THE CO_2 DENSITY VARIATION IN THE SUPERCRITICAL EXTRACTION OF ANET ESSENTIAL OILS

Manuela Zorca, I. Găinar* and Daniela Bala

abstract: The supercritical fluid extraction of anet essential oil was studied using CO_2 as solvent. The effect of CO_2 density variation in the range of 0.225 g/ml to 0.662 g/ml was analyzed. Chemical analysis revealed that oils extracted under different supercritical CO_2 extraction conditions possessed a different percentage composition. Oil obtained by hydrodistillation was also compared with the extracted oils.

Introduction

The application of extraction process using supercritical fluids is based on the experimental observation according that carbon dioxide has a great dissolution capacity of solutes (terpenes) compatible with it in point of the molecular polarity, near its critical point (P_c = 73.75 bar, T_c = 30.9°C, ρ_c = 0.468 g/ml). In the critical region, the small pressure, and/or temperature variations determine a great variation of carbon dioxide density [1÷3].

Increasing of carbon dioxide dissolution capacity due to increasing of its density allows the increasing of process yield and of extract quality (because of extraction of compounds with polar functions). The concentration of solute in supercritical phase depends also on its volatility; the volatile compounds and those with lower molecular weight are more soluble. The data analysis of terpenes solubility in supercritical carbon dioxide indicates that at lower CO_2 density (40-50ºC and 80-90 bar), terpenes are more soluble than diterpenes, paraffin and oil acids. At high CO_2 density (40-50ºC and 100-200 bar), hydrocarbonated and oxygenated terpenes are complete miscible in carbon dioxide. Concomitantly the solubility of high molecular weight is increasing. In order to obtain a selective extraction of volatile compounds, it is indicated to using of low density carbon dioxide [4-6].

Experimental

The study of carbon dioxide density variation was performed on the supercritical CO_2 extraction (Supercritical Fluid Extraction, SFE) from anet seeds (*Anethum graveolens*, fam. *Apiaceae*). In order to obtain anet essential oil, the semicontinuous processing vegetal

* Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, bd. Elisabeta 4-12, sect. 3, 030018, Bucharest, Romania

Analele Universităţii din Bucureşti – Chimie, Anul XVI (serie nouă), vol. I, pag. 43 – 47

matrix was used with fractional separation of extract in two separators operated in series. A schematic representation and further details on this apparatus have been given elsewhere [7]. Extractions (called SFE-1, SFE-2 and SFE-3) were performed at three different extraction conditions regarding CO_2 density, pressure and temperature; for SFE-1: 0.225 g/ml, 80 bar, 50ºC; for SFE-2: 0,403 g/ml, 100 bar, 50ºC, and respective SFE-3: 0.662 g/ml, 120 bar, 40ºC. The flow rate of carbon dioxide was kept constant, 2.0 kg/h, as well as the separation conditions: 80 bar and –10ºC for separator S_1 and 18 bar and 15ºC for separator S_2. The extraction time for all three supercritical extraction processes was the same, 120 minutes.

Results and discussions

Chemical analysis of anet essential oils obtained by supercritical CO_2 extraction (SFE-1, SFE-2 and SFE-3) has been performed by GC-MS. Analytical procedure were described in a previous paper [8]. The chemical compounds and their concentration, contained in extracted oil are given in Table 1.

Table 1. Percentage composition of anet 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	4.50	0.18	0.20	0.28	0.13
α-Pinene	4.78	0.09	0.11	0.14	0.17
Camphene	4.90	0.22	0.19	0.13	0.08
Sabinene	5.32	0.13	0.07	0.11	0.05
β-Pinene	5.55	0.05	–	0.08	0.14
β-Myrcene	5.73	0.07	0.12	0.15	0.05
α-Phellandrene	5.97	2.84	3.41	1.57	1.78
p-Cimene	6.30	0.53	0.32	0.40	0.21
Limonene	6.56	33.79	30.67	33.30	35.25
1,8-Cineol	6.69	0.41	0.25	0.12	0.10
γ-Terpinene	7.04	1.27	1.16	0.95	1.19
Menth-2-en-1-ol	7.14	1.87	1.42	1.28	0.88
Linalool	8.37	0.92	1.27	0.96	1.00
Trans-Menthone	8.81	0.24	0.31	0.10	0.08
Isomenthone	9.03	0.07	–	–	0.06
Neomenthol	9.31	0.12	0.11	0.22	0.17
Cis-Menthol	9.44	0.08	–	–	0.09
Dihydrocarvone	9.58	1.45	2.78	1.65	1.01
Dihydrocarveol	9.71	0.50	0.47	0.53	0.28
Carveol	9.86	1.98	2.02	2.00	1.31

Table 1. ***continued***

Compound	Rt[a](min)	HD%	SFE-1%	SFE-2%	SFE-3%
Carvone	10.23	49.95	52.55	53.42	53.70
Piperitone	10.31	0.24	0.25	0.18	0.12
Carvacrol	10.90	0.14	0.17	0.18	0.19
Timol	11.22	0.25	0.23	0.15	0.12
δ-Elemene	11.45	0.09	–	0.22	0.25
α-Cubebene	11.57	0.38	0.19	0.06	0.05
α-Copaene	11.82	0.33	0.28	0.12	0.08
β-Elemene	12.22	0.12	0.09	0.09	0.17
β-Caryophyllene	12.73	0.31	0.22	0.14	0.10
α-Humulene	13.15	0.08	0.10	0.16	0.17
γ-Muurolene	13.53	0.18	0.19	0.21	0.11
Germacrene	13.64	0.45	0.43	0.32	0.19
γ-Cadinene	13.87	0.07	–	–	0.14
Calamenene	14.05	0.12	0.09	0.11	0.06
Caryophyllen oxide	14.87	0.23	0.11	0.10	–
Humulene oxide	15.14	0.14	0.10	0.26	0.25
Bisabolol oxide	16.77	0.11	0.12	0.31	0.27

[a]Rt = retention time (min)

The characteristic chemical compounds of anet oil are limonene (hydrocarbon monoterpene) and carvone (oxygenated monoterpene). Their concentration in essential oil is higher than 80%. For comparison purposes the GC-MS analysis of the oil obtained at increasing values of carbon dioxide density, one can observe the increasing of these compounds concentration (Fig. 1). The limonene concentration increased from 30.67 (SFE-1) at 33.30% (SFE-2) and 35.25% (SFE-3). Concerning carvone, its concentration increased from 52.55% (SFE-1) at 53.42% (SFE-2) and 53.70% (SFE-3)

In Fig. 2 we presented a comparison study of concentration variation for monoterpenes and sesquiterpenes in supercritical extracted oils. The superior quality of essential oil is due to oxygenated monoterpenes and generally to oxygenated compounds. Hydrocarbon monoterpenes and sesquiterpenes did not participate at the extract flavor. In addition, these compounds can give unspecific, nasty smell (odour) [5,7,9]. One remark that the increasing of CO_2 density leaded to increasing of hydrocarbon monoterpenes (35.93% in extracted oil by SFE-1, 36.71% in extracted oil by SFE-2 and 38.84 % in extracted oil by SFE-3) and to decreasing of oxygenated monoterpenes concentration (61.43% in extracted oil by SFE-1, 60.46% in extracted oil by SFE-2 and 58.80% in extracted oil by SFE-3). According to these results we can conclude that by using carbon dioxide with density of 0.662 g/ml (SFE-3) low quality anet oil was obtained in comparison with those obtained with CO_2 with density 0.225 g/ml (SFE-1).

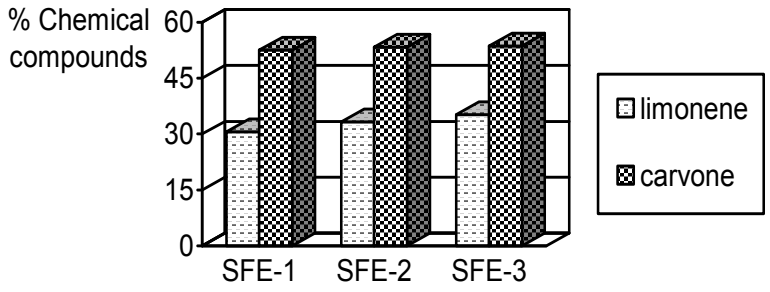

Fig. 1 *The characteristic anet essential oil compounds.*

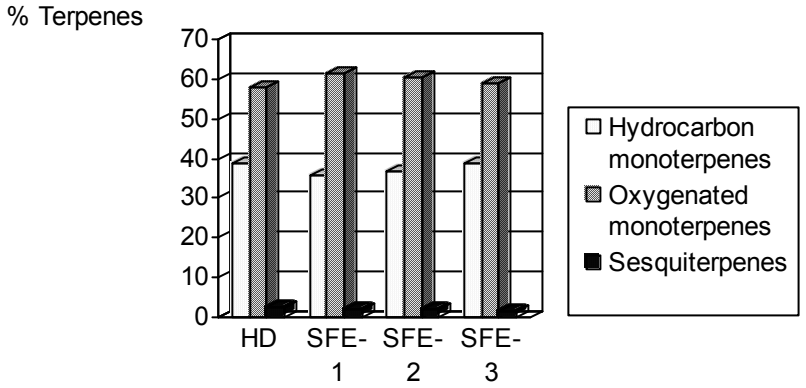

Fig. 2 *Percentages by weight of terpenes obtained by hydrodistillation (HD) and by supercritical fluid extraction (SFE).*

The anet oil was extracted also by hydrodystillation (HD). 50 grams of seeds and 1000 cm^3 were used. Mass of resulted oil was 2.9459 g and the yield of HD process was 5.89%, higher than supercritical carbon dioxide extraction processes. The HD oil quality was inferior. Analyzing the data from table 1 we can see that by HD , oxygenated monoterpenes have a lower concentration (57.83%) and sesquiterpenes have a higher concentration (2.61%), in comparison with oils extracted with supercritical carbon dioxide (figure 2). In addition, the carvone concentration in oil obtained by hydrodistillation is just 49.95%.

From quantitative point of view, the CO_2 density variation had an opposite effect: the yield of SFE processes were increased at increasing density. The time evolution of SFE processes yield is plotted in Fig. 3.

The partial and total extraction yield was measured by weighting the oil recovered in the second separator at the various extraction times: 15, 30, 60, 90 and 120 minutes from the beginning of supercritical extraction. One can see an increasing of yield extraction with

almost 1% (from 3.95% in SFE-1 at 4.77% in SFE-3) with increasing of carbon dioxide density from 0.225 g/ml to 0.662g/ml.

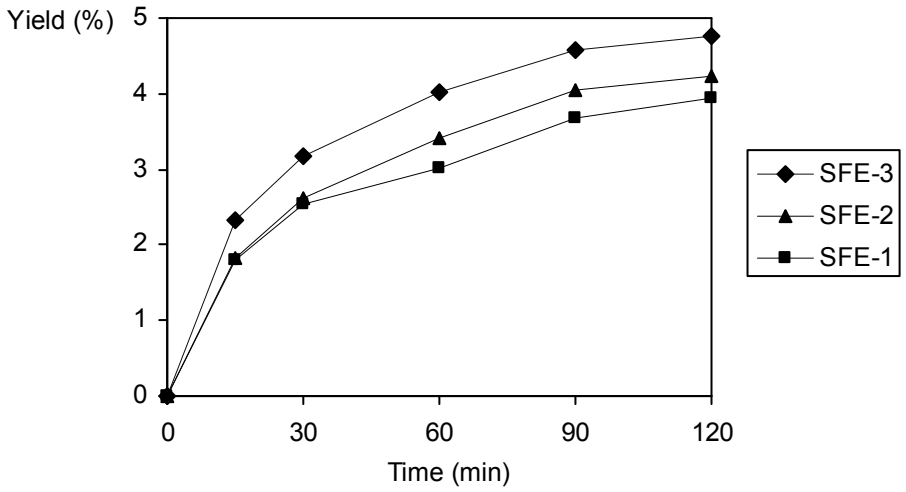

Fig. 3 *Anet essential oil yield against extraction times, at different CO_2 density.*

Conclusions

With increasing the density of supercritical solvent, carbon dioxide, from (0.225 to 0.662) g/cm^3, the concentration of monoterpenes is modified: the concentration of hydrocarbon monoterpenes increased from 35.93% to 38.84%, and concentration of oxygenated monoterpenes decreased from 61.43% to 58.80%. With increasing of supercritical carbon dioxide density we observed an increasing of anet yield extraction from 3.95% to 4.77%.

REFERENCES

1. Stahl, E., Quirin, K. W. and Gerard D. (1987) **Verdichtete Gase zur Extraction und Raffination**, Springer Verlag, Berlin
2. Di Giacomo, G., Brandani, V., Del Re, G. and Mucciante, V. (1989) *Fluid Phase Equilib.* **52**, 405.
3. Tufeu, R., Subra, P. and Plateaux, C. (1993) *J. Chem. Thermodynam.,* **25**, 1219.
4. Reverchon, E., Donsi, G and Pota, F. (1992) *It. J. Food Science*, **3**, 187.
5. Reverchon, E., Ambruosi, A. and Senatore, F. (1994) *J. Flavour and Fragrance* **9**, 19.
6. Reverchon, E. (1997) *J. Supercritical Fluids* **10**, 1.
7. Găinar, I., Vîlcu, R. and Mocan, M. (2002) *Anal. Univ. Buc.-Chimie* **XI** (vol. I), 63.
8. Găinar, I., Mocan, M. and Vîlcu, R. (2002) *Rev. Chim*. (Bucureşti) **53**(1), 78.
9. Della Porta, G. (1998) *Tecniche analitiche*, ISASF, Chia Laguna, 84.