SUPERCRITICAL CO_2 EXTRACTION OF ESSENTIAL OIL FROM CORIANDER FRUITS

Manuela Zorca, I. Găinar * and Daniela Bala

abstract: Supercritical CO_2 extraction of oil from coriander was performed on a laboratory apparatus. A two-stage separation procedure was added to extraction to induce the fractional separation of the extracts by selective precipitation of the undesidered compounds. Detailed GC-MS analysis of the products was performed to assess the best extraction and the best separation conditions. The best overall performance of the process resulted from the extraction performed at 90 bar and 50°C and from the separation conducted at 90 bar, -5°C in the first separator and 15 bar, 10°C in the second separator, respectively. The coriander oil produced by supercritical CO_2 extraction and fractionation was compared to the oil obtained by classical hydrodistillation. The oil yield of the extraction process was measured at various extraction times.

Introduction

The extraction of flavours and fragrances using supercritical CO_2 is usually performed by means of a process based on single stage extraction and one step separation. A viscous extract can be obtained due to simultaneous extraction and recovery of the fragrance compounds and of cuticular waxes. Moreover, if CO_2 densities over about 0.5 g/cm^3 are used, also fatty acids and their methyl esters, triglycerides, colouring matters, etc, can be extracted.

It has been recently demonstrated that, by analyzing the extraction mechanism involved in supercritical fluid extraction (SFE) processes, essential oils and cuticular waxes are however coextracted from vegetable matters even at optimum extraction pressure and temperature [1]. Cuticular waxes show very low solubility in supercritical CO_2 but they are located on the vegetable surface. Therefore, they can be extracted by simple washing. On the contrary, the essential oil compounds show very high supercritical CO_2 solubility [2] but are located in the internal part of the vegetable matter. Thus, a complex mass transfer mechanism is involved in the extraction of their fragrance compounds. It is for this reason that different solubility and mass transfer mechanisms produce a simultaneous extraction of both compound families [1]. Nevertheless, it is possible to obtain pure essential oils by inducing the selective precipitation of the extract in two or more separators operated in series [1,3]. For this purpose, it is necessary to select adequate pressure and temperature conditions that produce the selective supersaturation and precipitation of solutes. By means

* Faculty of Chemistry, Department of Physical Chemistry, University of Bucharest, 4-12 Regina Elisabeta, 030018 Bucharest, Romania

Analele Universităţii din Bucureşti – Chimie, Anul XV (serie nouă), vol. II, pag. 79-83

of this technique, the complete separation of cuticular waxes from the essential oil has been achieved for various vegetable matters like rosemary, marjoram, chamomile and peppermint [1,3÷5].

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 [6÷9]. In the present work, experiments have been performed on coriander fruits (*Coriandrum sativum*, fam. *Apiaceae*). The aim of this work was to apply supercritical CO_2 extraction and fractional separation process, to isolate coriander essential oil. The oil was then compared to the product obtained by hydrodistillation (HD). The extraction yield was also measured at various extraction times.

Experimental

Tests on coriander 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 [6]. About 300 g of comminuted coriander fruits were submitted to extraction. A CO_2 flow rate of 2.0 kg/h was used. Fractional separation, exploited in two stages, was obtained setting the first separator at 90 bar and -5°C and the second one at 15 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 [6]. Yield (η) of the produced essential oils has been evaluated. The plant material was also subjected to hydrodistillation for 180 minutes according to the standard procedure [10].

Results and discussions

Optimum extraction conditions were studied in the pressure range from 80 to 120 bar and for temperatures between 40 and 55°C. Extraction conditions that produce higher than about 0.6 g/cm^3 CO_2 densities were not tested since such densities produce low extraction selectivity; i.e., the coextraction of higher molecular weight compounds. To assess the optimum oil composition, GC-MS analysis of the extract was performed at each extraction condition. Optimum extraction conditions resulted: pressure 90 bar and temperature 50°C.

Table 1 shows the identification and the percentage composition of compounds in coriander oil extracted by SFE. 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 compounds isolated were practically the same as those extracted by the SFE process.

The higher percentages in supercritical oil (SFE) and hydrodistilled oil (HD) compounds are: linalool (72.10% and 45.31%), γ-terpinene (3.52% and 2.04%), limonene (3.25% and 2.86%), α-pinene (3.07% and 2.90%), and camphor (2.68% and 0.73%). There are some exceptions: p-cimene (4.04% and 12.44%), geranyl acetate (2.86% and 10.62%). In oil extracted by hydrodistillation a lot of components are not found.

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

Compound	Rt(min)	HD	SFE
Tricyclene	4.36	0.06	0.06
α-Thujene	4.55	0.08	–
α-Pinene	4.70	2.90	3.07
Camphene	4.90	0.24	0.20
Δ^3-Carene	5.21	0.08	–
Sabinene	5.35	0.14	0.24
β-Pinene	5.65	0.12	0.09
β-Myrcene	5.78	0.96	1.01
α-Phellandrene	5.95	0.11	0.08
p-Cimene	6.37	12.44	4.04
Limonene	6.52	2.86	3.25
γ-Terpinene	7.07	2.04	3.52
cis-Linalool oxide	7.15	0.10	0.41
trans-Linalool oxide	7.30	0.08	0.39
α-Terpinolene	7.46	0.16	0.06
Linalool	8.34	45.31	72.10
Camphor	8.71	0.73	2.68
Borneol	8.98	–	0.15
4-Terpineol	9.11	0.05	tr
α-Terpineol	9.40	0.16	0.41
Nerol	10.04	0.12	0.32
Geraniol	10.26	0.55	1.98
Carvone	10.49	0.05	–
Bornyl acetate	10.62	2.48	0.17
Trans-Menthyl acetate	10.90	4.50	0.26
Citral	11.07	0.18	0.44
trans-Anethole	11.15	3.96	0.09
Neryl acetate	11.60	8.73	0.30
Geranyl acetate	11.86	10.62	2.86
β-Caryophillene	12.79	–	0.15
β-Farnesene	13.00	0.08	0.13
α-Humulene	13.12	–	0.06
Germacrene	13.62	–	0.05
γ-Cadinene	13.87	0.11	0.30
Nerolidol	14.50	–	0.07

Table 1. (*continued*)

Compound	Rt(min)	HD	SFE
Caryophillene oxide	14.81	–	0.48
Viridiflorol	14.95	–	0.19
Bisabolol oxide	16.87	–	0.39

Rt = retention time (min)

The yield of coriander oil was measured by weighting the oil recovered in the second separator at the optimized extraction and fractionation conditions, at various extraction times. The maximum oil yield was 1.16% by weight of the charged material, id est somewhat lower than the yield found by the supplier using hydrodistillation (1.62%).

Fig. 1 shows the supercritical extraction yield as a function of time for mean particle size of 0.5 mm and for a CO_2 flow rate of 2.0 kg/h.

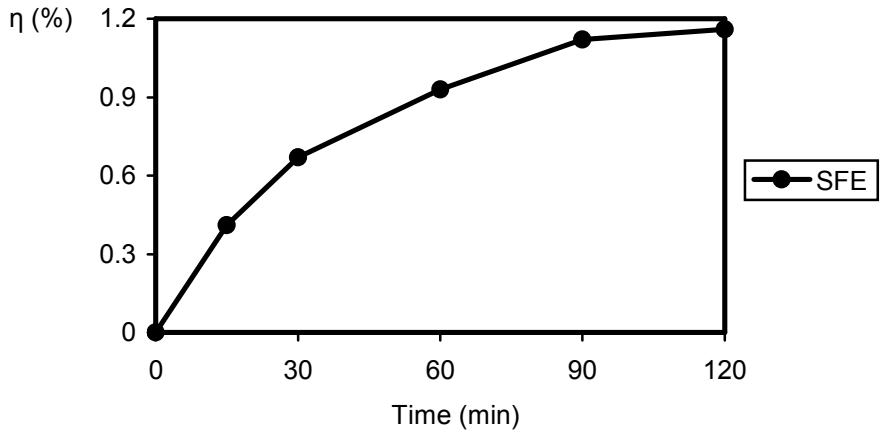

Fig. 1: *Coriander oil yield at various extraction times.*

Conclusions

For the studied conditions of extraction and fractionation, the results lead us to choose P = 90 bar and T = 50°C as the best ones to obtain the coriander essential oil. Linalool is the principal component extracted. At 90 bar and 50°C the linalool content in the essential oil extracted by SFE is greater than 72%. The yield obtained from hydrodistillation was 1.62% while from SFE at the optimum conditions was 1.16%.

REFERENCES

1. Reverchon, E. (1992) *J. Supercritical Fluids* **5**, 256.
2. Stahl E. and Gerard D. (1985) *Perfumer and Flavorist* **10**, 29.
3. Reverchon, E. and Senatore F. (1992) *J. Flavour and Fragrance* **7**, 227.

4. Reverchon, E. and Senatore, F. (1994) *J. Agric. Food Chem.* **42**, 154.
5. Reverchon, E., Ambruosi, A. and Senatore, F. (1994) *J. Flavour and Fragrance* **9**, 19.
6. Găinar, I., Vîlcu, R. and Mocan, M. (2002) *Anal. Univ. Buc.-Chimie* **XI** (vol. I), 63.
7. Găinar, I., Vîlcu, R. and Mocan, M. (2002) *Revue Roumaine de Chimie* **47(1-2)**, 29.
8. Vîlcu, R., Mocan, M. and Găinar, I. (2003) *Anal. Univ. Buc.-Chimie* **XII** (vol. I- II), 297.
9. Găinar, I. and Zorca, M. (2005) *Anal. Univ. Buc.-Chimie* **XIV** (vol. I-II), 287.
10. *********Farmacopeea Română* (1993) Ediția a X-a, Ed. Medicală, Bucureşti, 1064.