INFLUENCE OF THE PROCESS PARAMETERS ON SUPERCRITICAL CO_2 EXTRACTION OF FENNEL ESSENTIAL OIL

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abstract: The aim of this study was to investigate the most convenient conditions of solvent flow rate in order to obtain the essential oil from fennel with supercritical CO_2 and compare the corresponding yield with that of the oil obtained by hydrodistillation. The collected extracts were analyzed by GC-MS and the relative composition of the oils was determined.

Introduction

Supercritical fluid extraction (SFE) is receiving great attention in the agrochemical field. It can be used as an analytical method to prepare samples from complex natural products, but it can also be applied as an industrial process to obtain new or improved-quality products from vegetable matter. CO_2 is the most widely used among the possible solvents in SFE because it is cheap, simple to use and shows a great affinity to lipophilic compounds to be extracted. Some attempts to use other solvents such as nitrous oxide have been performed; cosolvent addition to CO_2 has been studied too.

Essential oil production is one of the industrial processes that can be improved by the adoption of SFE. In fact, the traditional techniques can produce thermal degradation of the product (hydrodistillation) or its pollution by organic solvents (solvent extraction). SFE of essential oils has been attempted by several authors, but the products obtained usually shows a waxy consistency due to the simultaneous extraction of the oil, cuticular waxes and other undesiderable compounds. It has been assessed that cuticular waxes can be eliminated by fractional separation of the supercritical extracts by using two or more separators operating in series at adequate process conditions. Fatty acids and their derivatives can be completely eliminated in the extract by adopting adequate SFE process conditions [1].

At the University of Bucharest, we developed a laboratory scale SFE plant that allows the fractional separation of supercritical extracts. This process arrangement is very effective in obtaining high quality essential oils [2÷5]. In the present work, experiments have been performed on fennel fruits (*Foeniculum vulgare*, fam. *Apiaceae*). The objective is to study

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the influence of CO_2 flow rate on the composition of oils and on the yield of the extractions.

Experimental part

Tests on fennel fruits were performed on a laboratory unit based on an extraction vessel equipped with two separators operated in series. A schematic representation and further details on this apparatus have been given elsewhere [2]. About 100 g of comminuted fennel fruits were submitted to extraction in each run. Extractions (called SFE-1, SFE-2 and SFE-3) were performed at three different CO_2 flow rate: 1.0, 1.5 and 2.0 kg/h. Fractional separation, exploited in two stages, was obtained setting the first separator at 90 bar and -5°C and the second one at 18 bar and 10°C. These conditions allowed a very efficient fractionation. In the first stage only cuticular waxes have been precipitated, while in the second one a yellow liquid has been obtained. Chemical analysis of the extraction products has been performed by GC-MS. Analytical procedures were described elsewhere [2]. Yield (η) of the produced essential oils has been evaluated. The plant material was also subjected to hydrodistillation (HD) for 180 minutes according to the standard procedure [6].

Results and Discussion

The percentage composition of the fennel oil obtained under SFE conditions is given in the Table 1. CO_2 flow rate increased from 1.0 kg/h for SFE-1 to 2.0 kg/h for SFE-3 that justifies the difference in composition between the extracts obtained under these conditions. The major contribution comes from trans-anethole, which represents 61-64% of the SFE oil composition.

The SFE extracts were also compared with the fennel oil isolated by hydrodistillation. The results of a detailed analysis of the hydrodistilled oil (HD) are again given in Table 1. The compounds isolated were practically the same as those extracted by the SFE process. The hydrodistilled oil possessed the higher percentage of estragole, 6.01% against 4.20-4.96% for SFE fennel oils.

Table 1. Percentage composition of fennel oil isolated by supercritical CO_2 extraction (SFE) and hydrodistillation (HD). The percentages are based on GC peak areas.

Compound	Rt[a] (min)	HD%	SFE-1%	SFE-2%	SFE-3%
α-Thujene	4.45	0.12	0.14	0.15	0.12
α-Pinene	4.50	2.05	2.28	1.57	1.09
Camfene	4.81	0.27	0.31	0.39	0.24
Δ^3-Carene	5.10	0.09	0.11	–	tr[b]
Sabinene	5.29	0.15	0.09	0.10	0.13
β-Pinene	5.30	0.14	0.13	0.14	0.11
β-Myrcene	5.57	0.61	0.45	0.39	0.28
α-Phellandrene	5.83	0.48	0.26	0.32	0.25

Compound	Rt[a] (min)	HD%	SFE-1%	SFE-2%	SFE-3%
p-Cimene	6.24	0.93	0.42	0.25	0.23
Limonene	6.39	1.77	0.54	0.60	0.53
1.8-Cineole	6.42	1.18	0.52	0.11	0.10
Cis-β-Ocimene	6.65	0.10	0.07	0.05	–
Trans-β-Ocimene	6.85	0.05	–	0.07	tr
γ-Terpinene	6.90	0.76	0.71	0.31	0.22
α-Terpinolene	7.30	0.19	0.14	0.12	0.10
Linalool	7.64	0.22	0.32	0.36	0.13
Fenchone	8.23	20.29	23.29	24.05	25.38
α-Thujone	8.47	0.13	0.09	0.14	0.06
Fenchol	8.64	0.05	tr	0.09	0.09
Camphor	8.75	0.38	0.58	0.41	0.17
Trans-Menthone	8.84	0.12	0.11	0.14	0.08
Isomenthone	9.02	tr	0.07	0.05	–
Trans-Menthol	9.16	–	0.09	0.10	0.12
4-Terpineol	9.21	0.27	0.14	0.18	0.09
Dihydrocarvone	9.46	0.33	0.17	0.15	0.16
Estragole	10.78	6.01	4.96	4.20	4.23
p-Anisaldehyde	10.84	0.96	0.40	0.46	0.41
Cis-Anethole	10.97	0.45	0.68	0.66	0.54
Trans-Anethole	11.11	59.09	61.18	62.77	64.09
Dihydrocarveol acetate	11.47	0.70	0.41	0.34	0.28
Hydrocarveol acetate	11.63	0.56	0.32	0.35	0.11
Eugenol	11.78	0.52	0.57	0.42	0.32
Methyleugenol	11.91	0.18	0.08	0.17	0.09
β-Caryophyllene	12.53	0.28	0.25	0.20	0.15
β-Bisabolene	13.72	0.57	0.12	0.19	0.10

[a] Rt = retention time (min)

[b] tr = traces (<0.05%)

The characteristic fennel essential oil compounds are fenchone (23.29-25.38%), estragole (4.20-4.96%) and trans-anethole (61.18-64.09%). Fenchone is the specific contributor to the fennel flavour. The oil extracted under SFE-3 conditions had a higher content of fenchone (25.38%) and trans-anethole (64.09%) compared with the SFE-1 and SFE-2 oils and a lower content of estragole (4.23%) (see Fig. 1).

The oxygenated monoterpenes are considered to be the main constituents of the aroma of many essential oils. In the fennel oil extracted under SFE-3 conditions, oxygenated monoterpenes content amounted to 26.38% compared with 25.38% SFE-1 conditions. On the contrary, hydrocarbon monoterpenes were only 3.07% for SFE-3, 4.21% for SFE-2 and 5.23% for SFE-1 (see Fig. 2).

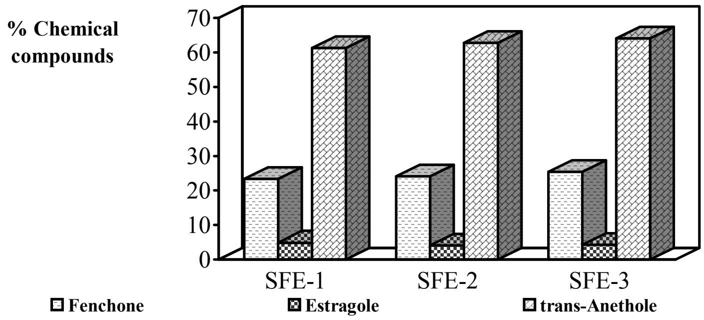

Fig. 1 *The characteristic fennel essential oil compounds*

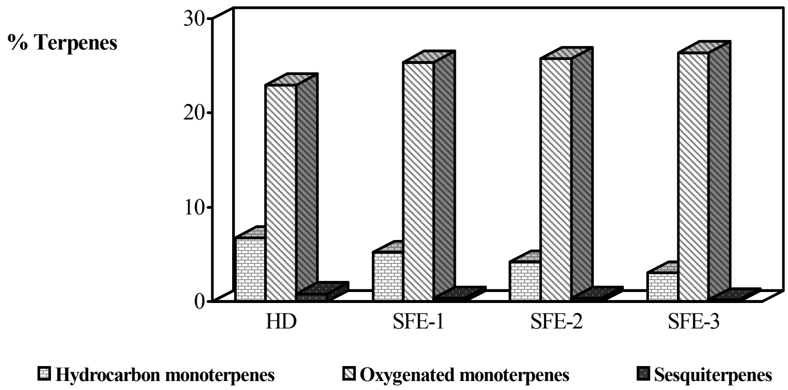

Fig. 2 *Percentages by weight of terpenes obtained by supercritical fluid extraction (SFE) and by hydrodistillation (HD).*

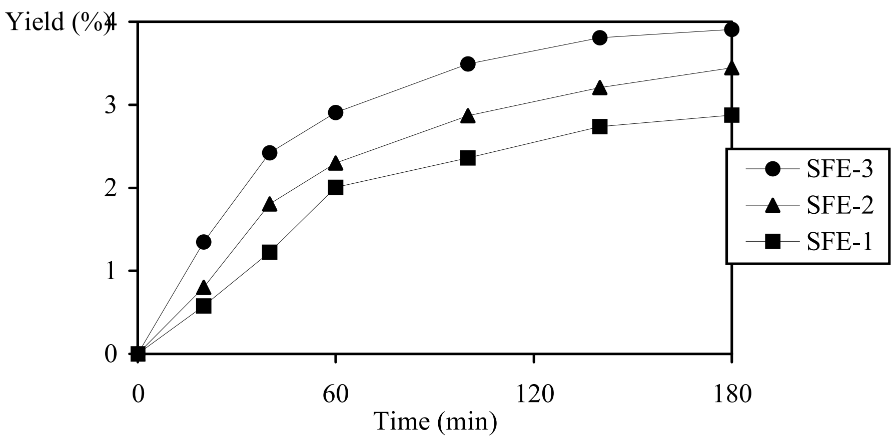

Fig. 3 *Fennel essential oil yield against extraction time, at different CO_2 flow rate.*

Conclusions

Trans-anethole is the principal extracted component. At 2.0 kg/h CO_2 flow rate the trans-anethole content in the essential extracted oil is greater than 64%. The obtained products show higher quality than those obtained by hydrodistillation (see Table 1). The changes of the solvent flow rate have a relevant effect on the extraction yield and can serve to improve the SFE technology. The extraction yield increases (2.88-3.91%) by increasing of CO_2 flow rate. The essential oil yields obtained by SFE were compared. In the case of fennel (see Fig. 3), the maximum obtained yield was of about 3.91% (by weight of the charged material) at SFE-3 conditions.

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