

## HIGH-PRESSURE EXTRACTION USING SUPERCRITICAL CO<sub>2</sub>

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Supercritical CO<sub>2</sub> extraction of oil from lavender inflorescence 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 supersaturation and precipitation of the undesired 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, 0°C in the first separator and 15 bar, 5°C in the second separator, respectively. The lavender oil produced by supercritical CO<sub>2</sub> extraction and fractionation was compared to the oil obtained by classical hydrodistillation. The major difference between the two products resulted in the linalyl acetate content. This compound was found to be 31.82% of the oil produced by supercritical fluid extraction and as 16.05% of the hydrodistilled oil. The difference can be ascribed to the hydrolysis of part of the compound during hydrodistillation. The oil yield of the extraction process was measured at various extraction lengths.

### Introduction

Extraction may be defined as the removal of individual components from a mixture by means of suitable solvents, traditionally low-boiling organic substances, such as methanol, ethanol, dichloromethane, etc. However, because some of these substances are toxic, efforts are now being made to avoid their use. An alternative to these solvents is provided by high-pressure extraction using supercritical gases. This extraction method is based on the principle that substances dissolve at a much higher rate in supercritical gases than would normally be expected at a given vapour pressure. CO<sub>2</sub> has proven especially well suited for the extraction of natural substances. The low critical temperature of 31°C allows particularly delicate handling of natural substances. Moreover, CO<sub>2</sub> is not only readily available, but may also be obtained at relatively low prices.

The extraction of flavours and fragrances using supercritical CO<sub>2</sub> (SFE) 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<sub>2</sub> densities over about 0.5 g/cm<sup>3</sup> are used, also fatty acids and their methyl esters, triglycerides, colouring matters, etc, can be extracted. Thus, although never explicitly mentioned by the various authors, the conventional CO<sub>2</sub> SFE technique does not produce fragrance compounds alone; i.e., it is not possible to isolate essential oil.

It has been recently demonstrated that, by analyzing the extraction mechanism involved in SFE processes, essential oils and cuticular waxes are however coextracted from vegetable matters even at optimum extraction pressure and temperature [1]. Cuticular waxes show

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very low solubilities in supercritical CO<sub>2</sub> 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<sub>2</sub> solubilities [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 solubilities 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 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].

Stahl et al. [6] reported a previous study on lavender extraction in which liquid CO<sub>2</sub> was used. These authors state that the extract showed high contents of linalool and linalyl acetate. The high percentage of the latter compound is particularly important because the conventional steam distillation process leads to partial hydrolysis of linalyl acetate and thus lowers the value of the product. However, by using liquid CO<sub>2</sub> high solvent densities are involved that lead to very low extraction selectivities: high molecular weight lipophilic compounds contained in the vegetable matter, that do not contribute to the fragrance of the extract, can also be extracted.

The aim of this work was to apply supercritical CO<sub>2</sub> extraction and fractional separation process, to isolate lavender essential oil. The oil was then compared to the product obtained by hydrodistillation. The extraction yield was also measured at various extraction lengths.

## Experimental part

Tests on lavender were performed on a laboratory unit based on a 350 cm<sup>3</sup> extraction vessel equipped with two separators. Further details on this apparatus have been given elsewhere [7]. A CO<sub>2</sub> flowrate of 1.0 kg/h was used.

The extracts were analyzed by a GC-MS apparatus formed by a Varian 3400 GC coupled to a Finnigan 800 Ion Trap Detector (ITD, software version 4.1). Analytical procedures were described in a previous work [7]. Compound percentages were calculated by GC peak area integrations computed without correction factors.

About 250 g of comminuted lavender flowers (*Lavandula augustifolia*, fam. *Lamiaceae*) was submitted to extraction in each run, for 180 min. The maximum lavender oil yield was measured at the end of an exhaustive SFE run. It resulted in 1.64% by weight of the material charged in the extractor. Similar material was submitted to conventional hydrodistillation (HD) for 180 min according to the standard procedure [8]. The HD oil yield was 2.95%.

## Results and discussion

Optimum extraction conditions were studied in the pressure range from 80 to 120 bar and for temperatures between 40 and 60°C. Extraction conditions that produce higher than about 0.6 g/cm<sup>3</sup> CO<sub>2</sub> densities were not tested since such densities produce low extraction selectivities; i.e., the co-extraction 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.

The yield of lavender 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 1.64% by weight of the charged material. It was assumed equal to 100% in the Fig. 1.

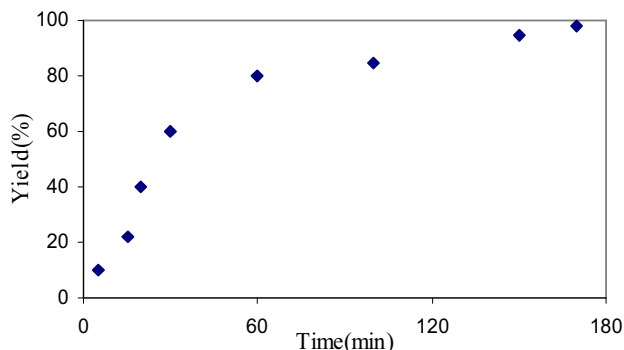


Fig. 1: Lavender oil yield at various extraction times.

Table 1 shows the identification and the percentage composition of compounds in lavender oil extracted by SFE. For comparison purposes the analysis of the oil obtained by conventional hydrodistillation (HD) is reported too. No paraffins precipitated together with the oil: the fractional precipitation technique resulted to be very selective.

The higher percentages in supercritical and hydrodistilled oil compounds are: camphor, 1,8-cineole, linalool and linalyl acetate. They correspond to the most significant ones, as indicated by an extensive work performed on several lavender and lavandin cultivars [9].

One major difference appeared between the SFE and HD extracts: the former contains 27.32% of linalool and 31.82% of linalyl acetate, while the latter contains 38.07% of linalool and only 16.05% of linalyl acetate. Linalyl acetate was partly decomposed during hydrodistillation and converted into other compounds. Therefore, these products confirm the opinion that in the case of thermal labile compounds the conventional hydrodistillation technique can greatly modify the extract with respect to the starting composition of the vegetable matter.

The oil obtained by hydrodistillation showed a sensible odour difference compared to the starting lavender inflorescence whereas the odour of the SFE oil was considered not distinguishable from that of the starting material.

**Table 1. Percentage composition of lavender oil isolated by supercritical CO<sub>2</sub> extraction (SFE) and by hydrodistillation (HD), respectively; the percentages are based on GC peak areas.**

Compound	Retention time (min)	SFE (%)	HD (%)
$\alpha$ -Thujene	4.54	-	0.08
$\alpha$ -Pinene	4.69	0.39	0.41
Camphene	4.81	0.07	-
Sabinene	5.33	-	0.22
1-Octen-3-ol	5.58	0.16	0.27
$\beta$ -Pinene	5.61	0.77	1.18
$\beta$ -Myrcene	5.73	1.42	1.53
Hexyl acetate	6.07	0.05	0.08
<i>o</i> -Cymene	6.28	0.15	0.41
<i>p</i> -Cymene	6.33	0.06	0.17
1,8-Cineole	6.65	5.92	4.85
<i>cis</i> - $\beta$ -Ocimene	6.80	1.59	1.02
<i>trans</i> - $\beta$ -Ocimene	6.99	1.42	1.38
Menth-2-en-1-ol	7.05	0.12	0.05
<i>cis</i> -Linalool-oxide	7.10	0.75	1.09
<i>trans</i> -Linalool-oxide	7.44	1.02	1.31
Linalool	8.07	27.32	38.07
Camphor	8.67	8.10	7.12
Borneol	8.76	2.71	3.20
Lavandulol	8.84	0.82	0.34
4-Terpineol	8.92	2.12	2.00
$\alpha$ -Terpineol	9.11	1.07	3.02
Hexyl butyrate	9.44	0.27	0.32
Nerol	9.76	0.10	0.09
Geraniol	10.13	0.71	1.10
Linalyl acetate	10.36	31.82	16.05
Neryl acetate	11.64	0.14	0.91
Geranyl acetate	11.96	0.23	1.85
$\beta$ -Caryophyllene	12.43	1.68	2.71
Aromadendrene	12.61	0.66	0.95
$\alpha$ -Bergamotene	12.84	0.32	0.87
$\beta$ -Farnesene	13.06	2.41	2.01
$\gamma$ -Muurolene	13.53	0.22	0.88
$\gamma$ -Cadinene	13.88	0.34	0.17
$\alpha$ -Bisabolol	15.13	5.07	4.29

## Conclusions

For the studied conditions of extraction and fractionation, the results lead us to choose  $P = 90$  bar and  $T = 50^\circ\text{C}$  as the best ones to obtain the lavender essential oil. The yield

obtained from hydrodistillation was 2.95% while from SFE at the optimum conditions was 1.64%.

## 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., Ambrosi, A. and Senatore, F. (1994) *J. Flavour and Fragrance* **9**, 19.
6. Stahl, E., Quirin, K. W. and Gerard, D. (1987) **Verdichtete Gase zur Extraction und Raffination**, Springer Verlag.
7. Găinar, I, Vilcu, R. and Mocan, M. (2002) *Anal. Univ. Buc.* **XI**, 63.
8. **Farmacopeea Română** (1993) Edit. Medicală, București, 1064.
9. Tucker, A. O., Maciarello, M. J. and Howell, J. T. A. (1984) *Perfumer and Flavorist* **9**, 49.