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THE POTENTIAL OF SUPERCRITICAL CO_2 AS A SOLVENT IN THE EXTRACTION OF PEPPERMINT ESSENTIAL OIL

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abstract: Dried leaves of peppermint were used as a matrix for supercritical CO_2 extraction of essential oil. An extraction vessel of 1.5 L and two separators of 0.25 L were used to carry out studies at 50˚C and 80 bar. The essential oil was analyzed by GC-MS and its composition was compared with that of the oil obtained by hydrodistillation.

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Introduction

Supercritical fluid extraction (SFE) has many potential advantages compared to traditional processes, when selected compounds have to be extracted from natural matter. Indeed, it is possible to process the material with a non-harmful fluid like CO_2, the extracts are solvent free and it is possible to modulate the selectivity of the supercritical solvent to obtain the fractionation of complex mixtures. However, to perform a successful extraction or fractionation the choice of the right process scheme is also important. Indeed, it frequently occurs that, even when suitable values of pressure and temperature have been chosen, it is not possible to avoid the coextraction of several compound families. This is because vegetable matter frequently contains many lipophilic compounds, which show a good affinity with supercritical CO_2. If the supercritical extraction is carried out in a single stage separation, the extracts obtained present a solid consistency due to the simultaneous extraction of the oil (terpenes) and the cuticular waxes. However, it is possible to obtain the essential oil by supercritical CO_2 extraction adopting a fractional separation at least in two stages. Choosing optimal pressure and temperature, is possible to precipitate the undesirable compounds in the first separator and the essential oil in the second one [1-3].

At the University of Bucharest, it was 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 in

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order to obtain the essential oil from peppermint with supercritical CO_2. 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 from dried peppermint leaves (*Mentha piperita*, fam. *Lamiaceae*) 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 experimental set up has been described in an early paper [4]. About 300 g of comminute peppermint leaves were submitted to supercritical fluid extraction. A CO_2 flow rate of 1 kg/h was used for an extraction time of 180 minutes. Fractional separation, exploited in two stages, was obtained setting the first separator at 80 bar and 0˚C and the second one at 20 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 elsewhere [4]. The vegetal material was also submitted to conventional hydrodistillation (HD) according to the standard procedure [5]. The yield of the two processes has been evaluated.

Results and discussions

Table 1 shows the identification and the percentage composition of compounds in peppermint oil extracted by supercritical fluid extraction (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 (HD) is reported too. The isolated compounds were practically the same as those extracted by the SFE process.

The higher percentages in hydrodistilled oil (HD) and supercritical oil (SFE) compounds are trans-menthol (35.26% and 37.06%) and trans-menthone (24.41% and 26.20%).

Table 1 Percentage composition of peppermint oil isolated by hydrodistillation (HD) and by supercritical fluid extraction (SFE).

Compound	Rt[a](min)	HD %	SFE %
α-Pinene	4.09	0.19	0.23
Sabinene	5.35	0.16	0.08
β-Pinene	5.31	0.31	0.47
β-Myrcene	5.51	0.11	0.30
Octan-3-ol	5.59	0.10	0.15
p-Cimene	6.35	0.06	0.08
1,8-Cineole	6.55	4.27	4.89
cis-β-Ocimene	6.56	0.25	0.41
Menth-2-en-1-ol	7.08	0.10	0.25

Table 1 *continued*

Compound	Rt[a](min)	HD %	SFE %
Linalol	7.20	0.06	–
Camphor	8.39	0.14	0.17
trans-Menthone	8.55	24.41	26.20
cis-Menthone	8.58	3.07	3.58
Neomenthol	9.10	1.45	1.07
trans-Menthol	9.29	35.26	37.06
cis-Menthol	9.37	0.23	0.43
α-Terpineole	9.41	–	0.07
Dihydrocarveol	9.56	0.11	0.37
Pulegone	9.59	0.35	0.94
Carvone	10.01	0.07	0.53
Piperitone	10.12	0.62	0.49
Linalyl acetate	10.27	1.21	0.72
Neomenthyl acetate	10.34	2.90	1.59
trans-Menthyl acetate	10.35	6.38	10.17
cis-Menthyl acetate	10.51	1.98	1.02
δ-Elemene	11.31	0.07	–
α-Cubebene	11.50	0.09	0.06
α-Copaene	11.58	–	0.05
β-Bourbonene	12.03	0.54	0.31
β-Elemene	12.17	0.81	0.45
β-Caryophyllene	12.19	2.53	1.09
Aromadendrene	12.22	–	0.08
β-Gurjunene	12.37	0.59	0.16
β-Farnesene	12.47	0.42	0.13
α-Humulene	13.11	0.31	0.18
γ-Muurolene	13.15	0.45	0.14
γ-Cadinene	13.22	5.79	3.86
γ-Elemene	13.34	0.51	0.10
Calamenene	13.41	0.30	0.23
Spatulenol	14.17	0.62	0.16
Caryophyllene-oxide	14.36	0.64	0.32
Viridiflorol	14.55	0.29	0.18
Guaiol	15.01	0.61	0.15
γ-Cadinol	15.20	0.97	0.70
Bisabolol-oxide	16.29	0.67	0.38

[a]Rt = retention time

The characteristic peppermint essential oil compounds are: menthone, menthol, pulegone, piperitone and menthyl-acetates. The menthone and menthol were the cis and trans geometrical isomers, but the trans isomers prevail. In the little concentration was synthetized the neomenthol which is a steric isomer of menthol. The peppermint specific aroma is constituted by the menthol isomers and by the menthyl-acetates. The study of the GC-MS analyses relieved different concentration of these compounds in the two oils (see Fig. 1). The isomers of menthol and menthyl-acetates were extracted in a higher percentage in the supercritical oil: 38.56% and 12.78% compared to the hydrodistilled oil (36.94% and 11.26%).

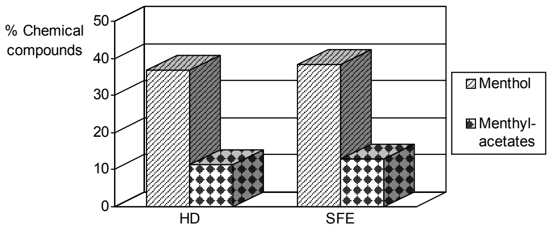

Fig. 1 *The characteristic peppermint essential oil compounds.*

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: they can give decomposition or polymerization reactions [6,7]. In Fig. 2 one can see a comparison, for the two peppermint oils, with regard of the terpenes composition. In the case of the SFE peppermint essential oil, only 6.84% was constituted by hydrocarbon sesquiterpenes. The oxygenated monoterpenes concentration was higher (76.05%) in the SFE oil.

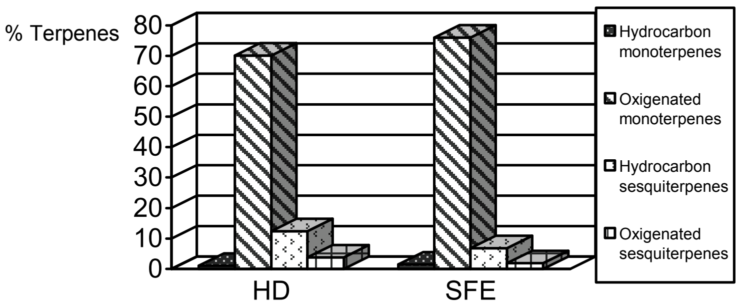

Fig. 2 *Percentages by weight of terpenes obtained by hydrodistillation (HD) and by supercritical CO_2 extraction (SFE)*

The oxygenated compounds (oxygenated monoterpenes, oxygenated sesquiterpenes and menthyl-acetates) presents highest concentration in the SFE oil (90.72%) compared to HD oil (85.20%). They are all specific contributors to the peppermint flavour. In the Fig. 3 is presented the graphic comparison of the oxygenated compounds isolated by two of the extraction methods.

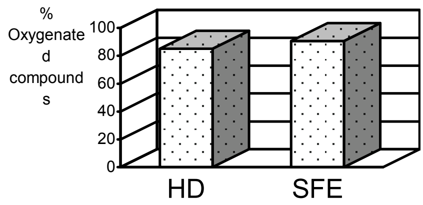

Fig. 3 *The oxygenated peppermint essential oil compounds.*

The yield of peppermint essential oil at the SFE conditions was 2.14% by weight of the charged material and by using hydrodistillation was 3.23%.

Conclusions

For the studied conditions of supercritical CO_2 extraction and fractionation, the results lead us to choose a pressure of 80 bar and a temperature of 50˚C as the best process parameters for the obtainining of peppermint essential oil. Trans-menthol is the principal extracted component. At 80 bar and 50˚C the trans-menthol concentration in the essential oil extracted is greater than 37%. The yield obtained from hydrodistillation process was greater in comparison with SFE process at the optimum conditions, but in the case of SFE the quality of oil is better (the concentration of oxygenated monoterpenes was higher).

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