SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF ROSEMARY ESSENTIAL OIL

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abstract: The supercritical fluid extraction of rosemary essential oil was studied using CO_2 as solvent. The effect of mean particle size of rosemary leaves in the range of 0.2 to 1.0 mm was analyzed in a series of experiments at 40°C and 100 bar. The colected extracts were analyzed by GC-MS and the relative composition of the essential oil was determined.

Introduction

After two decades of industrial development, supercritical fluids applications to natural products extraction/fractionation, both for food and pharmaceutical products, are continuing to slowly spread worldwide still with a wide potential as high quality products are more and more required and environment/health problems are more and more considered. In the meantime, numerous new applications of supercritical fluids are investigated and are beginning to reach large-scale development.

One of the most studied problems in supercritical fluid extraction (SFE) is the research of the optimum conditions for the extraction of flavour characteristic compounds from herbs, flowers and roots. In fact, on this matter many works are avaible in the scientific literature [1÷5]. The supercritical solvent is a rule CO_2 and the SFE process usually adopted consists of one separation stage only. This process arrangement revealed to be not suitable to obtain essential oils: it produces concrete like extracts, due to coextraction of cuticular waxes. Moreover, when the SFE has been conducted in non optimized conditions, the simultaneous extraction of some further families of unwanted compounds like fatty acids and their methyl esters has been produced. It has been demonstrated that it is necessary to adopt more complex process schemes to realize a better extraction selectivity [6].

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 [7÷11].

In the present work, experiments have been performed on rosemary (*Rosmarinus officinalis*, fam. *Lamiaceae*) leaves. The objective is to study the influence of mean particle size on the composition of oils and on the yield of the extractions.

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Experimental part

Tests on rosemary leaves were performed on a laboratory unit based on a 350 mL extraction vessel equipped with two separators operated in series with a volume of 250 mL each. A schematic representation and further details on this apparatus have been given elsewhere [8].

About 250 g of dried and comminuted rosemary leaves were submitted to extraction in each run. A CO_2 flow rate of 1.2 kg/h and an extraction period of 120 min were used. Extractions (called SFE-1, SFE-2 and SFE-3) were performed at three different mean particle sizes: 0.2, 0.5 and 1.0 mm. Chemical analysis of the extraction products has been performed by GC-MS. Analytical procedures were carefully described elsewhere [8]. Yield (η) of the produced essential oils has been evaluated.

Results and Discussion

The optimal extraction conditions of 100 bar and 40°C were determined on the laboratory apparatus on a different rosemary leaves. Fractional separation, exploited in two stages, was obtained setting the first separator at 100 bar and 0°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.

In Table 1 the identification and the area percentage of all the compounds were proposed. This data confirm that the produced rosemary essential oil does not contain unwanted compounds and is free of cuticular waxes.

Table 1. Percentage composition of rosemary oil isolated by supercritical CO_2 extraction. The percentages are based on GC peak areas.

Compound	Rt[a]	SFE-1 (%)	SFE-2 (%)	SFE-3(%)
Tricyclene	4.30	0.07	0.10	0.09
α-Thujene	4.40	-	-	0.17
α-Pinene	4.50	9.17	9.05	11.52
Camphene	4.82	4.02	2.98	2.43
Δ^3-Carene	5.12	0.40	0.35	0.22
Sabinene	5.27	0.41	0.21	0.18
β-Pinene	5.39	1.82	1.54	1.59
β-Myrcene	5.56	0.22	0.38	0.41
p-Cimene	6.24	1.69	1.52	1.87
Limonene	6.36	0.49	0.67	0.40
1,8-Cineole	6.47	23.85	25.16	24.20
Linalool	7.69	4.01	3.72	3.08
Fenchone	8.29	1.75	1.93	1.51
Camphor	8.59	13.92	15.09	12.55
Borneol	8.77	17.80	18.11	18.02
4-Terpineol	8.91	2.04	1.36	2.30
α-Terpineol	9.24	1.62	0.93	1.78
Verbenone	9.94	6.71	6.88	6.26
Linalyl acetate	10.02	0.08	0.19	0.23

Isobornyl acetate	10.36	1.75	2.21	3.95
Timol	11.12	-	0.10	0.21
α-Cubebene	11.44	0.25	0.12	0.23
Methyl Eugenol	11.94	-	-	0.18
α-Selinene	12.36	0.30	0.32	0.25
β-Caryophyllene	12.57	3.08	2.37	2.77
α-Santalene	12.61	0.21	0.14	0.11
β-Gurjunene	12.71	0.19	0.13	-
β-Farnesene	12.97	0.19	0.15	0.11
α-Humulene	13.06	1.10	0.76	0.48
γ-Muurolene	13.39	0.27	0.27	0.14
β-Bisabolene	13.79	0.58	0.72	0.37
γ-Cadinene	13.84	0.81	1.05	1.12
Calamenene	13.99	0.34	0.35	0.28
Caryophyllene oxide	14.73	0.29	0.37	0.44
Humulene oxide	15.14	0.25	0.18	0.10
α-Santalol	15.71	0.14	0.34	0.24
Bisabolol oxide	16.88	0.18	0.25	0.21

[a]Rt = retention time (min).

As a rule, essential oils are complex mixtures of various compounds families. Among these constituents, oxygenated terpenes are considered the aroma responsible compounds. On the contrary, hydrocarbon terpenes do not contribute to odour formation and negatively influence the product stability: they can give decomposition or polymerization reactions [12]. In the case of the SFE-2 rosemary essential oil, only 15.28% (by area) was constituted by hydrocarbon terpenes (16.60% in the case of SFE-1 and 17.01% in the case of SFE-3).

The characteristic rosemary essential oil compounds are α-pinene (9.05%-11.52%), 1,8-cineole (3.08%-4.01%), camphor (12.55%-15.09%), borneol (17.80%-18.11%) and verbenone (6.26%-6.88%) (see Fig. 1). They are all specific contributors to the rosemary flavour.
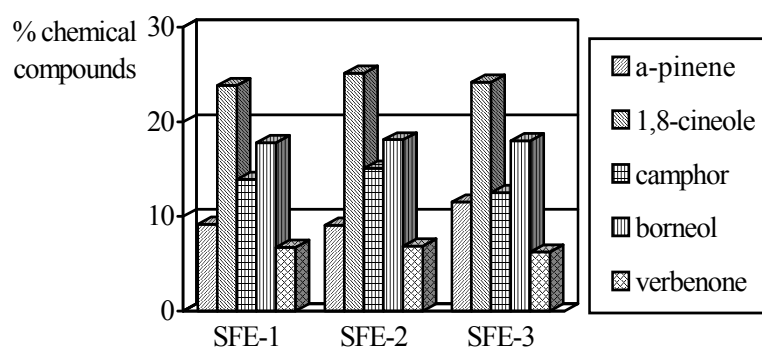

Fig. 1: *The characteristic rosemary essential oil compounds.*

The yield of the extraction process has been measured at different mean particle sizes: figure 2 shows the results for 0.2, 0.5 and 1.0 mm mean particle sizes and for extraction times up to 120 minutes. The essential oil yield (0.81%, 1.03% and 0.94%) is markedly influenced by the variation of the mean particle size of the treated material. This results can

be explained taking into account the mass transfer mechanism involved in the extraction process. In fact, it has been demonstrated that in SFE of essential oils the controlling stage is constituted by the internal diffusion resistance [6]. Then, higher particle sizes produce an increase of the diffusion length and the extraction process is slowed down.
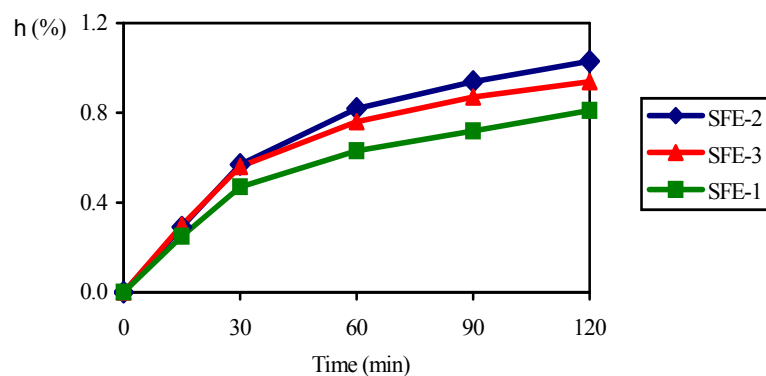
Fig. 2: *Rosemary essential oil yield against extraction time, at different particle size*.

Conclusions

These results confirm the importance of particle size in the SFE of essential oils. It is not possible to operate with the smallest particle size possible because comminution techniques can induce degradation of same thermolabile compounds.

REFERENCES

1. Stahl, E., Quirin, K.W., Glatz, A., Gerard, D. and Rau, G. (1984) *Ber. Bunsenges Phys. Chem.* **88**, 900.

2. Sankar, K.U. (1989) *J. Sci. Food Agric.* **48**, 483.

3. Reverchon, E. and Senatore, F. (1992) *J. Flavour and Fragrance* **7**, 227.

4. Poiana, M., Reverchon, E., Sicari, V., Mincione, B. and Crispo, F. (1994) *Ital. J. Food Sci.* **4**, 459-466.

5. Mendez-Santiago, J. and Teja, A.S. (2000) *Ind. Eng. Chem. Res.* **39**, 4767.

6. Reverchon, E. (1992) *J. Supercritical Fluids* **5**, 256.

7. Găinar, I., Mocan, M. and Vîlcu, R. (2002) *Rev. Chim. (Bucureşti)* **(53) 1**, 78-80.

8. Găinar, I., Vîlcu, R. and Mocan, M. (2002) *Anal. Univ. Buc.-Chimie* **XI** (vol. I), 63-67.

9. Găinar, I., Vîlcu, R. and Mocan, M. (2002) *Revue Roumaine de Chimie* **47(1-2)**, 29-32.

10. Vîlcu, R., Găinar, I. and Mocan, M. (2002) *Anal. Univ. Buc.-Chimie* **XI** (vol. II), 167-171.

11. Vîlcu, R., Mocan, M. and Găinar, I. (2003) *Anal. Univ. Buc.-Chimie* **XII** (vol. I- II), 297-302.

12. Reverchon, E., Ambruosi, A. and Senatore, F. (1994) *J. Flavour and Fragrance* **9**, 19.