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Analytical Methods

Supercritical carbon dioxide extraction of volatile oil from Italian coriander seeds

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ABSTRACT

Supercritical CO_2 fluid extraction of the volatile oil from Italian coriander seeds was carried out under different conditions of temperature (40 and 50 °C), pressure (90, 100 and 150 bar), mean particle size (0.4, 0.6 and 0.8 mm) and CO_2 flow rate (0.79, 1.10 and 1.56kg/h) in order to evaluate their influence on the yield and composition of the volatile oil. Hydrodistillation with the same mean particle sizes was performed and used as a comparative method. The best supercritical fluid extraction conditions were found to be 90 bar, 40 °C, 1.10 kg/h and 0.6 mm. The chemical composition of each supercritical fluid extraction sample was analysed by GC and GC–MS and the global composition was compared with that obtained by hydrodistillation. The dominant components were linalool (65–79%), γ-terpinene (4–7%), camphor (3%), geranyl acetate (2–4%), α-pinene (1–3%), geraniol (1–3%) and limonene (1–2%). Moreover, supercritical fluid extraction samples were collected at specific intervals of amount of CO_2 consumed, during each extraction, and the contribution of the main volatile components from each sample, for the global volatile compositions, was evaluated. In general, the first sample of each extraction contained up to 50% of the mass of each component.

1. Introduction

The importance of aromatic and medicinal plants for pharmaceutical, food and fragrance industries is mainly due to a small fraction, the volatile oil. Depending on the extraction method used, the volatile oil composition may change leading to deviations from the natural odour of the plant (Anitescu, Doneanu, & Radulescu, 1997; Catchpole, Grey, & Smallfield, 1996).

HD (hydrodistillation) and SD (steam-distillation) are the traditional methods to isolate essential oils from aromatic plants, although these two methods present some problems, namely, hydrolysis and thermal degradation. To overcome these limitations, an alternative method, SFE (supercritical fluid extraction), has been applied (Bruno, Nieto de Castro, Hamel, & Palavra, 1993, chap. 11; Reverchon & De Marco, 2006). Supercritical fluids provide a higher solubility of the components of the volatile oil, as well as improved mass-transfer rates. Moreover, the manipulation of parameters as temperature and pressure leads to the extraction of different components, which can be useful when a particular component is required (Anitescu et al., 1997; Catchpole et al., 1996; Illés, Daood, Perneczki, Szokonya, & Then, 2000; Mendiola, Herrero, Alejandro Cifuentes, & Elena Ibañez, 2007; Pourmortazavi & Hajimirsadeghi, 2007; Reverchon & De Marco, 2006). Since some of the supercritical CO_2 extracted oil present a flavour resembling the original material, development of industrial applications has been carried out (Moyler, 1993, chap. 6). Recently, a published review indicates that the number of independent patents in the area had reached 8600 (Schütz, 2007).

Coriander (*Coriandrum sativum* L.) is an annual Apiaceae (Umbelliferae) herb which grows in the Mediterranean countries and is widely used in food and pharmaceutical industries. In traditional medicine, seeds are used against gastrointestinal problems, rheumatism, pain in the joints and recent studies have also demonstrated a hypoglycaemic action and effects on carbohydrate metabolism (Wangesteen, Samuelsen, & Malterud, 2004). It has also been reported the antimicrobial effect of coriander leaves and seeds against several microorganisms (Delaquis, Stanich, Girard, & Mazza, 2002; Lo Cantore, Iacobellis, De Marco, Capasso, & Senatore, 2004). In food industry, leaves and seeds are employed as condiment, being used to flavour various commercial foods as liqueurs, teas, meat products and pickles (Illés et al., 2000).

As it is common in the Apiaceae family, the volatiles of coriander are accumulated in internal secretory structures, called ducts or vittae, which are present in stems, leaves and seeds (Evans, 1996). The Portuguese Pharmacopoeia indicates a minimum essential oil content of 3 ml/kg (dried plant) for coriander seeds (Farmacopeia Portuguesa VIII, 2005).

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The composition of the volatile oil isolated from coriander seeds was already studied by some authors using different extraction methods, namely SD (Anitescu et al., 1997; Machado, Gomes de Azevedo, Nunes da Ponte, & Sardinha, 1993; Smallfield, van Klink, Perry, & Dodds, 2001), HD (Kerrola & Kallio, 1993) and SFE (Anitescu et al., 1997; Catchpole et al., 1996; Illés et al., 2000; Kerrola & Kallio, 1993; Machado et al., 1993). However, concerning SFE, Machado et al. (1993), Kerrola and Kallio (1993) and Anitescu et al. (1997) only used one extraction condition of pressure and temperature, while Illés et al. (2000) studied the composition of the coriander oil at a higher range of pressures (from 100 to 350 bar), obtaining fatty acids besides the volatile oil. Catchpole et al. (1996) also reported the influence of particle size and flow rate on extraction conditions of 250 bar and 40 °C.

The aim of this work was to study the influence of the various process parameters as pressure, temperature, particle size and CO_2 flow rate on the extraction yield and composition of the volatile oil from Italian coriander seeds, comparing the extracts with those obtained by HD. The evolution of the extraction was also studied and the samples collected during the process were analysed to understand how they influence the final composition of the volatile oils. These studies were carried out in the course of an experimental program involving several aromatic plants such as rosemary (Coelho et al., 1997), pennyroyal (Reis-Vasco, Coelho, & Palavra, 1999), fennel (Coelho, Pereira, Mendes, & Palavra, 2003) and savory (Coelho et al., 2007).

2. Materials and methods

2.1. Supercritical fluid extraction apparatus

The SFE apparatus used in this work was described in detail by Reis-Vasco et al. (1999). Briefly, the main parts of the apparatus are a diaphragm pump, an extraction vessel with an internal volume of 1 l and two separators of 0.27 l each, operating in series. A back-pressure regulator is used to control the pressure, which is measured with a Bourdon type manometer and the total volume of CO_2 is determined with a dry test meter. A preset temperature in the extraction vessel is achieved with the aid of a water jacket. Furthermore, the CO_2 (99.995% purity) used in the studies was supplied by Air Liquide (Lisbon, Portugal).

2.2. Plant material

Seeds from commercial Italian coriander (L'Ortolano, Cesena, Italy) were ground with a commercial mill and frozen with liquid N_2 to avoid the loss and thermal degradation of the volatile oil. Several sieves, with various mesh sizes, were used to collect different fractions. After this process, the different fractions were kept at −20 °C in dark bottles and mean particle sizes of about 0.4, 0.6 and 0.8 mm were used for the extractions.

To determine the moisture content of the plant material used in the extractions, a sample of untreated seeds (without grinding) was oven-dried at 100 °C until a constant weight (72 h). A value of 8.5% was obtained.

2.3. Extraction

Volatile oil was isolated by SFE. About 100 g (d.w.) of coriander seeds were placed inside the extractor between two layers of glass wool. Different experimental conditions were used and the process parameters were studied in the following order: pressure (90, 100 and 150 bar), temperature (40 and 50 °C), mean particle size (0.4, 0.6 and 0.8 mm) and flow rate (0.79, 1.10 and 1.56 kg/h).

For the fractionation steps, a pressure of 80 bar and a temperature of −8 °C, in the first separator, and 20 bar and −15 °C, in the second one, were considered appropriate. The quantities of the volatile oils collected in the second separator were determined gravimetrically (w/w).

Samples were collected at specific intervals (0.19, 0.56, 1.11, 1.85, 2.77, 3.90 and 4.40 kg of CO_2 consumed) to study the evolution of the extraction. The chemical composition of the volatile oil was calculated after the analysis of each sample taking into account their relative weights to the total mass of oil. The isolated samples were also used to understand how the time of the extraction influences the oil composition.

To obtain the essential oil, HD was carried out for 4 h, in a Clevenger apparatus, using 40 g (d.w.) of seeds with the mean particle size of 0.4, 0.6 and 0.8 mm.

2.4. Gas chromatography

Quantitative analyses were performed in a Hewlett-Packard 5890 gas chromatograph (HP, Waldbronn, Germany), equipped with a flame ionization detector (FID) and a fused-silica DB-5 capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm; J&W, Folsom, CA, USA). Oven temperature was programmed isothermally to 40 °C, during 2 min, then was raised at 3 °C/min to 230 °C, and finally increased at 5 °C/min to 310 °C and held at this temperature for 15 min. The injector and detector were set at the same temperature, 310 °C. Helium was used as a carrier gas flowed at a rate of 24 cm/s and the split ratio was 1:50. The percentage composition of the oils was computed by the normalization method from the GC peak areas without using response factors.

2.5. Gas chromatography–mass spectrometry

The GC–MS unit consisted of a Perkin Elmer Autosystem XL gas chromatograph (Perkin Elmer, Shelton, CT, USA) equipped with DB-1 fused-silica column (30 m × 0.25 mm i.d., film thickness 0.25 μm; J&W Scientific Inc., Agilent Technologies, Santa Clara, CA, USA), and interfaced with Perkin Elmer Turbomass mass spectrometer (software version 4.1, Perkin Elmer, Shelton, CT, USA). A different program was used. Oven temperature was programmed, 45–175 °C, at 3 °C/min, subsequently at 15 °C/min up to 300 °C, and then held isothermal for 10 min; injector and detector temperatures, 280 °C and 290 °C, respectively; transfer line temperature, 280 °C; ion trap temperature, 220 °C; carrier gas, helium, adjusted to a linear velocity of 30 cm/s; split ratio, 1:40; ionization energy, 70 eV; ionization current, 60 μA; scan range, 40–300 u; scan time, 1 s.

The identification of the components was assigned by comparison of their retention indices, relative to C9–C16 *n*-alkanes indices and GC–MS spectra from a home-made library, based on the analyses of reference oils, laboratory-synthesised components and commercial available standards.

2.6. Scanning electron microscopy (SEM)

Plant material was prepared for SEM as previously reported (Figueiredo & Pais, 1994). Plant material was fixed with 1.5% glutaraldehyde (GA) in 0.05 M sodium cacodylate buffer, pH 7.0, for 45 min at room temperature, under shaking. After 1–2 min at reduced pressure (0.03 bar) the fixative agent was substituted by 3% GA in 0.1 M sodium cacodylate buffer, pH 7.0, for 120 min at room temperature, under shaking. The material was rinsed thoroughly in the same buffer and post-fixed with a 1% osmium tetroxide aqueous solution for 120 min at room temperature, under shaking. After dehydration in a graded acetone series, the material was dried by the critical point drying method in a Polaron E3500

(Quorum Technologies, Ringmer, United Kingdom). Dried specimens were sputter coated with gold in a Polaron E5350 and the observations were made at 15 kV in a Jeol JSM T220 scanning electron microscope (Tokyo, Japan).

3. Results and discussion

Different SFE extraction conditions of coriander seeds were used to study the influence of the pressure, temperature, mean particle size and solvent flow rate on the yield and composition of the volatile oil (Table 1). All the volatile oil samples showed a pale yellow colour, except for 150 bar where the extract was yellowish. The volatile oil was also compared with the essential oil obtained by hydrodistillation using the same particle size (Table 1). The composition of the volatile oils and essential oils isolated from coriander, obtained under the different parameters studied, are listed in Table 1 considering the order of the components elution on a DB-5 column.

Taking into account the global volatile oil chemical composition and that of the essential oil, oxygen-containing monoterpene fraction dominated all the oil samples (73–86% for SFE and 76–82% for HD). On the other hand, the monoterpene hydrocarbon fraction showed a relative amount lower in SFE (9–16%) than in HD (17–22%). For both cases, SFE and HD, linalool (65–79% for SFE and 67–72% for HD), γ-terpinene (4–7% for SFE and 5–7% for HD), camphor (3% in both cases), geranyl acetate (2–4% for SFE and 1–3% for HD), limonene (1–2% for SFE and 3% for HD), geraniol (1–3% for SFE and 3% for HD) and α-pinene (1–3% for SFE and 2–3% for HD) are the main components (Table 1).

3.1. Influence of the pressure

The influence of three different pressures (90, 100 and 150 bar) on the volatiles isolated from coriander was studied using a temperature of 40 °C, a mean particle size of 0.6 mm and a flow rate of 1.10 kg/h (Table 1).

At 90 bar and 100 bar, the yield (% in g/g d.w.) was 0.38 and 0.40% (Table 2 and Fig. 1), respectively, and the extract was mainly composed of volatile components (97% and 95%; Table 1). At 100 bar the yield was similar to that obtained at 90 bar, but the contamination with other components was higher. For 90 and 100 bar, 3.90 kg of CO_2 were necessary to extract all the volatile oil, which corresponded to 210 min of extraction, at a flow rate of 1.10 kg/h. At 150 bar more time was needed to achieve the maximum yield due to the co-extraction of non-volatile components not present in the essential oil (almost 15% of the extract; Table 2 and Fig. 1). Although, the total amount of recovered oil increased at higher pressures, the selectivity decreased due to fatty acids and other heavy components contamination. Anitescu et al. (1997), using extraction conditions of 150 bar and 50 °C, also observed the co-extraction of fatty acids and esters and the total yield obtained was similar to that of the present work (0.61% *vs.* 0.58%). Using pressures from 100 to 350 bar, Illés et al. (2000) also extracted triglycerides, besides volatile components, which is in agreement with these results.

Table 1
Global percentage composition of essential oil (obtained by HD) and volatile oil (obtained by SFE)

Extraction method		Hydrodistillation			Supercritical fluid extraction							
Pressure (bar)					90					90	100	150
Temperature (°C)					40					50	40	40
Particle size (mm)		0.40	0.60	0.80	0.40	0.60			0.80	0.60	0.60	0.60
Flow rate (kg/h)					1.10	0.79	1.10	1.56	1.10	1.10	1.10	1.10
Components	RI											
α-Thujene	1010	t	t	t	t	t	t	t	t	t		t
α-Pinene	1017	2.2	2.5	3.4	3.4	1.5	1.5	1.2	2.8	2.1	1.3	1.9
Camphene	1032	0.3	0.3	0.4	0.3	0.2	0.2	0.1	0.3	0.2	0.1	0.2
Sabinene	1060	0.2	0.1	0.2	0.2	0.1	0.1	0.1	0.2	0.2	0.3	0.1
β-Pinene	1063	0.3	0.4	0.4	0.4	0.2	0.2	0.8	0.4	0.3	0.2	0.3
Myrcene	1081	2.0	2.8	2.7	1.1	0.9	1.0	1.2	1.2	0.9	1.0	0.9
α-Terpinene	1109	0.4	0.5	0.5	0.2	0.1	0.2	0.2	0.2	0.1	0.1	0.1
p-Cymene	1117	1.2	1.3	1.5	1.1	0.8	0.8	0.7	1.0	1.1	0.9	0.9
Limonene	1122	2.5	3.1	3.4	1.7	1.3	1.4	1.5	1.8	1.4	1.5	1.4
cis-β-Ocimene	1125	t	t	t		t	t		t	0.1	t	0.2
trans-β-Ocimene	1146	1.1	1.7	1.6	0.3	0.3	0.4	0.6	0.5	0.3	0.4	0.3
γ-Terpinene	1158	6.3	6.8	7.2	6.7	5.1	5.0	4.6	6.3	5.6	5.4	5.1
trans-Sabinene hydrate	1166	t	t	t	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
cis-Linalool oxide	1173	t	t	t	t	t	t	t	t	t	t	t
n-Octanol	1173	t	t	t	t	t	t	t	t	t	0.2	t
Terpinolene	1191	0.8	0.9	1.0	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5
Linalool	1210	72.3	67.6	66.5	74.0	72.4	75.9	77.6	73.4	78.8	75.3	65.2
Camphor	1254	3.0	3.0	3.3	3.3	3.0	3.1	3.2	3.2	3.4	3.1	2.5
Citronellal	1265	0.1	0.1	0.1	0.1	t	0.1	t	t	t		t
Borneol	1279	0.1	0.1	0.1	t	0.1	0.1	t	0.1	t	t	0.2
Terpinen-4-ol	1292	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2
α-Terpineol	1305	0.4	0.4	0.4	t	0.1	0.1	t	t	0.1	t	0.1
Citronellol	1360	t	t	t	t	t	t	t	t	0.1	0.5	0.1
Geraniol	1378	2.8	2.7	2.6	2.0	2.3	2.9	2.2	2.2	0.9	1.5	1.9
Geranyl acetate	1513	2.8	2.8	2.4	2.7	2.7	3.5	3.1	2.7	1.5	2.5	2.6
Identified components		98.7	97.6	97.9	98.2	91.9	97.3	97.9	97.3	97.9	95.1	84.9
Grouped components												
Monoterpene hydrocarbons		17.0	20.6	22.4	15.9	11.1	11.3	11.6	15.4	12.8	11.7	12.0
Oxygen-containing monoterpenes		81.7	77.0	75.5	82.3	80.8	86.0	86.4	81.9	85.1	83.2	72.9
Other volatile components		t	t	t	t	t	t	t	t	t	0.2	t

The SFE was performed under different conditions of pressure, temperature, mean particle size and flow rate.
Retention index relative to C9–C16 *n*-alkanes on the DB-5 column, t – trace (<0.05%).

Table 2
Yield of the samples collected during the extractions performed

Pressure (bar)	90						100	150
Temperature (°C)	40					50	40	40
Mean particle size (mm)	0.40	0.60			0.80	0.60	0.60	0.60
Flow rate (kg/h)	1.10	0.79	1.10	1.56	1.10	1.10	1.10	1.10
Mass of CO_2 (kg)	Yield (%)							
0.19	0.19	0.12	0.13	0.15	0.12	0.06	0.12	0.16
0.56	0.26	0.26	0.21	0.20	0.20	0.11	0.21	0.28
1.11	0.36	0.35	0.28	0.23	0.26	0.12	0.29	0.36
1.85	0.40	0.41	0.34	0.25	0.29	0.14	0.35	0.44
2.77	0.43	0.43	0.36	0.27	0.31	0.15	0.39	0.52
3.50	–	–	–	–	–	0.16	–	–
3.90	0.44	0.44	0.38	0.27	0.32	–	0.40	0.57
4.40	–	–	–	–	–	–	–	0.58

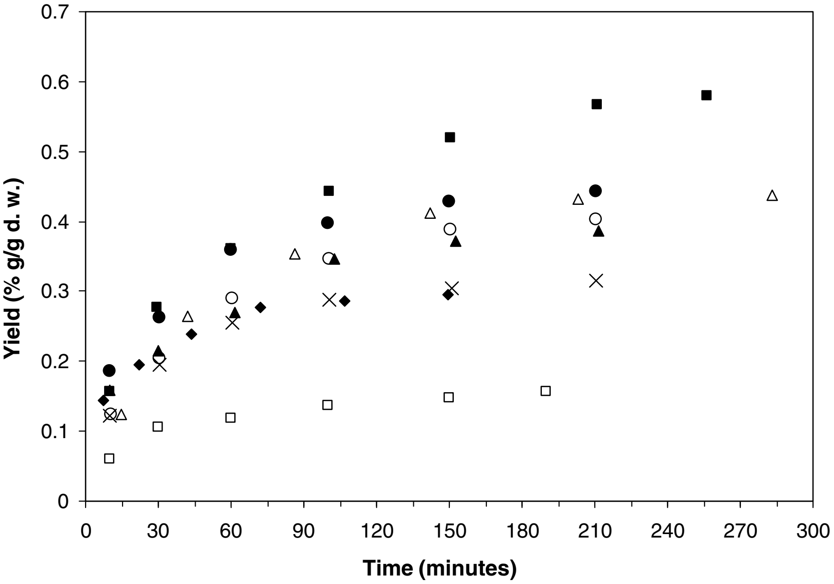

Fig. 1. Comparison between the volatile oil yields obtained for different SFE conditions: pressure and temperature (▲ – 90 bar/40 °C, □ – 90 bar/50 °C, ○ – 100 bar/40 °C and ■ – 150 bar/40 °C) for a mean particle size of 0.6 mm and a flow rate of 1.10 kg/h; mean particle size (● – 0.4 mm, ▲ – 0.6 mm, × – 0.8 mm) using 90 bar, 40 °C and a flow rate of 1.10 kg/h; and flow rate (Δ – 0.79 kg/h, ▲ – 1.10 kg/h, ♦ – 1.56 kg/h) for 90 bar, 40 °C and 0.6 mm of mean particle size.

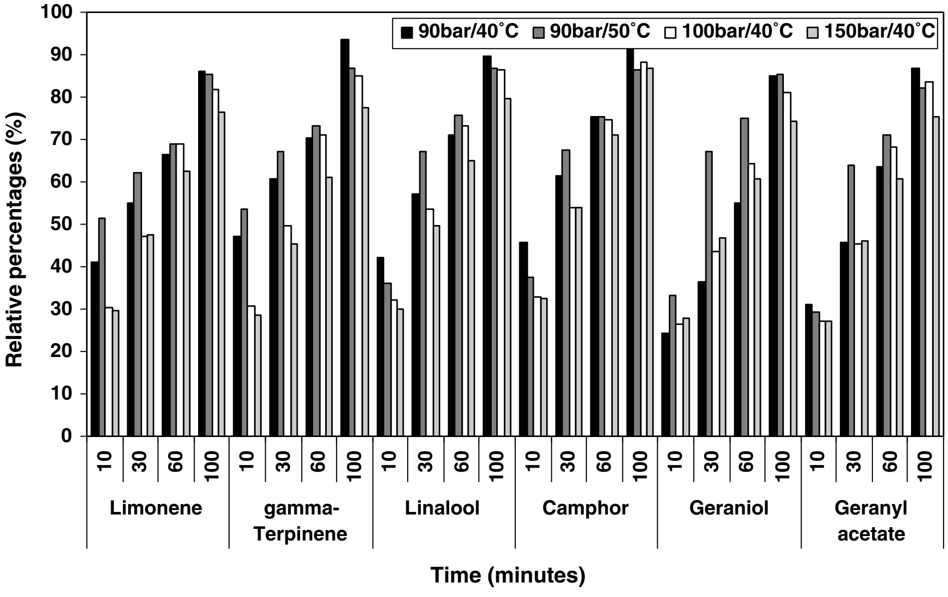

Fig. 2. Relative percentage of the main components extracted by SFE with different pressures (90, 100 and 150 bar) and temperatures (40 and 50 °C), using 0.6 mm of particle size and 1.10 kg/h of flow rate. Results are only shown for the first four samples collected.

In terms of volatile compositions, no major differences were found in the volatiles extracted at different pressures. Linalool (65–76%), γ-terpinene (5%), camphor (3%), geranyl acetate (3–4%), geraniol (2–3%), limonene (1–2%) and α-pinene (1–2%) occurring within the previous recorded ranges (Table 1). Due to the reasons presented before, a pressure of 90 bar was adopted in the subsequent experiments.

The samples collected at different times were analysed to understand the behaviour of the main components (linalool, γ-terpinene, camphor, geranyl acetate, geraniol and limonene) during the extraction time, i.e., when they were preferentially released (Fig. 2). Differences are more evident at the beginning of the extraction (in the first four samples) reason why only these results are presented in Fig. 2. Although the extraction was carried out for 210 min (90 and 100 bar) and 255 min (150 bar), for all the main components, almost 27–47% was extracted after only 10 min and at the end of 100 min only 7–25% of these compounds remained in the plant matrix. It was also observed that the highest percentages were obtained, in general, for the lowest pressure (90 bar), meaning that at 150 bar other compounds, besides hydrocarbon and oxygen-containing monoterpenes, competed for the CO_2, and were additionally extracted.

3.2. Influence of the temperature

The influence of the temperature was studied using extraction conditions of pressure, flow rate and particle size of 90 bar, 1.10 kg/h and 0.6 mm, respectively. The experiments were carried out for 200–210 min, which correspond, as explained above, to a consumption of 3.90 kg of CO_2 (Table 2 and Fig. 1).

Although the yield at 40 °C was higher than that obtained at 50 °C (0.38% *vs.* 0.16%) due to the higher density ($\rho = 485$ *vs.* 285 kg m^{-3}) and, therefore, solvent power of CO_2, volatile oil composition was similar (Table 1). But taking into account the best compromise between the yield and composition of the volatile oil, 40 °C was selected.

Temperature seemed to promote the rapid release of the monoterpene hydrocarbons from the plant matrix, as could be observed after only 10 min (Fig. 2). For the oxygen-containing monoterpenes the opposite behaviour was observed, except for geraniol (Fig. 2). However, the positive effect of the temperature was noticed for all the components (even the oxygen-containing monoterpenes) in the subsequent samples. As it was observed for the assay of different pressures, at the end of 100 min, at 40 °C and 50 °C, only 7–18% of these compounds were not extracted yet. However, at 50 °C it was necessary a longer extraction time to reach the same relative percentages obtained for 40 °C at the end of 100 min.

3.3. Influence of the particle size

The study of the influence of the mean particle size was performed using the following experimental conditions: 90 bar, 40 °C, 1.10 kg/h and 210 min of extraction (Table 2, Fig. 1).

As in the case of the previously assayed parameters, no major differences were found in the SFE volatiles composition, extracted with different mean particles sizes, linalool (73–76%), γ-terpinene (5–7%), camphor (3%), geranyl acetate (3–4%), geraniol (2–3%), limonene (1–2%) and α-pinene (2–3%) maintaining similar relative amounts (Table 1).

From the point of view of the morphology, the schizocarpic coriander fruits (seeds) show two dry segments (mericarps) attached to a more or less deeply forked central stalk (carpophore; Fig. 3A). Internally, the oil is secreted in ducts located in the pericarp of the fruit (Fig. 3B) and these ducts are damaged during grinding, leading to the release of the oil which produces an external film around the endosperm particles (Fig. 3C). So, the highest yield was obtained for the smallest particle size, indicating that more ducts were damaged and, therefore, the oil was more accessible to carbon dioxide. Although the best yield was achieved with 0.4 mm, the mean particle size of 0.6 mm was selected for the other experiments due to practical reasons.

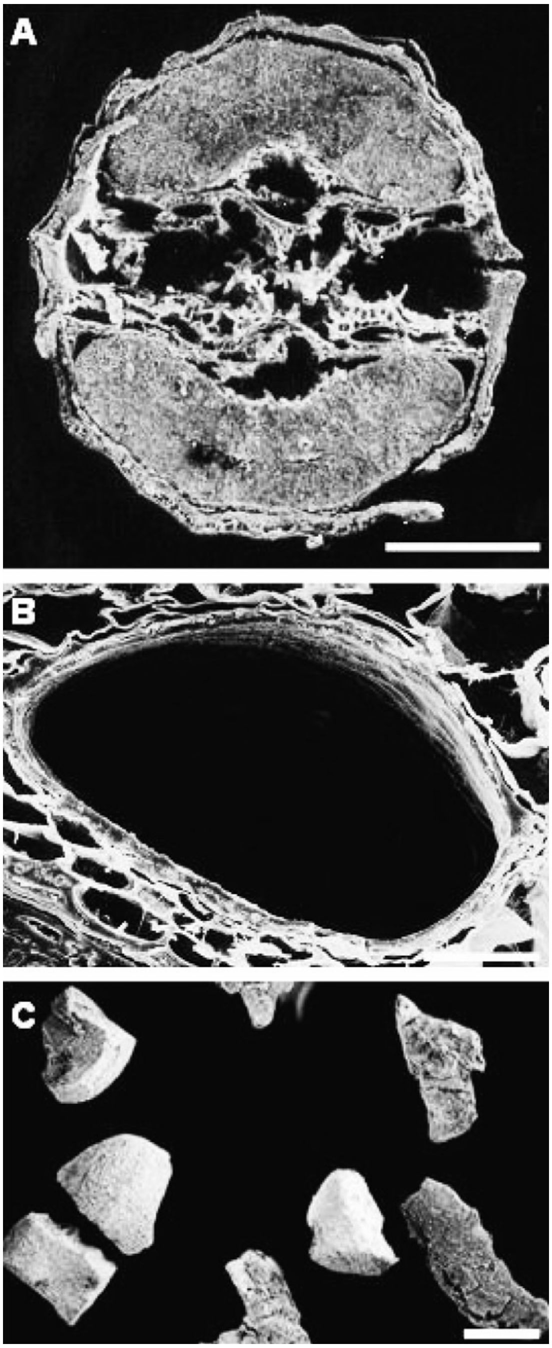

Fig. 3. Scanning electron microscopy images of coriander seeds. (A) Transversal section of coriander seed (bar = 1 mm); (B) ventral duct (bar = 50 μm); (C) particles obtained after seed grinding in 1 mm sieve (bar = 1 mm).

This parameter also influenced the composition of the samples collected during the extraction process. Except for geraniol, the smallest mean particle sizes (0.4 and 0.6 mm) promoted the initial release of the main components being, for instance, 47% of limonene present in the sample collected after 10 min. At the end of 100 min higher relative percentages of monoterpene hydrocarbons were obtained, using a mean particle size of 0.4 mm and for oxygen-containing monoterpenes using 0.8 mm (Fig. 4).

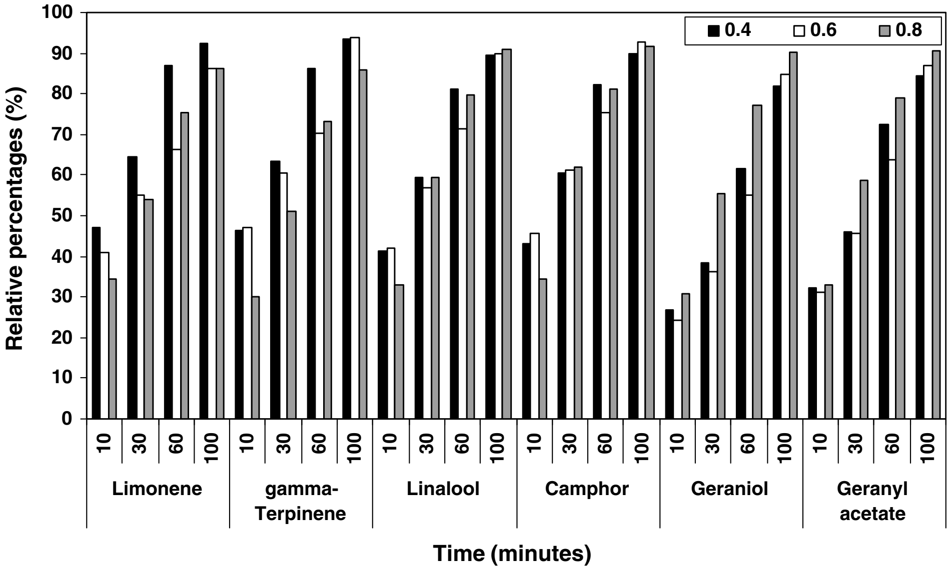

Fig. 4. Relative percentage of the main components extracted by SFE with different mean particle sizes (0.4, 0.6 and 0.8 mm) at 90 bar, 40 °C and 1.10 kg/h. Results are shown only for the first four samples collected.

For the three particle sizes studied, the SFE yields were similar to those observed for HD: from the mean particle size of 0.4–0.8 mm, the yields obtained for SFE were 0.44, 0.38 and 0.32, respectively, while for HD they were 0.42%, 0.38% and 0.31%. Hydrodistillation performed with entire seeds resulted in a yield of 0.34%.

3.4. Influence of the flow rate

When evaluating the influence of flow rates of 0.79, 1.10 and 1.56 kg/h in the yield and composition of the volatile oil (Table 2, Fig. 1), all extractions were carried out using 3.90 kg of CO_2.

The increase of the flow rate reduced the time required to obtain the complete extraction. However, the total yield decreased (for 1.56 kg/h, 0.30%). One possible explanation can be that the volatile oil and the CO_2 had shorter contact time and the solvent may leave the plant matrix without dissolving all the solute that it could solubilize. However, the decrease of the yield with the increase of flow rate had no influence in the global composition of the volatile oil. The main components remaining within ranges are: linalool (73–78%), γ-terpinene (4–6%), camphor (3%), geranyl acetate (3–4%), geraniol (2–3%), limonene (1–2%) and α-pinene (1–2%; Table 1).

4. Conclusions

The parameters under study showed different influences on the volatile oil extracted. Pressure and temperature control both its yield and composition, since a slight variation of these parameters leads to a change in the density of the supercritical solvent. As the pressure rises (at the same temperature), the solvent also solubilizes non-volatile components that contaminate the volatile oil. However, working at pressures between 90 and 100 bar, the composition of the volatile oil is closed to that obtained with hydrodistillation. Taking into account the general variation of the composition with time, at the lowest pressure (90 bar) and during the first 30 min of extraction, the highest percentages of the main components were obtained, both for hydrocarbons and oxygen-containing compounds. Concerning the temperature, an increase (at the same pressure) leads to a decrease of the density of the CO_2, resulting in a lower yield and in an initial composition of the oil richer in monoterpene hydrocarbons. Therefore, moderate pressure and temperature extraction conditions of 90 bar and 40 °C, minimized the co-extracted compounds and optimized the composition of the volatile oil, as it was similar to that of the essential oil obtained from the same species.

The present study showed, also, that a decrease in the particle size improved the volatiles' yield, since more ducts were destroyed during the milling process. Although the global composition was not affected by the mean particle size, more monoterpene hydrocarbons were isolated, in the beginning of the extraction, with particles around 0.4 mm while the opposite occurred for the 0.8 mm particles.

The increase of the flow rate reduced the time required to obtain the complete extraction, although the achieved yield was not the same for all the tested flow rates, due to the different time contact of the solvent with the plant matrix. Furthermore, this parameter had no influence on the composition of the volatile oil.

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