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ISOLATION AND FRACTIONAL SEPARATION OF TARRAGON ESSENTIAL OIL BY SUPERCRITICAL FLUID

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abstract: The experimental results of supercritical CO_2 extraction on tarragon essential oil at 50˚C and 90 bar are presented. The chemical composition and the yield of the supercritical extract are compared with those of the tarragon oil isolated by conventional hydrodistillation method.

key words: supercritical fluid; supercritical extraction; supercritical carbon dioxide; essential oils; tarragon

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Introduction

The supercritical fluid extraction (SFE) of the compounds responsible for the fragrances contained in vegetable matter is a promising field for the industrial application of supercritical fluid processing. Indeed, there is a considerable interest in replacing the steam distillation and solvent extraction processes traditionally used to obtain these products.

The characteristic smell of plant materials is usually the results of the complex interactions occurring among hundreds of compounds. Correct reproduction of the natural fragrance in a concentrated extract is therefore a complex task. The presences of thermolabile compounds, the possibility of hydrolysis and of hydrosolubilization are serious obstacles in the reproduction of natural fragrances. Moreover, severe legislative restrictions are currently being proposed to eliminate solvent residues in these products when used in the food, pharmaceutical and cosmetic industries.

By using different extraction techniques, a variety of products can be obtained. “Concretes” and “oleoresins” are extracts obtained using organic solvents on fresh or dried vegetable matter. These products become quasi-solid at room temperature after the removal of the solvent. A typical concrete extracted by hexane contains all the lipophilic compounds which

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constitute the vegetable matter. An “absolute” is a liquid product obtained by post-processing a concrete with ethanol and subsequently removing the solvent. A “volatile oil” is a liquid product obtained by post-processing a concrete by steam distillation. An “essential oil” can be defined as the volatile material present in plants. As a rule, it consists of a complex mixture of terpenes, oxygenated terpenes, sesquiterpenes and oxygenated sesquiterpenes. Essential oils can also contain diterpenes and some specific compounds which cannot be classified as belonging to any of the above-mentioned compound families. Other compounds which can be extracted from vegetable matter and can be found in concretes, absolutes and oleoresins are fatty acids and fatty acid methyl esters, colouring matters, coumarins, psoralens, sterols and flavones.

CO_2 is the most popular SFE solvent. The critical parameters of CO_2 are 31^0C and 73.8 bar. The advantages of supercritical carbon dioxide are its mild operation conditions, gaseous standard state under ambient conditions, its non-toxicity and its relatively low cost compared with organic solvents [1].

At the University of Bucharest, we developed a laboratory scale SFE plant that allows the extraction and fractional separation of essential oils from herbaceous matters. The aim of this study was to investigate the conditions of extraction and fractional separation more convenient in order to obtain the essential oil from tarragon with supercritical CO_2. The therapeutic properties of tarragon oil are anti-rheumatic, aperitif, digestive, deodorant, emmenagogue, stimulant and vermifuge. Tarragon oil stimulates the appetite and has a pronounced effect on the sluggish digestive system. It can be helpful for anorexia, dyspepsia, flatulence, hiccups, internal spasm, nervous indigestion, etc**.** The chemical composition and the yield of the supercritical extract were compared with those of the oil isolated by conventional hydrodistillation method.

Experimental

Supercritical CO_2 extraction on dried leaves of tarragon (*Artemisia dracunculus*, fam. *Asteraceae*) was performed on a SFE plant based on an extractor of 1.5 L and two separators of 0.25 L. A schematic representation on this laboratory unit has been given elsewhere [2]. Extraction conditions were studied in the pressure range from 80 to 120 bar and for temperatures between 40 and 55°C. About 300 g of comminute tarragon leaves were submitted to supercritical fluid extraction. A CO_2 flow rate of 1.5 kg/h was used for an extraction time of 120 minutes. Fractional separation, exploited in two stages, was obtained setting the first separator at 90 bar and –10˚C and the second one at 15 bar and 5˚C. These conditions allowed an efficient fractionation. In the first stage only cuticular waxes have been precipitated, while in the second one a colourless liquid has been obtained. The collected extracts were analyzed by GC-MS procedure, which was described in a previous paper [2]. The vegetal material was also submitted to conventional hydrodistillation (HD) according to the standard procedure [3]. The yield of the two processes has been evaluated.

Results and discussion

Table 1 shows the identification and the percentage composition of compounds in tarragon oil extracted by supercritical fluid extraction. No paraffin precipitated together with the oil: the fractional precipitation technique resulted to be very selective. For comparison purposes the analysis of the oil obtained by conventional hydrodistillation is reported too. The isolated compounds were practically the same as those extracted by the SFE process.

Table 1 Percentage composition of tarragon oil isolated by hydrodistillation (HD) and by supercritical CO_2 extraction (SFE), respectively; the percentages are based on GC peak areas.

No.	Compound	Rt[a] (min)	HD%	SFE%
1	α-Thujene	4.34	0.17	0.09
2	α-Pinene	4.51	0.82	0.82
3	Camfene	4.88	0.06	0.08
4	Δ^3-Carene	5.10	0.10	0.09
5	Sabinene	5.28	0.12	0.21
6	β-Pinene	5.31	0.28	0.17
7	α-Fenchene	5.45	0.05	–
8	β-Myrcene	5.50	0.08	–
9	β-Phellandrene	5.93	0.51	0.67
10	α-Terpinen	6.07	–	0.10
11	p-Cimene	6.28	0.16	0.18
12	Limonene	6.33	3.27	2.54
13	1.8-Cineole	6.45	–	0.09
14	cis-β-Ocimene	6.67	4.09	3.67
15	trans-β-Ocimene	6.88	3.87	3.26
16	γ-Terpinene	6.90	0.09	0.05
17	trans-Linalool-oxide	7.37	0.41	0.59
18	Linalool	7.69	1.71	2.05
19	Camphor	8.39	0.38	0.31
20	4-Terpineol	8.97	2.04	2.74
21	Carvone	10.02	0.25	0.16
22	Bornyl acetate	10.50	1.53	1.34
23	Estragole	10.74	63.75	62.89
24	trans-Anethole	11.16	1.21	0.92
25	Citronelyl acetate	11.51	–	0.17
26	Eugenol	11.72	1.30	1.12
27	Geranyl acetate	11.84	1.11	1.28
28	Methyl-eugenol	11.92	6.51	7.53

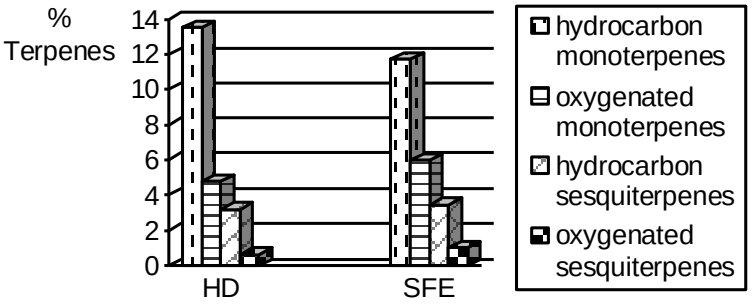
29	β-Elemene	12.16	0.83	0.76
30	β-Caryophyllene	12.51	0.96	0.95
31	β-Farnesene	12.99	0.11	0.69
32	α-Humulene	13.08	0.28	0.31
33	γ-Muurolene	13.33	0.34	0.14
34	δ-Cadinene	13.83	0.65	0.58
35	Nerolidol	14.40	0.46	0.68
36	Spatulenol	14.71	0.17	0.32
37	cis-Asarone	15.51	2.33	2.45

[a] Rt = retention time (min)

The higher percentages in hydrodistilled oil (HD) and supercritical oil (SFE) compounds are estragol (63.75% and 62.89%), methyl-eugenol (6.51% and 7.53%), cis-β-ocimene (4.09% and 3.67%) and trans-β-ocimene (3.87% and 3.26%).

The essential oils are complex mixtures of various compounds families. Among these constituents, oxygenated terpenes are considered responsible for the aroma of the oils. On the contrary, hydrocarbon terpenes do not contribute to odour formation and negatively influence the product stability [4, 5]. In Fig. 1 one can see a comparison with regard of the terpenes composition, for the two tarragon oils.

By the classification of the terpenic components is observed a superior quality of SFE extract (remarked at the organoleptic examinations too). In the case of the SFE tarragon essential oil, only 11.75% was constituted by hydrocarbon monoterpenes. The oxygenated monoterpenes concentration is greater (5.94%) in the SFE oil.



Percentages by weight of terpenes obtained by hydrodistillation (HD) and by supercritical CO_2 extraction (SFE).

The estimated yield of tarragon essential oil obtained by SFE was 0.42% and those obtained by HD was 0.57%.

Conclusions

For the studied conditions of supercritical CO_2 extraction and fractionation, the results lead us to choose a pressure of 90 bar and a temperature of 50˚C as the best ones to obtain the tarragon essential oil. Estragol is the principal component extracted. At 90 bar and 50˚C the estragol concentration in the essential oil extracted is greater than 62%. SFE extracted oil has a superior quality: only 11.75% was constituted by hydrocarbon monoterpenes and oxigenated monoterpenes concentration is greater (5.94%) in SFE oil than in HD extracted oil. At optimum conditions the yield obtained from hydrodistillation process was 0.57% while from SFE process was 0.42%.

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