

Isolation of *Coriander* Oil: Comparison Between Steam Distillation and Supercritical CO₂ Extraction

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Ripe fruits of *Coriander sativum* L. were extracted by steam distillation and by supercritical fluid extraction (SFE), using CO₂ in a two-stage separation system. An inexpensive thermal expansion procedure for supercritical fluid delivery has been developed. The identification of components was performed by gas chromatography–mass spectrometry (GC–MS). The percentage composition of the 40 identified compounds was compared with the composition of a commercial coriander oil extracted by hydrodistillation. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Essential oils represent a small fraction of a plant's composition but confer the characteristics for which aromatic plants are used in the pharmaceutical, food and fragrance industries. Essential oils have a complex composition, containing from a few dozen to several hundred constituents, especially hydrocarbons (terpenes and sesquiterpenes) and oxygenated compounds (alcohols, aldehydes, ketones, acids, phenols, oxides, lactones, acetals, ethers and esters). Both hydrocarbons and oxygenated compounds are responsible for the characteristic odours and flavours. The proportion of individual compounds in the oil composition is very different: from traces to over 90% (D-limonene in orange oil). The aroma of each oil is the result of the combination of the aromas of all components. Trace components are very important, since they give the oil a characteristic and natural odour. Thus, it is very important that the natural proportion of the components is maintained during extraction of the essential oils from plants by any procedure. From this viewpoint, the supercritical fluid extraction (SFE) technique (in which there has been important developments in the last few years) presents some remarkable advantages in comparison with the

classical procedures, steam distillation and liquid solvent extraction. By using SFE, the natural characteristics of the oils are kept and thermal degradation or hydrolysis and solvent contamination are avoided. SFE offers a rapid method for extraction of oils from complex matrices as well as high selectivity for certain compounds, depending on the extraction conditions.

Numerous papers describe the extraction of volatile oils from solid plant material by SFE on analytical and preparative scales.^{1–5}

This paper reports a very simple SFE technique for coriander fruits and compares it to the conventional approach of steam distillation. SFE allows for a continuous modification of solvent power and selectivity by changing the supercritical fluid density. Nevertheless, a high density and one-stage subcritical separation, when the yield of the extracted material is high, is unsuitable due to the simultaneous extraction of many unwanted compounds, especially cuticular waxes and lipids.^{6,7} SFE at relative high density of CO₂ (~ 0.7 g/cm³), followed by separation of the extract in multiple-stage separators at different pressure and temperature values, overcomes this undesirable situation. Coriander oil, used extensively in seasonings and perfumes, is usually obtained by steam or hydrodistillation (6–9 hours) of the partially dried ripe fruits of *Coriander sativum* L. The major areas of cultivation are Russia, Egypt, Morocco, The

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Netherlands, Romania, India, China and the USA. The oil is pale yellow with the odour of linalol, its major component. Other minor components were identified previously by Tashinen and Nykanen⁸ but in recent years many different GC approaches, such as headspace GC for volatile compounds, GC–matrix isolation–Fourier transform infra-red spectrometry (FTIR),^{9–11} or GC–FTIR–MS¹² have been used for characterization of this oil.

EXPERIMENTAL

Plant Material

On the basis of the results of preliminary experiments, 300 g of ripe fruits of *Coriander sativum* L. were dried and ground to an approximate size of 0.4 mm. The essential oil content, determined by 5 hours steam distillation at 600–700 Torr and 80–90°C, was about 0.65%.

Supercritical Fluid Extraction (SFE)

The SFE bench-scale apparatus (Fig. 1) consists of a 1 litre stainless steel extractor (SFE-V) and two separators (S_1 , S_2) assembled in series, the first with an inner volume of 100 ml and the second with 300 ml. The desired pressure and temperature values in S_1 and S_2 were maintained by valves V_2 – V_4 by adequate regulation of CO_2 flow rates, measured by a flowmeter (FM).

The filling of the extraction vessel with CO_2 was made directly from a moderately heated cylinder (60–80°C) fitted with a dip tube. The cooling Joule–Thomson effect, appearing by opening the valve V_1 , permits the transfer of CO_2 in a condensed phase due to the pressure dropping after V_1 at very low temperature ($T_{\text{subl}} = -78.5^\circ\text{C}$). CO_2 transferred becomes a supercritical fluid by heating at temperature value of the extraction process (over 32°C, the critical value). A high density is reached as a function of the amount transferred and the supercritical temperature value (given by the thermostat T). The system is essentially maintenance-free, with virtually no moving parts.

The dynamic method at 50°C and 150 bar and an extraction period of 180 minutes at 50 ml/min were used. The above-mentioned parameter values were selected after a number of experiments and were considered as the optimum conditions for both acceptable yield and selectivity. The yield of various fractions was measured by weight with respect to the material charged in the extractor.

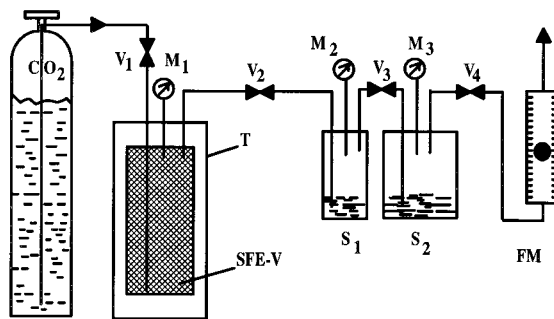


Fig. 1. Schematic diagram of the SFE Apparatus.

Steam Distillation

A similar batch of ripe coriander fruits (ground to 0.4 mm) was also steam-distilled for 5 hours at 600–700 Torr and 80–90°C to minimize the thermal degradation of the more labile compounds. The essential oil obtained by this procedure was compared with a commercial essential oil (FARES SA Orastie, Romania), obtained by hydrodistillation, and with the oil obtained by SFE.

Gas Chromatography–Mass Spectrometry Analysis (GC–MS)

GC–MS data were obtained using a Fisons Instruments MD 800 gas chromatograph–mass spectrometer equipped with a split–splitless injector (250°C) and with a fused silica DB-5 column (15 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific). Helium was used as carrier gas, with a flow rate through the column of 1.2 ml/min (at 40°C) and septum purge of 4 ml/min. The split ratio was 1:50, and the volume of injected samples was 0.4 μl. The GC oven was programmed as follows: 40°C (5 min)–120°C (10 min) at 5°C/min, then to 250°C (5 min) at 4°C/min, and finally to 280°C at 5°C/min. The interface temperature was 280°C. Data acquisition was performed with MassLab Software for the mass range 35–480 a.m.u. with a scan speed of 1 scan/sec. The ionization energy of electrons was 70 eV. The identification of compounds was based on a comparison of their mass spectra with NIST mass spectral library (National Institute of Standardization, USA) and by relative retention time of compounds identified previously.¹² The percentage composition of the essential oil was computed in each case from GC peak areas without using correction factors.

Table 1. Comparative percentages of the identified compounds in *Coriander* oils

Compound	Kováts RI ^a	Comm. oil	Steam dist. oil	SFE oil
1 α -Thujene	928	trace	trace	0.1
2 α -Pinene	936	3.3	2.3	2.8
3 Camphene	951	0.6	0.4	1.5
4 Sabinene	975	0.1	0.3	0.9
5 β -Pinene	980	1.0	0.3	0.9
6 6-Methyl-5-hepten-2-one	983	0.1	0.1	0.1
7 β -Myrcene	990	1.2	0.8	1.0
8 Δ^3 -Carene	1006	1.1	0.3	0.3
9 α -Terpinene	1018	0.1	0.1	0.1
10 <i>p</i> -Cymene	1026	4.9	4.0	4.0
11 Limonene	1030	2.4	2.3	2.7
12 1,8-Cineole	1033	trace	0.1	0.1
13 δ -Terpinene	1059	4.6	3.5	3.5
14 <i>cis</i> -Linalol oxide	1073	0.6	0.2	0.4
15 <i>trans</i> -Linalol oxide	1089	0.8	0.3	0.4
16 Linalol	1103	63.8	62.8	61.9
17 Camphor	1147	5.5	5.6	5.6
18 Borneol	1168	0.1	0.1	0.1
19 Menthol	1174	trace	0.1	0.1
20 Terpinene-4-ol	1179	0.6	0.5	0.5
21 <i>p</i> -Cymen-8-ol	1184	trace	0.1	0.3
22 <i>cis</i> -Hex-3-enyl butyrate	1186	trace	0.1	0.2
23 α -Terpineol	1192	1.0	0.9	0.6
24 <i>cis</i> -Dihydrocarvone	1198	–	0.1	0.1
25 β -Citronellol	1226	0.1	0.3	0.2
26 Neral	1241	0.1	0.1	0.2
27 Carvone	1245	0.5	1.0	1.0
28 Geraniol	1253	1.8	2.8	2.2
29 Geranial	1270	trace	0.1	0.2
30 Anethole	1287	0.7	0.4	0.4
31 Thymol	1289	trace	0.1	0.1
32 Carvacrol	1299	trace	0.1	0.2
33 Geranyl formate	1301	–	trace	0.2
34 Eugenol	1357	0.1	2.6	1.4
35 Neryl acetate	1363	0.1	0.1	0.2
36 Geranyl acetate	1382	1.0	1.8	2.4
37 β -Caryophyllene	1428	trace	2.1	0.8
38 α -Humulene	1463	trace	0.3	0.2
39 Eugenyl acetate	1526	–	trace	0.2
40 β -Caryophyllene oxide	1594	trace	trace	0.2
Unidentified compounds		3.8	2.9	1.7

^aOn DB-5.

RESULTS AND DISCUSSION

Extractions performed at various CO₂ densities showed that extraction at $P = 150$ bar and $T = 50^\circ\text{C}$ ($\rho = 0.7$ g/cm³) minimized the co-extraction of unwanted compounds but increased the yield of the flavour fraction. To perform the separation of unwanted compounds (cuticular waxes, such as C₂₅–C₃₃ *n*-paraffins and lipids such as esters of fatty acids) and the oil, the best

parameters were $P = 60$ bar and $T = 10^\circ\text{C}$ for the first separator and $P = 30$ bar and $T = 0^\circ\text{C}$ for the second. These parameters were maintained at the above-mentioned values by different flow-rates of supercritical CO₂ through the pipes and separators (different intensities of Joule–Thomson effect obtained by different opening level of valves V₂–V₄).

The yield of the oil recovered for the second separator in the SFE as described was 0.61% compared with 0.65% using the steam distillation procedure at 600–700 Torr and 80–90°C.

The oils obtained by SFE, steam distillation and a commercial oil (FARES SA) were examined by GC–MS. One hundred compounds were observed in the oils obtained by distillation (i.e. compounds with an area peak greater than 0.01% from area peak of the linalol) in comparison with 140 in the case of the oil obtained by SFE. The 40 identified compounds (over 96% from total oil composition) are presented in Table 1 as a function of the Kováts retention index (RI).

The percentage composition of each oil is also presented. It is noteworthy that the oil extracted by SFE has a composition quite similar to that of the oil obtained by steam distillation at 600–700 Torr, but several important differences can be observed between these oils and the commercial oil. The percentage of the most desired oxygenated compounds is higher in oil obtained by SFE. Some fatty acids and ester traces were also extracted by SFE but these do not have a negative influence in the oil quality.

Organoleptic comparison of the SFE oil with the commercial oil showed that the aroma of the first was more intense and more pleasant.

CONCLUSIONS

A simple SFE procedure combined with a two-stage separation of the extract gives a coriander oil in comparable yield and avoids the thermo-degradation of some important compounds observed in commercial oil obtained by hydro-distillation.

Essential oils are generally expensive (from several to several thousand US dollars per kg) compared to 'duplicate oils' (synthetics combined with natural oils). But such 'reconstituted' oils usually lack certain odour notes of the natural products because of the absence of trace components, tending to have a more 'chemical' odour.

SFE appears to be a cost-effective technique at laboratory scale, but an accurate economic evaluation for larger-scale units requires supplementary experiments. It offers the advantages of a low operating temperature and no solvent residue with positive effects in oils' quality. For design purposes it is necessary to calculate the composition of supercritical phase for all possible conditions.

The coriander essential oil obtained by SFE presents some quantitative and qualitative differences that give a superior aroma compared with a commercial oil obtained by hydrodistillation.

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