed as a function of time. Results for both separated fractions, essential oil, and waxes, were different. The oil composition varied with time, probably because of the different diffusion times inside the vegetable matrix of the various families of compounds constituting the oil. However, the composition of the waxy fraction was essentially constant throughout the extraction process. This different behavior exhibited by components of essential oil and waxes was attributed to their different location inside the vegetable matter.

Modeling the SCE of rock rose oil was attempted using three models proposed in the literature for studying the SCE of natural products. The fitting of the data was quite satisfactory in all cases, but the model assuming the matrix particles to be spherical and a nonhomogeneous initial distribution of solute within the particles predicted the data best. The use of this model allowed us to obtain a first estimate of the solid-phase and fluid-phase mass transfer coefficients of the essential oil.

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