

Comparative Analysis of the Oil and Supercritical CO₂ Extract of *Elettaria cardamomum* (L.) Maton

BRUNO MARONGIU,* ALESSANDRA PIRAS, AND SILVIA PORCEDDA

Dipartimento di Scienze Chimiche, Università degli Studi di Cagliari, Cittadella Universitaria di Monserrato, SS 554, km 4,500, 09042 Cagliari, Italy

The volatile oil of *Elettaria cardamomum* (L.) Maton seeds was obtained by supercritical CO₂ extraction (SC-CO₂). The effect of the extraction conditions on the yield and composition of the resulting cardamom volatile oil was examined by testing two pressure values, 9.0 and 11.0 MPa; two temperatures, 40 and 50 °C; two flow rate values, 0.6 and 1.2 kg/h; and two particles size values, 250–425 and >850 μm. The extraction conditions that gave the highest yield, *Y* (grams of extract per gram of seeds), of 5.5%, were as follows: pressure, 9.0 MPa; temperature, 40 °C; carbon dioxide flow, $\phi = 1.2$ kg/h; and particles sizes in the range of 250–425 μm. Waxes, recovered as traces, were entrapped in the first separator set at 9.0 MPa and –10 °C. The oil was recovered in the second separator working at 1.5 MPa and 10 °C. The main components were as follows: α -terpinyl acetate, 42.3%; 1,8-cineole, 21.4%; linalyl acetate, 8.2%; limonene, 5.6%; and linalool, 5.4%. A comparison with the hydrodistilled oil, obtained at a yield of 5.0%, did not reveal any consistent difference. In contrast, the extract obtained using hexane, *Y* = 7.6%, showed strong composition differences. Indeed, the volatile fraction of the extract was made up mainly of the following: limonene, 36.4%; 1,8-cineole, 23.5%; terpinolene, 8.6%; and myrcene, 6.6%.

KEYWORDS: *Elettaria cardamomum* (L.) Maton; essential oil; supercritical carbon dioxide

INTRODUCTION

Extraction by compressed carbon dioxide, CO₂, known as supercritical fluid extraction (SFE), is a good technique for the production of flavors and fragrances from vegetable matter. Indeed, there is considerable interest in this technique replacing steam distillation, hydrodistillation, and solvent extraction – processes traditionally used to obtain essential oils and similar products. With these techniques, a variety of products can be obtained. “Concretes” and “oleoresins” are extracts obtained using organic solvents on fresh or dried vegetable matter. A typical concrete extracted by hexane contains all of the lipophilic compounds that make up vegetable matter. A “volatile oil” is a liquid product obtained by postprocessing a concrete by steam distillation. An “essential oil” can be defined as the volatile material present in plants (*1*), usually obtained by cold pressing and water or steam distillation. As a rule, it consists of a complex mixture of hydrocarbon and oxygenated mono- and sesquiterpenes. Essential oils can also contain diterpenes and specific compounds that cannot be classified as belonging to any of the compound families mentioned above. Other compounds that can be extracted from vegetable matter and are found in concretes and oleoresins are fatty acids and fatty acid methyl esters (FAMES), coloring matters, coumarins, psoralens, sterols, and flavones.

The extract, made up of fragrant compounds obtained by SFE, is sometimes called volatile oil or more commonly essential oil. Conventional processes of extraction often require additional steps, such as the separation of the extractant, and are usually inferior to CO₂ in selectivity. In addition, the lower temperature in SFE prevents thermal degradation, and the low water content limits the hydrolytic process. Volatile concentrates obtained by SFE do not have the high molecular mass compounds normally co-extracted by conventional solvents, and their scent is more similar to the starting material than those obtained by water- or steam-distillation. On account of its chemical and physical properties, compressed carbon dioxide is used almost exclusively to extract volatiles or aroma substances for human nutrition and for the pharmaceutical and perfume industries. It is safe, nontoxic, noncombustible, and inexpensive, and its critical temperature and pressure are not high (31.06 °C; 7.38 MPa) (*2*). Supercritical CO₂ behaves like a lipophilic solvent, but its advantage over liquid solvents is that its selectivity is adjustable and can be set to values ranging from gaslike to liquidlike. To obtain a pure essential oil by SFE, it is necessary to work with carbon dioxide at low density. To study the SFE of flavors and fragrances, an accurate chemical characterization is necessary, because as a rule essential oils contain tens or hundreds of compounds. Moreover, it is important to make sure that no compounds with undesired characteristics are present, as even trace amounts could greatly reduce the quality of the product. Particle size, extraction time, and solvent flow rate should also

* Author to whom correspondence should be addressed [telephone +39 070 6754412; fax +39 070 6754388; e-mail maronb@unica.it].

be taken into account for a complete knowledge of the SFE process. These parameters affect the extraction rate and/or yield of the process. Also, extraction time can affect the composition of the extracted material.

Elettaria cardamomum (L.), cardamom, also called small cardamom (3), is to be distinguished from large cardamom (*Amonum subulatum* Roxb.). Originally from the tropical regions of Asia (4), it grows to 4 m and is cultivated extensively nowadays especially in India. The seeds, of a green color, are collected before maturation to avoid opening of the teguments and subsequent loss of fragrance. Cardamom seeds are widely used as a spice, being one of the most expensive. Its oil is used in a large number of beauty products. It was used as an anti-putrefactive during embalmment. Cardamom is used as a carminative, and in Northern Europe it is used in baking and pastry-making. In recent years, a few studies have been published on the biological activity of cardamom essential oil. They showed a moderate inhibitory activity against the fungus *Aspergillus flavus* (3), and a marked antispasmodic action and significant analgesic and anti-inflammatory activity (5). Naik and Mahaswari (6) performed a few extractions in a high-pressure Soxhlet apparatus with liquid carbon dioxide, at 58 bar and room temperature, on different matrixes including cardamom seeds. In 1991, Gopalakrishnan and Narayanan (7) published their results on the extraction of a mix of volatile oil with a heavier fraction from cardamom seeds with supercritical CO₂ in the batch mode. It has been reported (8) that when CO₂-extracted cardamom oil is used fresh, even though of better quality, it deteriorates faster than the distilled oil. The objectives of this study have been to isolate the essential oil of cardamom using carbon dioxide at supercritical conditions in a semi-batch apparatus, and to identify the compounds making up the oil. Moreover, the influence of several operative conditions has been investigated with special attention to the yield and the composition of the extracts obtained at different conditions. The SFE volatile oil has also been compared with oils obtained by hydrodistillation, HD, and extraction with hexane, SE.

MATERIALS AND METHODS

Materials. *E. cardamomum* (L.) Maton seeds were supplied by Minardi (Bagnacavallo-Ravenna, Italy). Seeds (pods) were used as received. The water content was 14% (w/w) on a dry basis. Before utilization, the vegetable matter was ground with a Malavasi mill (Bologna, Italy), taking care to avoid overheating. A large amount of ground material was employed in SE and HD. The material destined to SFE was split into two lots, using mechanical sieving, with particle sizes, d_p , in the range (250–425) and >850 μm , respectively. Hexane (purity $\geq 99.5\%$) was supplied by Fluka (Buchs, Switzerland); CO₂ (purity 99%) was supplied by SIO (Società Italiana Ossigeno, Cagliari, Italy).

SFE Apparatus. Supercritical CO₂ extractions were performed in a laboratory apparatus, equipped with a 400 cm³ extraction vessel, operating in the single-pass mode of CO₂, through a fixed bed of ground material. The length of the bed particles was 20 cm. About 280 g of material was charged in each run. The two fractions of the extract were recovered in two separator vessels of 300 and 200 cm³, respectively, connected in series. The first separator was cooled using a thermostated bath (Neslab, model CC-100II, accuracy of 0.1 °C). The second separator allowed discharge of the liquid product at the desired time intervals. In this section, the temperature was maintained at the desired value, using a heating ribbon wrapped around the pipe between the two separators, and by means of a water thermostated system connected to the second separator. A high-pressure diaphragm pump, Lewa – model EL 1, with a maximum capacity of 6 kg/h, pumped liquid CO₂ at the desired flow rate. CO₂ was then heated to the extraction temperature in a thermostated oven controlled by a PID controller,

Table 1. Variation with Extraction Time, t , of the Chromatographic Area Percentages of the Main Classes: Hydrocarbon Monoterpenes, HM; Oxygenated Monoterpenes, OM; and Oxygenated Sesquiterpenes, OS, in Which the Constituents of Cardamom Volatile Oil Can Be Grouped^a

t/min	HM	OM	OS
	[9.0; 40], $Y(\text{w/w})\% = 5.5$		
60	9.1	90.1	0.8
120	5.2	87.9	1.2
180	3.7	84.4	1.0
240	3.9	94.4	
	[11.0; 50], $Y(\text{w/w})\% = 5.1$		
60	8.0	90.7	1.2
120	4.4	92.6	1.1
180	3.2	91.7	1.1
240	3.1	97.0	

^a Operative conditions common to all runs were $\phi_{\text{CO}_2} = 1.2 \text{ kg/h}$ and $d_p = 250\text{--}425 \mu\text{m}$. The pressure and temperature of extraction are denoted [P/MPa ; $t/^\circ\text{C}$]. Percent yields, $Y(\text{w/w})\%$, are also given.

model 2116 (Eurotherm). Extraction was carried out in a semi-batch mode: batch charging of vegetable matter and continuous flow solvent. The carbon dioxide flow was monitored by a calibrated rotameter (Shorate, model 1355) located after the last separator. The total CO₂ delivered during an extraction test was measured by a dry test meter. Temperatures and pressures along the extraction apparatus were measured by thermocouple and Bourdon-tube test gauges, respectively. The pressure was regulated by high-pressure valves under manual control. Experiments were carried out at different conditions in the extraction section. In the first separator, the temperature was set at -10°C and the pressure was set at the same value as in the extraction section. No repeated runs were carried out.

Hydrodistillation. Hydrodistillation was performed for 4 h in a circulatory Clevenger-type apparatus up to exhaustion of the oil contained in the matrix. About 100 g of material was charged. No duplicate extractions were performed.

Solvent Extraction. Solvent extraction was performed at 25°C by maceration without agitation on about 12 g of matrix with hexane. After 24 h, the extract was decanted and filtered through a Watman No. 1 filter paper. The resulting filtrate was concentrated to an oily residue by removal of the solvent under vacuum in a rotating evaporator. No repeated extractions were carried out.

GC/MS Analysis. A Hewlett-Packard (Palo Alto, USA) 5890 series II gas chromatograph, GC, was employed. It was equipped with a split-splitless injector and a DB5-MS fused silica column; 5% phenylmethylpolysiloxane, 30 m \times 0.25 mm i.d., film thickness 0.25 μm . The used GC conditions were as follows: programmed heating from 60 to 280°C at $3^\circ\text{C}/\text{min}$ followed by 30 min under isothermal conditions. The injector was maintained at 250°C . Helium was the carrier gas at 1.0 mL/min; the sample (1 μL) was injected in the split mode (1:20). The GC was fitted with a quadrupole mass spectrometer, MS, model HP 5989 A. MS conditions were as follows: ionization energy 70 eV, electronic impact ion source temperature 200°C , quadrupole temperature 100°C , scan rate 1.6 scan/s, mass range (40–500) amu. The software adopted to handle mass spectra and the chromatogram was ChemStation. NIST98 (9), FLAVOUR, and LIBR (TP) (10) mass spectra libraries were used as references. Samples were run diluted in chloroform with a dilution ratio of 1:100. **Tables 1** and **2** show the chromatographic results, expressed as area percentages calculated without any response factor, as a function of Kováts' indices, I_K (11). Identifications were made by matching their mass spectra and I_K with those reported in the literature or those of pure compounds whenever possible.

RESULTS AND DISCUSSION

We conducted a comparison of cardamom SFE at different extraction conditions. Literature experimental data show that at extraction temperatures of 40 and 50°C and extraction

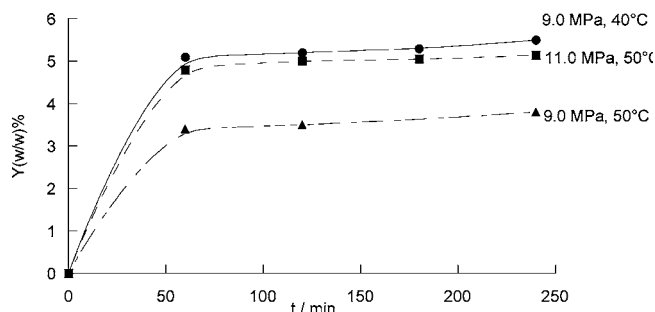
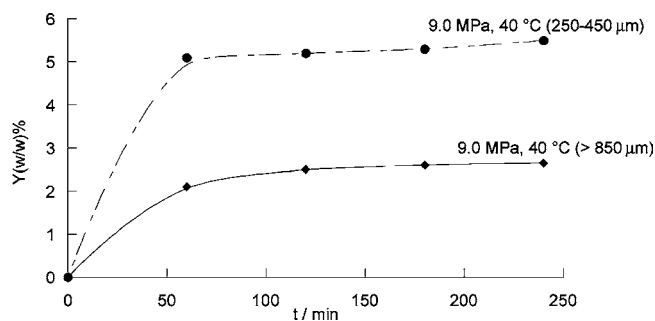
Table 2. Kovats' Indices, I_k , and Chromatographic Area Percentages of Compounds Found in Cardamom Volatile Oil Extracted by Supercritical Extraction at 9.0 MPa, 40 °C, and $\phi_{CO_2} = 1.2 \text{ kg/h}^a$

I_k	SFE1	SFE2	HD	SE	compound
872				0.5	<i>n</i> -nonane
902	0.5	0.4	0.2	0.5	tricyclene
911	0.9	1.1	1.3	0.6	α -pinene
948	3.2	3.1	3.0	0.5	sabinene
953	0.3	0.3	0.3	0.2	β -pinene
962	2.4	2.2	2.1	6.6	myrcene
975			0.2		<i>n</i> -octanal
982				1.5	α -phellandrene
992			0.3	2.7	α -terpinene
999				0.4	<i>p</i> -cymene
1000	5.6	3.7	3.5	36.4	limonene
1005	21.4	21.0	27.4	23.5	1,8-cineole
1016	0.3		0.2	3.2	(<i>E</i>)- β -ocimene
1027	0.4	0.4	0.6	3.3	γ -terpinene
1039	0.9	0.9	0.4		<i>cis</i> -sabinene hydrate
1051	1.0	0.8	0.7	8.6	terpinolene
1060				0.3	<i>p</i> -cymenene
1066	5.4	5.4	6.6	2.1	linalool
1085			0.1	0.5	<i>cis-p</i> -mentha-2-en-1-ol
1131			0.1		<i>p</i> -mentha-1,5-dien-8-ol
1143	0.7	0.7	2.1	0.8	terpin-4-ol
1156				1.8	<i>m</i> - α -terpineol
1160	2.8	3.2	5.0	0.4	α -terpineol
1182	0.7	1.0	0.2	0.3	<i>cis</i> -sabinene hydrate acetate
1190			0.1		hexyl 2-methyl butyrate
1204			0.3		neral
1221	8.2	8.6	3.3		linalyl acetate
1239	0.6	0.6	0.5	0.5	geranial
1285			0.1		<i>neo</i> -dihydrocarveol acetate
1297				0.2	methyl geranate
1325	42.3	44.2	37.7	0.3	α -terpinyl acetate
1334			0.3		neryl acetate
1354	1.6	1.4	1.7		geranyl acetate
1401			0.1		(<i>E</i>)- α -ionone
1427				0.8	(<i>E</i>)- β -farnesene
1454			0.1		γ -gurjunene
1458				0.5	γ -himachalene
1465				0.5	(<i>Z</i>)- α -bisabolene
1478				0.5	(<i>Z</i>)- γ -bisabolene
1528	0.8	1.1	0.8		(<i>E</i>)-nerolidol
1721			0.2	0.2	NI ^b
1723			0.3	0.2	NI
3037				0.5	triacontane
3237				0.7	diatriacontane
3465				0.3	tetraatriacontane

^a SFE1 refers to a charge with particles sizes in the range of 250–425 μm , and SFE2 refers to particles sizes >850 μm ; by hydrodistillation, HD; and by solvent extraction, SE. ^b Unidentified compound.

pressures in the range (9.0–11.0) MPa, high molecular-weight compounds should not be co-extracted with essential oil, because at these operating conditions their solubilities are negligible. In fact, because cuticular waxes, typically long-chain alkanes, are located on the surface of vegetable matter, their extraction is inevitable, even though they are not very soluble in supercritical CO₂ (12, 13) as compared to those of hydrocarbons and oxygenated mono- and sesquiterpenes (14, 15). The problem is overcome with a stepwise separation (16, 17) on the extracted product. Generally, two steps are sufficient. In the first stage, the temperature, typically set at –10 °C, induces the precipitation of waxes, while in the second stage a strong pressure drop causes the removal of gaseous carbon dioxide from the oil.

As stated above, several experimental parameters and preliminary treatments of the matrix affect the yield and/or composition of the extract. In this study, the considered parameters were as follows: temperature, pressure, time of extraction, solvent flow rate, and matrix granulometry.

**Figure 1.** Percentage yield, $Y(\text{w/w})\%$, of cardamom volatile oil obtained by SFE against extraction time at $\phi_{CO_2} = 1.2 \text{ kg/h}$, at d_p 250–425 μm , and at different conditions: 9.0 MPa, 40 °C; 9.0 MPa, 50 °C; and 11.0 MPa, 50 °C.**Figure 2.** Percentage yield, $Y(\text{w/w})\%$, of cardamom volatile oil obtained by SFE against extraction time at 9.0 MPa, 40 °C, $\phi_{CO_2} = 1.2 \text{ kg/h}$, and at two different values of d_p : 250–425 and >850 μm .

The extractions were carried out at the same operating conditions but by changing one parameter at a time. Extraction sets concerned two temperatures, 40 and 50 °C, two pressures, 9.0 and 11.0 MPa, two solvent flow rates, 0.6 and 1.2 kg/h, and two mean particle size values, 250–425 and >850 μm . **Figures 1–3** show the yields against time of extraction for some runs carried out at different operative conditions. The yield is defined as g extract/g seeds.

A higher pressure and a lower temperature, at a given extraction time, give a higher yield (**Figure 1**). The highest yield of 5.5% was obtained at 9.0 MPa, 40 °C, $\phi_{CO_2} = 1.2 \text{ kg/h}$, and d_p in the range of 250–425 μm .

Table 1 shows the percentages of different compound families, where the cardamom oil constituents can be grouped against time of extraction for some of the conducted runs, keeping $\phi_{CO_2} = 1.2 \text{ kg/h}$ and particles size 250–425 μm . The extractions were performed at the following conditions: 9.0 MPa, 40 °C (abbreviated [9.0; 40]) and [11.0; 50]. The oils presented a very high percentage of oxygenated monoterpenes, OM, and small amounts of hydrocarbon monoterpenes, HM, and oxygenated sesquiterpenes, OS. Hydrocarbon sesquiterpenes, HS, were absent. In this case, due to the large prevalence of oxygenated monoterpenes, the evolution in the rate of extraction of the different classes of compounds with time could not be distinctly observed, as in previous studies (18–20). In the SFE of cardamom seeds, HM showed a decreasing trend with time, while the OM were practically constant.

The differences observed in the composition of the volatile oils obtained by SFE at different operating conditions (see **Tables 1 and 2**) were not large from a qualitative or quantitative point of view, while the yields were quite different.

Essential oil is preferably located in vacuoles inside the cellular structure, and a large mass transfer resistance in the solid phase characterizes their extraction process. As a result,

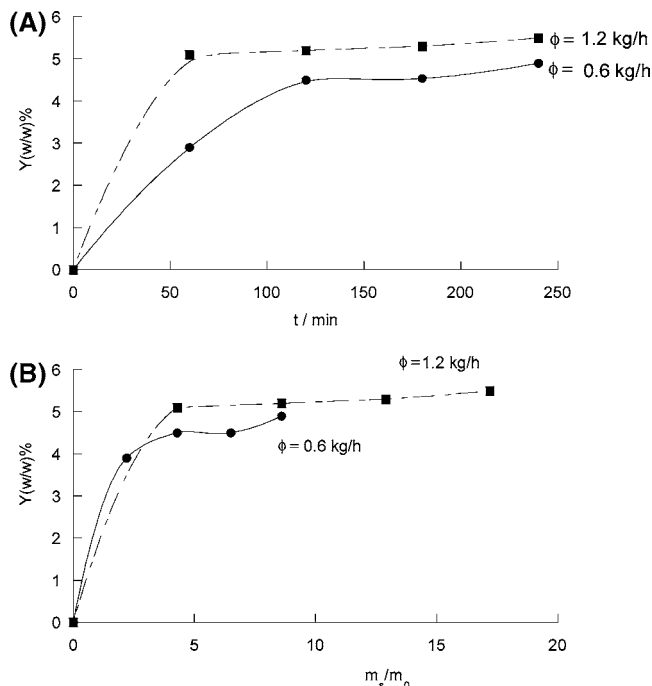


Figure 3. Percentage yield, $Y(w/w)\%$, of cardamom volatile oil obtained by SFE at 9.0 MPa, 40 °C, at d_p 250–425 μm and at two different values of solvent flow, $\phi_{\text{CO}_2} = 0.6$ and 1.2 kg/h: (A) against extraction time; (B) against m_s/m_0 , the specific amount of solvent.

volatile oil extraction can be controlled by mass transfer mechanisms.

If the internal mass transfer mechanism is the controlling step of the extraction process, extraction rates will largely depend on the length of the diffusion path, and, consequently, the time required to obtain a given yield of volatile oil will be affected by matrix particle size. As is indeed shown in **Figure 2**, the rate of extraction of cardamom volatile oil is affected by internal diffusion. A further experiment indirectly confirms the nature of the determining step in the SFE of cardamom seeds. For a given set of conditions, **Figure 3A** and **B** shows the $Y\%$ against time and against the corresponding m_s/m_0 , the specific amount of solvent (grams of CO_2 per gram of seeds). Because there is no major differences between the two extraction profiles, it is possible to deduce that the process is not affected by external diffusion.

Table 2 shows the detailed identification and area percentage of compounds found in the oils isolated by supercritical extraction at 9.0 MPa, 40 °C, $\phi_{\text{CO}_2} = 1.2$ kg/h. The run performed on a charge of matrix with particle sizes in the range of 250–425 μm was named SFE1, and the one with $d_p > 850$ μm was named SFE2. The relative compositions practically coincide, but the yields of the runs were different: 5.5% and 2.6% for SFE1 and SFE2, respectively. Comminution simply makes a greater amount of oil available without affecting its nature. The results on the composition of the oils obtained by hydrodistillation and hexane extraction are also reported in **Table 2**. The main compounds responsible for the fragrance of cardamom oil were α -terpinyl acetate, 42.3% in SFE versus 37.7% in HD; 1,8-cineole, 21.4% in SFE versus 27.4% in HD; linalyl acetate, 8.2% in SFE versus 3.3% in HD; and linalool, 5.4% in SFE versus 6.6% in HD. The oils have a similar composition. The oil obtained by hydrodistillation at a yield of 5.0% contained 86% of oxygenated compounds. A similar amount was also present in the oils obtained by SFE. Supercritical extraction avoided partial hydrolysis of linalyl acetate,

which occurs when vapor is used as a distillation medium. SFE cardamom oil contained 8.2%, while the hydrodistilled oil only contained 3.3% of this compound.

The semisolid dark green extract obtained by SE with hexane gave a yield (w/w) of 7.6%. Its volatile fraction contained a relatively high percentage of hydrocarbon monoterpenes (65%), but it was lower than the percentage in the SFE and HD oils. The main differences in extract quality are clear on comparing the volatile fraction obtained by SE to that obtained by SFE. The major constituents of oleoresin are as follows: limonene, 36.4% SE versus 5.6% SFE1; 1,8-cineole, 23.5% SE versus 21.4% SFE1; terpinolene, 8.6% SE versus 1.0% SFE1; and cuticular waxes, 1.5% SE versus 0% SFE1. The extract obtained by SE was not only polluted by the organic solvent, but it also contained cuticular waxes that worsened the quality of the oil. α -Terpinyl acetate, which was 42.3% in the SFE1 extract, was only 0.3% in the hexane extract. This difference was due to thermal degradation of α -terpinyl acetate, which at 80–90 °C causes a great amount of limonene with lesser amounts of terpinene and terpinolene to form (21). This process probably occurred during evaporation of the solvent in the rotating evaporator.

Comparative data in the literature are rare. In an HD oil obtained at a yield of 8%, Nirmala Menon (22) found α -terpinyl acetate, 29.0%; 1,8-cineole, 28.5%; and linalool, 3.8%, as main compounds. Naik and Maheshwari (6) reported the composition of the two main constituents, 1,8-cineole and α -terpinyl acetate, which were present as 33.3% and 20.9%, respectively, in liquid CO_2 extract and as 40.4% and 12.0%, respectively, in the HD oil. Gopalakrishnan and Narayanan (7) tested the extraction of the essential oil of cardamom seeds with SC-CO_2 in a batch mode apparatus in the 40–60 °C temperature range and at pressures ranging from 10 to 60 MPa. They found a fairly constant yield of the total extract with pressure, at 40 °C, from 7.6% at 10 MPa to 7.9% at 30 MPa at a contact time of 3 h. The nonvolatile fraction percentage in the total extract varied from 4.5% at 10 MPa to 9.4% at 50 MPa. These results probably depend on the adopted operative modality. This paper has shown that an essential oil of cardamom of good quality can be obtained at a satisfactory yield with a semi-batch apparatus.

LITERATURE CITED

- (1) *Encyclopedia of Food Science and Technology*; Wiley: New York, 1992.
- (2) Angus, S.; Armstrong, B.; De Reuck, K. M.; Altunin, V. V.; Gadeskii, O. G.; Chapela, G. A.; Rowlinson, J. S. *International Thermodynamic Tables of the Fluid State, Carbon dioxide*; Pergamon Press: Oxford, UK, 1983.
- (3) Atta-Ur-Rahman, Choudhary, M. I.; Ahmed, A.; Iqbal, M. Z.; Demirci, B.; Demirci, F.; Baser, K. H. C. Antifungal activities and essential oil constituents of some spices from Pakistan. *J. Chem. Soc. Pak.* **2000**, *22*, 60–65.
- (4) Leung, A.; Foster, S. *Enciclopedia delle piante medicinali*; Edizioni Aporie: Roma, Italy, 1999.
- (5) Al-Zuhair, H.; El-Sayeh, B.; Ameen, H. A.; Al-Shoor, H. Pharmacological studies of cardamom oil in animals. *Pharmacol. Res.* **1996**, *34*, 79–82.
- (6) Naik, S. N.; Maheshwari, R. C. Separations of essential oils from plant materials by liquid carbon dioxide. *VTT Symp.* **1989**, *102* (Non-Waste Technol. Vol. 1), 355–366.
- (7) Gopalakrishnan, N.; Narayanan, C. S. Supercritical carbon dioxide extraction of cardamom. *J. Agric. Food Chem.* **1991**, *39*, 1976–1978.
- (8) Gopalakrishnan, N. Studies on storage quality of CO_2 -extracted cardamom and clove bud oils. *J. Agric. Food Chem.* **1994**, *42*, 796–798.

- (9) NIST/EPA/NIH Mass Spectral Library, National Institute of Standard and Technology, 1998.
- (10) Adams, R. P. *Identifications of Essential Oils by Ion Trap Mass Spectroscopy*; Academic Press: New York, 1989.
- (11) Kováts, E. Gas chromatographic characterization of organic substances in the retention index system. *Adv. Chromatogr.* **1965**, *1*, 229–247.
- (12) McHugh, M. A.; Seckner, A. J.; Yogan, T. High-pressure phase behavior of binary mixtures of octacosane and carbon dioxide. *J. Ind. Eng. Chem. Fundam.* **1984**, *23*, 493–499.
- (13) Reverchon, E.; Russo, P.; Stassi, A. Solubilities of solid octacosane and triacontane in supercritical carbon dioxide. *J. Chem. Eng. Data* **1993**, *38*, 458–460.
- (14) Stahl, E.; Gerard, D. Solubility behaviour and fractionation of essential oils in dense carbon dioxide. *Perfum. Flavor.* **1985**, *10*, 29–37.
- (15) Richter, M.; Sovova, H.; Kucera, J. Solubility of monoterpenes in supercritical carbon dioxide. 2nd International Symposium on High-Pressure Engineering: Erlangen, Germany, 1990.
- (16) Stahl, E.; Quirin, K. W.; Gerard, D. *Verdichtete gase zur extraktion und raffination*; Springer-Verlag: Heidelberg, 1987.
- (17) Reverchon, E. Fractional separation of SFE extract from majorana leaves: mass transfer and optimization. *J. Supercrit. Fluids* **1992**, *5*, 256–261.
- (18) Caredda, A.; Marongiu, B.; Porcedda, S.; Soro, C. Supercritical carbon dioxide extraction and characterization of *Laurus nobilis* essential oil. *J. Agric. Food Chem.* **2002**, *50*, 1492–1496.
- (19) Reverchon, E.; Taddeo, R.; Della Porta, G.; Extraction of sage oil by supercritical CO₂: Influence of some process parameters. *J. Supercrit. Fluids* **1995**, *8*, 302–309.
- (20) Cherchi, G.; Deidda, D.; De Gioannis, B.; Marongiu, B.; Pompei, R.; Porcedda, S. Extraction of *Santolina insularis* essential oil by supercritical carbon dioxide: influence of some process parameters and biological activity. *Flavour Fragrance J.* **2001**, *16*, 35–43.
- (21) Dupont, G.; Levy, J.; Marot, M. Effet Raman dans les composés terpéniques. IV. Sur les terpinènes et le terpinolène. *Bull. Soc. Chim. Fr.* **1933**, *53*, 393–400.
- (22) Nirmala Menon, A. Studies on the volatiles of cardamom (*Elleteria cardamomum*). *J. Food Sci. Technol.* **2000**, *37*, 406–408.

Received for review July 23, 2003. Revised manuscript received July 30, 2004. Accepted August 3, 2004. This work was supported by funds from the Regione Autonoma della Sardegna-Programma Comunitario Interreg (PIC-Interreg III).

JF034819I