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Food Chemistry 92 (2005) 143–149
Food Chemistry
www.elsevier.com/locate/foodchem

Extraction of fennel (*Foeniculum vulgare* Mill.) seeds with supercritical CO_2: Comparison with hydrodistillation

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Received 7 June 2004; accepted 16 July 2004

Abstract

Ground fennel (*Foeniculum vulgare* Mill.) seeds, growing wild in Montenegro, were extracted with supercritical CO_2 (SC-CO_2) at a flow rate of 0.2 kg CO_2/h under varying extraction conditions in order to determine yield, composition and organoleptic characteristics of extract. The extracts obtained were compared to fennel seed oil isolated by hydrodistillation. In the SC-CO_2, extracts as well in the hydrodistilled oil, the major compounds were *trans*-anethole (68.6–75.0%) and (62.0%), methylchavicol (5.09–9.10%) and (4.90%), fenchone (8.40–14.7%) and (20.3%), respectively. With pressure varying from 80 to 150 bar and temperature varying from 40 to 57 °C, it was found that, for the selected herb material, the optimal conditions of SC-CO_2 extraction (high percentage of *trans*-anethole, with significant content of fenchone and reduced content of methylchavicol and co-extracted cuticular waxes) are: pressure, 100 bar; temperature, 40 °C; extraction time, 120 min. Organoleptic tests confirmed that hydrodistilled oil possessed a less intense fennel seed aroma than extracts obtained by SC-CO_2.

Keywords: *Foeniculum vulgare* Mill.; Supercritical CO_2; Hydrodistillation; Essential oil; Cuticular wax; Anethole; Fenchone

1. Introduction

Fennel (*Foeniculum vulgare* Miller) is an annual, biennial or perennial plant, depending on the variety, belonging to Apiaceae family and is native to the Mediterranean area (Piccaglia & Marotti, 2001). It has been cultivated and introduced into many regions outside that zone; it is grown commercially in some of them, such as Russia, India, China and Japan (Volák & Stodola, 1998). Fennel has been known, since antiquity, as a medicinal and aromatic herb, commonly used to flavour liqueurs, breads, fishes, salads and cheeses (Garcia-Jiménez, Pérez-Alonso, & Velasco-Negueruela, 2000).

The third European Pharmacopoeia reports two fennel drugs, from bitter fennel fruits (*F. vulgare* Miller spp. *vulgare* var. *vulgare*) and sweet fennel fruits [*F. vulgare* Miller spp. *vulgare* var. *dulce* (Miller) Thellung]. The drug consists of the dry, ripe, whole cremocarps and mericarps (commonly called seeds), which contain 1–4% (v/w) of volatile oil whose major constituents are the phenylpropanoid derivative *trans*-anethole and fenchone (Miraldi, 1999). The oil is used as an ingredient of cosmetic and pharmaceutical products for its balsamic, cardiotonic, digestive, lactogogue and tonic properties.

The essential oil of aromatic herbs has usually been isolated either by hydrodistillation (Bilia, Fumarola,

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doi:10.1016/j.foodchem.2004.07.019

Gallori, Mazzi, & Vincieri, 2000; Guillén, Cabo, & Murillo, 1996) or extraction with classical solvents such as hexane or ethanol (Damjanović, Skala, Petrović-Djakov, & Baras, 2003), as traditional spice-processing methods. These techniques present serious drawbacks: Low extraction efficiency, long extraction time, toxic residual solvent in the products and deterioration of the thermally sensitive materials (Gámiz-Gracia & Luque de Castro, 2000). Much work has recently been done on the composition of fennel essential oil obtained by traditional techniques (Barazani et al., 2002; Bernath et al., 1999; Lawrence, 1995; Ruberto, Tiziana Baratta, Deans, & Damien Dorman, 2000).

The advantages of the supercritical fluid extraction (SFE) technique are well known by now and it is often regarded as an alternative to the traditional methods. It has been established as an environmentally benign technique for separating essential oil from the vegetable substrates. SFE exploits the unique properties of gases above their critical values: Liquid like density, high rates of mass transfer and tuneable selectivity that arises by varying temperature and pressure. SFE of flavours and fragrances has been reviewed by Kerrola (1995) and Reverchon (1997).

Carbon dioxide is the most widely used compressed fluid, especially for the extraction of natural products, because it is non-toxic, non-explosive, readily available, easily removable from the product and possesses convenient critical properties (T_c = 31.1 °C, P_c = 73.8 bar). Moreover, obtained extract retains the organoleptic characteristics of the starting spice material (Oszagyan et al., 1996; Reverchon & Senatore, 1992).

An attempt to extract fennel oil using liquid CO_2 in a Soxhlet type apparatus has been described by Naik, Lentz, and Maheshwari (1989). Subcritical water extraction (Gámiz-Gracia & Luque de Castro, 2000), SFE of Hungarian fennel (Simándi et al., 1999), and SFE extraction and mathematical modelling of fennel seed oil and essential oil (Reverchon, Daghero, Marrone, Mattea, & Poletto, 1999)have been reported previously.

The essential oil or oleoresins from fennel seeds are important ingredients for flavouring cosmetics, pharmaceuticals and food products; hence, the improvement of the quality of fennel oil is of economic importance. For this reason, the extraction of fennel seed oil using SC-CO_2 could have an industrial impact.

The aim of this work was to compare the SC-CO_2 extraction of fennel seed with hydrodistillation and to optimize the oxygenated compound contents, e.g., *trans*-anethole and fenchone. The influence of parameters, such as temperature, pressure and extraction time, on the extraction rate of essential oil and cuticular waxes was also studied. The compositions of the extracts and hydrodistilled oil obtained were analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC–MS).

2. Materials and methods

2.1. Collection and preparation of herb samples

Many factors can influence the amount of essential oil in aromatic herbs, e.g., climate and environmental conditions, season of collection, age of plants and, for fennel especially, the stage of ripening of the fruits. To avoid this influence in the present work, the ripe, greenish-brown seeds of growing wild fennel (*Foeniculum vulgare* Mill.) were collected manually from the same collection site in the Podgorica region (central south Montenegro), within two days, at the end of September, 2002. A voucher specimen was deposited in the Herbarium, Department of Biology, Faculty of Natural Sciences and Mathematics, University of Montenegro. The seeds were air-dried and stored in double layer paper bags at ambient temperature, protected from direct light until further analysis.

The initial water inherent in the herb seed was found to be 9.6% (w/w), using a Dean and Stark apparatus with *n*-heptane as the reflux solvent. Typically, a batch of 240 g of material was milled in a coffee mill and, after sieving, a mean particle diameter size of 0.9 mm was obtained. A typical particle size distribution is shown in Fig. 1. A prepared batch was kept in an air-tight resalable polypropylene bag and stored at 8 °C for a maximum of three days before use, in order to avoid losses of volatile compounds.

2.2. Reagents

Commercial carbon dioxide (99% purity, Tehno-gas, Novi Sad, Serbia and Montenegro) was used for extractions. HPLC grade chloroform and methanol were purchased from Riedel-de Haën, Germany. Standard samples for GC analyses were purchased from Fluka, Great Britain.

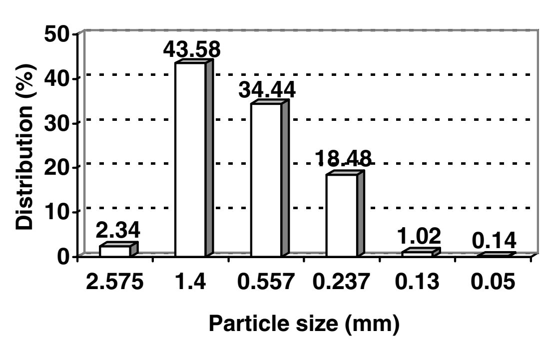

Fig. 1. Typical particle size distribution of the ground fennel seeds used in this work.

2.3. Hydrodistillation

Raw, as well as residual (after SC-CO_2 extraction), samples of ground fennel seed were subjected to hydrodistillation according to the fourth Yugoslav Pharmacopoeia in a Clevenger-type apparatus. The obtained oil was separated from water and the yield was determined in terms of dry basis yield, as g/100 g of dry herb; it was stored in a freezer at −4 °C until analyzed by GC and GC–MS.

2.4. Supercritical fluid extraction

Supercritical fluid extraction (SFE) was carried out with a laboratory-scale high-pressure extraction plant (NOVA – Swiss, Effretikon, Switzerland), described previously (Pekić, Zeković, Petrović, Lepojević, & Tolić, 1995). The main part and characteristics (manufacturer specification) of the plant were as follows: The diaphragm-type compressor (up to 1000 bar), extractor with an internal volume of 200 ml (p_{max} = 700 bar), separator with internal volume of 200 ml (p_{max} = 250 bar) and a maximum CO_2 mass flow rate of approximately 5.7 kg/h. The amount of fennel seed sample in the extractor was 80 g; pressure and temperature were investigated values; CO_2 flow rate was 0.2 kg CO_2/h; and the total extraction time was 4 h (samples were taken every half hour). Separator conditions were 14 bar and 25 °C. The obtained extracts were measured and stored in a freezer at −4 °C until analyzed by GC and GC–MS. The extraction degree (E_d) of essential oil obtained by SC-CO_2 was evaluated using Eq. (1)

$$E_d = 100\frac{M_{CO_2}(t)}{M_0} = 100\frac{M_{CO_2}(t)}{M_{CO_2} + M_{HD\ Res}}, \quad (1)$$

where M_0 refers to the initial mass (content) of essential oil in the herb sample. $M_{CO_2}(t)$ is the mass of essential oil extracted by supercritical CO_2 at time t, M_{CO_2} is the total essential oil mass extracted by CO_2 after 4 h, and $M_{HD\ Res}$ is the residual mass of essential oil isolated by hydrodistillation after CO_2 extraction. For cuticular waxes, the extraction curve points were calculated on dry basis yield, as g/100 g of dry herb. Each experiment was repeated twice.

2.5. GC and GC–MS analyses

GC analyses were performed using Ai Cambridge GC-94 gas chromatograph equipped with a FID and a DB-5 capillary column (30 m × 0.32 m, film thickness 0.25 μm). Oven temperature was programmed at 60 °C for 2 min, and then increased to 250 °C at a rate of 8 °C/min; injector and detector temperature were 120 and 270 °C, respectively. Helium as carrier gas was adjusted to a flow rate of 1.5 ml/min. A split flow of 11 ml/min was used. The constituents of essential oil and extracts were identified by comparing their retention times with those of available standards and their mass was calculated from a predetermined peak area response factor.

The GC–MS analyses were carried out using a Shimadzu QP 5050 GC–MS equipped with a PTE-5 capillary column with the same characteristics as the one used in GC. The column temperature was maintained at 60 °C for 2 min and than programmed to increase as follows: 60–300 °C at 4 °C/min. The temperature was 260 °C at the injection port and 300 °C at the interface. The samples, previously dissolved in chloroform:methanol (3:1), were injected (1 μl) in split mode with split ratio of 1:20 and the flow rate of the carrier gas (helium) was 1.5 ml/min; inlet pressure, was 16.8 kPa. The MS conditions were: The ionization voltage, 70 eV, scanning interval 0.5 s, detector voltage 1.3 kV and m/z range of 40–500. The components were identified by computer searching (using data base programme Class 5000) and comparing their mass spectral data with available standards and those in the WILEY229 and the NIST107 mass spectra libraries.

3. Results and discussion

In order to obtain the best conditions for the SC-CO_2 extraction of fennel seeds, experiments were performed at different pressure–temperature settings of the extractor and results were compared to hydrodistilled oil. The selection of pressure and temperature ranges is based on the fact that a great change in the density and dielectric constant of CO_2 occurs between 80 and 150 bar, and, in order to prevent the thermal degradation of some volatile oil compounds, the temperatures up to 57 °C are applied. The pressure varied from 80 to 150 bar and temperature from 40 to 57 °C and variations in the solvent density and the transport properties of the system were observed.

The total yields of fennel seed hydrodistilled oil and SC-CO_2 extracts at different temperatures and pressures are shown in Fig. 2.

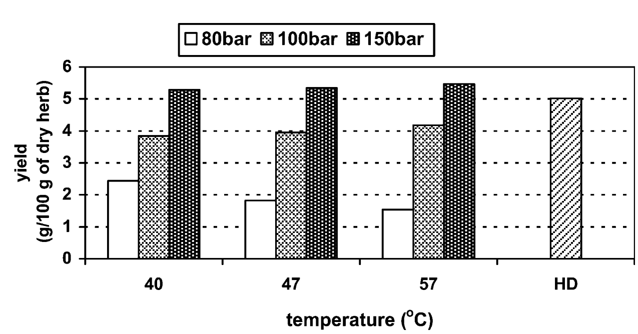

Fig. 2. Total yield of the hydrodistilled oil (HD) and SC-CO_2 extracts after 4 h of extraction.

At 80 bar, the total amount of the obtained extract is unusually small but, as pressure increases the amount of extracted material increases, (Fig. 2). It was found that at higher pressures (100 and 150 bar) the solubility of some compounds from vegetable matter pass from negligible to significant (Reverchon, 1997). This is explained by the fact that the density and viscosity of supercritical CO_2 change and, therefore, its extracting power increases. However, the high pressure is bound to result in greater cost for the extraction operating system, as well as stringent operation design and increased energy demand.

It should also be noted that the appearance of the extracts changed slightly with the increase of temperature and pressure. The colour, which is straw yellow when lower pressure and temperature are used, becomes darker, particularly with increasing temperature. Increased temperature, at 100 and 150 bar, has a favourable effect on the extraction efficiency although the change is not significant. However, when the temperature reaches 57 °C, extract quality probably begin to decrease according to the colour of the extracts. Moreover, elevated temperature could lead to decomposition of thermally labile active ingredients present in the final product (e.g., 1.8-cineole).

The chemical compositions of the SC-CO_2 extracts and hydrodistilled oil are shown in Table 1.

In the hydrodistilled oil, 19 compounds were identified, with major compounds being: *trans*-Anethole (62.0%), fenchone (20.3%) and methylchavicol (4.90%). In the SC-CO_2 extracts, 28 compounds were identified with major compounds being: *trans*-Anethole (68.6–75.0%), fenchone (8.40–14.7%) and methylchavicol (5.09–9.10%).

Hydrodistilled oil contained considerable higher percentages of fenchone (20.3%), α-pinene (2.81%), myrcene (1.68%) and limonene (3.15%) than SC-CO_2 extracts, (8.40–14.7%, 0.22–0.43%, 0.30–0.57% and 0.36–0.61%, respectively). In contrast, the SFE extracts contained a higher percentage of oxygenated compounds, especially methylchavicol and *trans*-anethole. Some oxygenated compounds, not found in hydrodistilled oil, were identified in insignificant amounts in SFE extracts, e.g., terpinen-4-ol (0.05–0.09%) and anisaldehyde (0.05–0.06%), while monoterpene *β*-ocimene was identified only in hydrodistilled oil (0.22%). This

Table 1
Relative percentage composition of fennel seed SC-CO_2 extracts and hydrodistilled oil

Compound	80 bar			100 bar			150 bar			HD
	40 °C	47 °C	57 °C	40 °C	47 °C	57 °C	40 °C	47 °C	57 °C	
α-Thujone	tr	tr	–	tr	–	–	0.05	tr	tr	0.05
α-Pinene	0.42	0.24	0.36	0.22	0.25	0.43	0.29	0.32	0.41	2.81
Camphene	0.08	–	–	0.07	0.06	0.11	0.05	0.07	0.12	0.34
Sabinene	0.19	0.21	0.29	0.18	0.19	0.18	0.25	0.21	0.19	0.56
Myrcene	0.41	0.50	0.57	0.42	0.30	0.46	0.35	0.35	0.37	1.68
α-Phellandrene	0.13	0.16	0.22	0.12	0.18	0.38	0.10	0.18	0.18	0.73
p-Cymene	0.05	tr	tr	0.05	–	tr	tr	–	–	0.28
Limonene	0.61	–	–	0.54	0.36	0.54	0.39	0.61	0.41	3.15
1.8 Cineole	0.71	0.69	0.70	0.20	0.17	0.03	0.24	0.25	0.13	1.20
β-Ocimene	–	–	–	–	–	–	–	–	–	0.22
γ-Terpinene	0.47	0.71	0.75	0.37	0.32	0.45	0.55	0.40	0.43	1.05
Fenchone	10.2	14.7	14.5	11.4	9.38	8.57	8.97	8.40	8.68	20.3
Camphor	Tr	tr	–	tr	0.05	–	tr	tr	–	0.58
Terpinen-4-ol	0.07	tr	–	0.09	–	–	–	0.05	–	–
Methyl chavicol	6.60	6.81	9.10	6.74	6.70	6.63	5.90	5.81	5.09	4.90
cis-Anethole	tr	tr	–	tr	tr	tr	tr	0.05	tr	tr
Anisaldehyde	0.06	0.05	tr	0.06	tr	–	–	0.05	0.05	–
trans-Anethole	72.8	71.8	69.3	73.3	75.0	74.3	68.6	69.1	69.9	62.0
Germacrene D	0.31	0.46	0.20	0.24	0.42	0.36	1.26	0.54	0.56	0.18
Tetradecanoic acid	0.14	0.52	0.46	0.13	0.60	0.45	0.99	0.67	1.27	–
Hexadecanoic acid	0.72	0.08	0.45	0.65	0.82	0.82	1.41	1.43	1.44	–
Tetradecane	2.05	0.44	0.44	1.58	1.17	1.07	1.43	2.50	1.50	–
1,2 Benzenedicarboxylic acid, dioctyl ester	0.17	0.14	0.46	0.35	0.16	0.84	0.66	0.90	1.10	–
Pentadecane	0.08	0.10	0.14	0.07	0.13	0.19	0.88	1.41	0.88	–
Pentacosane	0.12	0.54	0.52	0.12	0.17	0.71	1.11	1.04	1.09	–
1–Hexadecanol	0.40	0.05	0.05	0.4	0.83	0.68	0.95	1.05	1.07	–
Hexacosane	0.25	0.05	0.05	0.23	0.83	0.68	0.80	1.17	1.26	–
1–Octadecanol	0.37	0.06	0.05	0.36	0.67	0.75	1.42	0.64	1.17	–
7–Octadecanone	1.34	0.41	0.34	1.78	1.15	1.32	2.48	1.94	1.73	–
Total identified	98.7	98.7	99.0	99.6	99.9	99.9	99.1	99.1	99.0	100

tr < 0.05; HD, hydrodistilled oil.

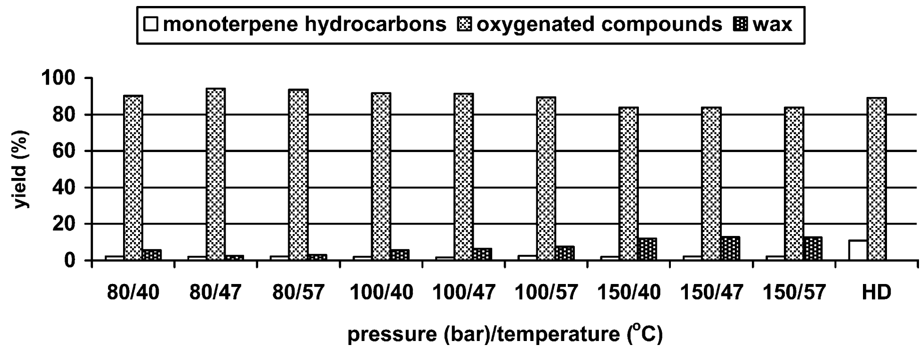

Fig. 3. Yield (%) of fennel seed extracts isolated by SC-CO_2 extraction and hydrodistillation (HD) with respect to grouped components.

indicates that degradation of the fennel essential oil during the hydrodistillation process was minimal. Only one sesquiterpene hydrocarbon with insignificant percentage was detected in fennel seeds, which is comparable with previously reported results (Ruberto et al., 2000).

A comparison between the essential oil obtained by hydrodistillation and SC-CO_2 extracts showed that, in the latter technique some undesired higher molecular weight compounds (waxes) were co-extracted with the essential oil (Table 1).

The co-extracted waxes consisted of paraffins as well as fatty acids, alcohols, esters, aldehydes and ketones. The major compounds were hexadecanoic acid (0.08–1.44%), tetradecane (0.44–2.50%) and 7-octadecanone (0.41–2.48%).

It can be seen from Fig. 3 that the content of non-volatile compounds increased with pressure (at 47 °C), from a minimum of 2.39% at 80 bar, over 6.53% at 100 bar to a maximum of 12.8% at 150 bar. The total percentage of monoterpene hydrocarbons in hydrodistilled oil is more than triple that of SC-CO_2 extracts, (10.8% against 1.66–2.55%, respectively). These are less valuable components since they contribute, only to a minor extent, to the aroma and tend to oxidize because of their unsaturated character. In contrast, the SC-CO_2 extracts, except at 150 bar, contained higher percentage of oxygenated compounds that strongly contribute to the fragrance. Therefore, the SC-CO_2 should give better reproduction of the natural aroma of the fennel seeds than the hydrodistilled oil. Organoleptic tests confirmed that hydrodistilled oils possess a less intense fennel seed aroma than extracts obtained by supercritical CO_2. Hydrodistilled oil aroma was also considered to be rather different from that of the starting herb material.

The effect of the SC-CO_2 extraction pressure, temperature and time on the essential oil extraction curves are shown in Fig. 4. At lower solvent densities (80 bar), very low extraction rates were observed. The extraction degree at this pressure was very low, less than 50% (Fig. 4(a)) Extraction rate was obviously limited by solubility of the essential oil in the supercritical CO_2. It was also noted that peaks corresponding to the low-boiling components of fennel oil, which occurred in the first hour of extraction, were lost in further stages (e.g., sabinene, camphene, limonene). At 80 bar, an increase in temperature led to a rather significant decrease of the extraction degree due to decline of the solvent density, probably dominating the increase of the solute vapour pressure (Fig. 4(a)). An opposite outcome was verified for 100 and 150 bar where the temperature alteration had a rather negligible influence on the essential oil yield (Figs. 4(b) and (c)).

At 100 and 150 bar, nearly 90% of the essential oil was extracted rather easily and quickly (after 120 min) whereas the last fractions were extracted very slowly (Figs. 4(b) and (c)). The fractions extracted in the first stage corresponded to the essential oil liberated from the glands damaged during the mechanical pre-treatment of the fennel seed. On the other hand, the slow extraction of the last fractions indicated that a portion of the essential oil was hidden within internal tissues or located within glands that survived pre-treatment. This stage showed typical diffusion-controlled characteristics.

The CO_2 flow rate and the extraction time were the main parameters that contributed to optimum extraction, i.e., a maximum yield at a minimum extraction time. At the selected flow rate of 0.2 kg CO_2/h, it was found experimentally that an extraction period of 120 min was sufficient for isolation of more than 90% of the essential oil available from the herb (except at 80 bar, as previously mentioned).

The cuticular waxes were extracted in insignificant amounts from the herb material (Fig. 5). The rate of extraction was negligible when lower density CO_2 was used (Fig. 5(a)). However, the increase of pressure (increase of CO_2 density) was accompanied by a significant increase of the extraction rate. The crossover pressures of typical cuticular waxes (octacosane and triacontane) were found within the range of 100–110 bar (Papamichail, Louli, & Magoulas, 2000). Therefore, it was not surprising that the yield of cuticular waxes increased at 100 bar and particularly at 150 bar (Figs. 5(b) and (c)).

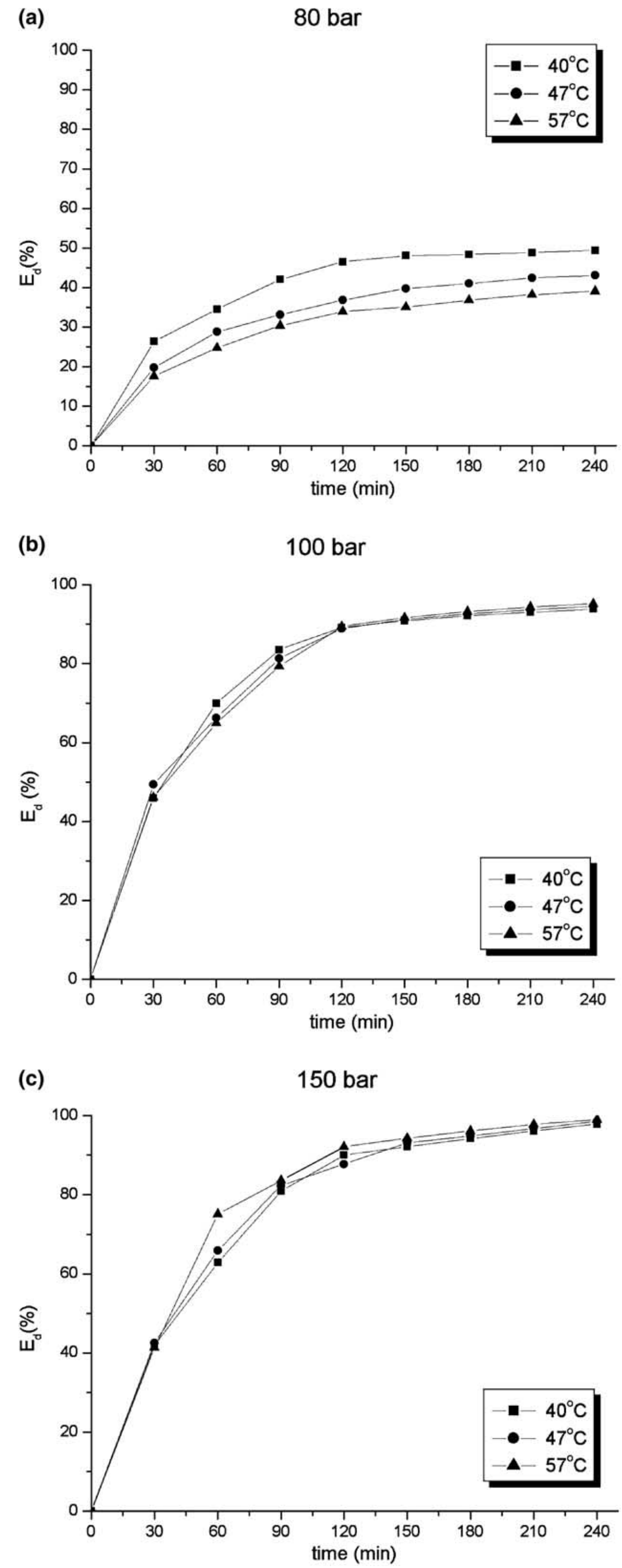

Fig. 4. Effects of the extraction pressure and temperature on the extraction degree of the essential oil.

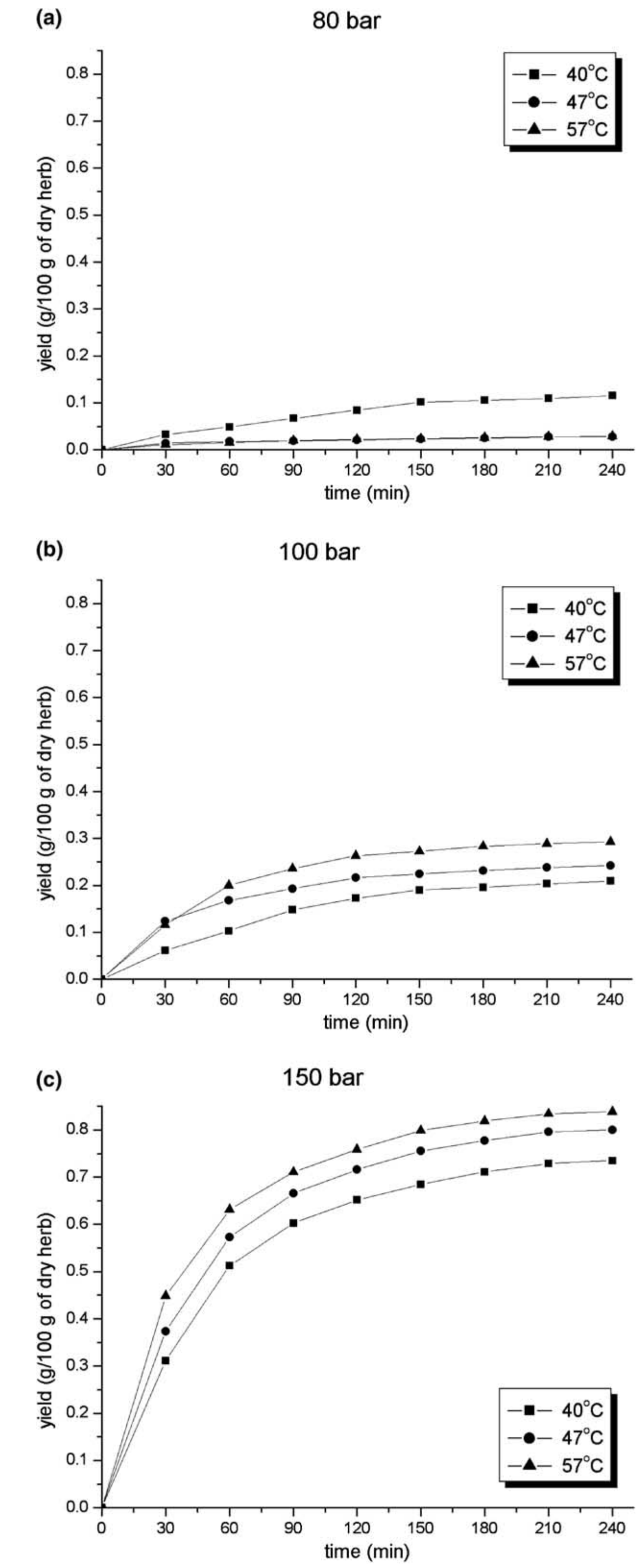

Fig. 5. Effects of the extraction pressure and temperature on the cuticular wax extraction curves.

The optimal chemical composition of fennel seed essential oil depends on the desired oil application. In the food industry, the most suitable type is fennel oil with a high percentage of *trans*-anethole, responsible for fennel seed aroma, while the pharmaceutical industry prefers essential oil with a higher percentage of fenchone. In both cases, the content of methylchavicol, which is assumed to be toxic to a certain degree, should be reduced. The optimal ratio of these compounds was obtained at 100 bar and 40 °C (Table 1).

4. Conclusions

Fennel seeds were extracted by varying CO_2 pressure from 80 to 150 bar and temperature from 40 to 57 °C. Supercritical CO_2 extraction of essential oil is accompanied by the co-extraction of unwanted cuticular waxes. However, SC-CO_2 extraction allowed optimization of the experimental conditions for selection of substances of interest, namely the oxygenated compounds, *trans*-anethole and fenchone. It was found that SC-CO_2 extracts generally contained higher percentages of oxygenated compounds that strongly contribute to the fragrance. Therefore, the SC-CO_2 extraction gives better reproduction of the natural aroma of the fennel seeds than does the hydrodistilled oil. For the selected herb material and CO_2 flow rate, the optimal conditions of SC-CO_2 extraction (high percentage of *trans*-anethole, with significant content of fenchone and reduced amount of methylchavicol and co-extracted cuticular waxes) were: Pressure, 100 bar, temperature, 40 °C and extraction time, 120 min.

Acknowledgements

We thank Mrs. Danijela Šuković (Center for Ecotoxicological Research, Podgorica, Serbia and Montenegro) for GC–MS analyses and Mr. Milan Janković for supplying the fennel seeds.

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