Comparison Between Coriander Volatile Oils Obtained by Supercritical CO_2 Extraction and Hydrodistillation

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Supercritical fluid extraction (SFE) with CO_2 of volatile oil from coriander (*Coriandrum sativum* L.) seeds was carried out at the temperature of 40ºC and pressures up to 150 bar with a flow apparatus using a two stage fractional separation technique.
Two ecotypes growing in different environmental conditions, one from Spain and the other from Italy, were studied. The best conditions of extraction (90 bar and temperature of 40 ºC), and separation (pressure of 70 bar and temperature of –8 ºC, in the first separator, and a pressure of 20 bar and a temperature of –5 ºC, in the second one), were used to assess the effect of different mean particle size.
The yield of the extraction and composition of the volatile oil were compared with those obtained by hydrodistillation. The study showed that the particle size of seeds influence the yield and the composition of the oil in SFE. The coriander oil was analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The main compounds identified in the oils were α-pinene (2.5%), myrcene (1.7%), linalool (74%), camphor (3.3%), geraniol (3%) and geranylacetate (1.3%)

INTRODUCTION

Coriander (*Coriandrum sativum* L.) is an annual Apiaceae herb, which grows in mediterranean countries, and is widely used in food and pharmaceutical industries. In traditional medicine, seeds are used in the treatment of gastrointestinal problems, rheumatism and pain joints. Recent studies have also demonstrated a hypoglycaemic action and effects on carbohydrate metabolism [1]. It has also been reported the antimicrobial effect of coriander leaves and seeds against several microorganisms [2,3]. Furthermore in food industry, leaves and seeds are employed as condiment, being used to flavour various commercial foods, as liqueurs, teas, meat products and pickles [4].
The composition of the oil isolated from coriander was studied by some authors using diferent extraction methods, namely steam distillation [5,6], hydrodistillation [7] and supercritical fluid extraction [4, 5, 7, 8]. Although hydrodistillation and solvent extraction are the common methods to isolate volatile oils from aromatic herbs these two methods present some problems like low extraction efficiency, long extraction time, toxic residual solvent in the products and deterioration of the thermally sensitive compounds. Therefore, over the last years, supercritical fluid extraction has received increasing attention due to the fact that supercritical fluids provide high solubility and improved mass-transfer rates and the manipulation of temperature and pressure allows the extraction of different components [4, 5, 8].

The aim of this work was to study the influence of various process parameters such pressure and particle size on the volatile oil extraction yield and composition of two different coriander ecotypes, one from Spain and the other grown in Italy.

MATERIALS AND METHODS

Supercritical Fluid Extraction Apparatus

The supercritical fluid extraction apparatus, with two separators, allows to carry out extraction studies in the temperature range of 25-60ºC, pressures up to 300 bar and flow rates of up to about 20 L/min [9,10]. The CO_2 (99.995% purity) used in the studies was supplied by Air Liquide (Portugal).

Plant Material

Seeds from Italian and Spanish coriander were ground with a commercial mill, frozen with liquid N_2 to avoid the loss and thermal degradation of the essential oil and kept at -20ºC in dark bags. Several sieves, of various mesh sizes, were used to collect and weigh several fractions, in order to determine the particle size distribution of the ground material. Mean particle size of 0.4, 0.6 and 0.8 mm were used. Supercritical extraction and hydrodistillation were performed with 100 g and 40 g of plant material, respectively.

Gas Chromatography and gas Chromatography-Mass Spectrometry

Quantitative analyses were performed in a Hewlett-Packard 5890 gas chromatograph, equipped with a flame ionisation detector (FID) and a fused-silica DB-5 capillary column (J&W; 30 m x 0.25 mm i.d., film thickness 0.25 μm). Oven temperature was programmed isothermally to 40 ºC, during 2 minutes, then was raised, at 3ºC/min, to 230 ºC, and finally increase at 5ºC/min, to 310 ºC and held at this temperature for 15 min. The injector and detector temperatures were, respectively, 310 ºC and 310 ºC. Helium was used as a carrier gas flowed at a rate of 24 cm/s, and the split ratio was 1:50.

The percentage composition of the essential oils and supercritical volatile oils were determined from GC peak areas and components were identified by GC-MS as previously reported [11] .

RESULTS AND CONCLUSIONS

The yields (mass of oil/mass of dried plant) of hydrodestillation (HD) and supercritical fluid extraction (SFE) at pressure of 90 bar, temperature of 40 ºC and flow rate 10.0 L/min of CO_2, are presented in Table 1. The yields of SFE were higher than those obtained by hydrodestillation. On the other hand the efficiency of SFE increased with the decrease of particle size of the plant. This effect was more important at 0.4 mm, where the SFE yield was higher.

Table 1: Comparison of extraction yields from coriander using hydrodestillation and supercritical fluid extraction with different particle size of plant material and ecotype at 40 ºC.

Mean particle size (mm)	Spanish ecotype		Italian ecotype		
	HD (%)	SFE (%) 90 bar	HD (%)	SFE (%) 90 bar	SFE (%) 150 bar
0.4	0.4	0.7	0.5	0.8	
0.6	0.4	0.5	0.5	0.6	1.1
0.8	0.4	0.5	0.5	0.6	

Table 2 shows the percentage composition of the detected components of the essential oil (HD) and volatile oil (SFE) in different conditions of particle size and ecotype. Twenty-five components were identified, representing 85-98 % of the total amount.
The obtained oils were dominated by hydrocarbons monoterpene and oxygenated monoterpenes.

Table 2: Percentage composition of coriander oils obtained by hydrodistillation and supercritical extraction at 40 ºC for three particles sizes and two ecotypes.

Components	Spanish ecotype				Italian ecotype				
	HD	SFE			HD	SFE			
		90 bar				90 bar			150 bar
		0.4	0.6	0.8		0.4	0.6	0.8	0.6
α-Thujene	t	t	t	t	t	t	t	t	t
α-Pinene	1.8	0.8	1.0	0.6	2.5	2.2	2.6	1.5	2.5
Camphene	t	0.1	0.1	0.1	0.3	0.2	0.3	0.2	0.3
Sabinene	t	0.1	0.1	0.1	0.2	0.2	0.2	0.1	0.2
β-Pinene	t	0.2	0.2	0.2	0.3	0.3	0.4	0.2	0.3
Myrcene	1.0	1.3	1.8	2.6	1.7	0.9	1.0	0.7	0.9
α-Terpinene	t	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1
p-Cymene	0.8	0.5	0.4	0.4	1.0	0.8	0.7	0.6	0.8
Limonene	1.1	0.9	1.1	1.5	1.7	1.3	1.3	1.2	1.4
cis-β-Ocimene	t	0.3	0.4	0.8	0.2	0.3	0.2	0.1	0.1
trans-β-Ocimene	0.4	0.6	0.9	1.4	0.6	0.2	0.2	0.1	0.2
γ-Terpinene	2.8	2.3	3.1	2.9	5.8	5.9	6.4	5.4	6.5
trans-Sabinene hydrate	t	0.1	t	t	0.1	0.1	0.1	0.1	0.1
cis-Linalool oxide	t	0.1	0.1	0.2	t	t	t	t	t
n-Octanol	t	0.1	0.1	0.2	t	t	t	t	t
Terpinolene	0.3	0.3	0.4	0.3	0.5	0.5	0.5	0.4	0.5
Linalool	73.2	69.3	59.1	62.7	74.3	74.4	73.1	65.2	72.7
Camphor	3.9	2.3	2.2	2.1	3.3	3.2	3.2	2.7	3.1
Citronellal	t	0.1	t	0.3	0.1	0.1	0.1	0.1	0.1
Borneol	1.0	0.7	0.7	0.8	0.1	0.1	0.1	0.1	0.1
Terpinen-4-ol	t	0.1	0.1	0.2	t	0.2	0.2	0.2	0.2
α-Terpineol	0.7	0.5	0.3	0.1	t	0.1	0.1	0.1	0.1
Citronellol	0.3	0.1	t	t	t	t	t	t	t
Geraniol	2.2	2.7	2.6	2.0	3.2	3.6	3.5	3.1	3.3
Geranylacetate	5.3	5.1	4.5	4.4	1.3	3.3	3.2	2.9	3.1
Identified components (%)	94.9	88.6	79.1	84.1	97.4	98.1	97.4	85.3	96.8
Grouped components (%)									
Monoterpene hydrocarbons	8.3	7.5	9.4	11.0	15.0	12.9	13.8	10.7	13.9
Oxygen-containing monoterpenes	86.6	81.0	69.5	72.9	82.3	85.2	83.6	74.5	82.8
Others	t	0.1	0.1	0.2	t	t	t	t	t

t = trace (<0.05 %)

The monoterpene hydrocarbons fraction was 8-14% of the essential and volatile oils and the oxygenated monoterpenes amount was 70-87 %, being linalool the principal constituent (70%). These results were similar to those obtained by others authors [5, 6, 7].
The two ecotypes present similar composition, being the principal difference the components geraniol, geranylacetate and γ-terpinene. It can be observed the increase of the content in oxygenated monoterpenes in SFE oils when the particle size decreases.
The effect of the extraction pressure was also studied. Figure 1 shows that the global yield of supercritical extraction increased with the pressure, from 90 to 150 bar at 40 ºC. The increase of pressure, for a fixed temperature, produced an increase on the density of the supercritical fluid, responsible by a higher dissolution of the heavier compounds. The analysis of the extract at 150 bar showed that the total amount of linalool decreased slightly and the process at high pressure seems to be less convenient to obtain the SFE volatile oil, since the total amount of waxes increase.

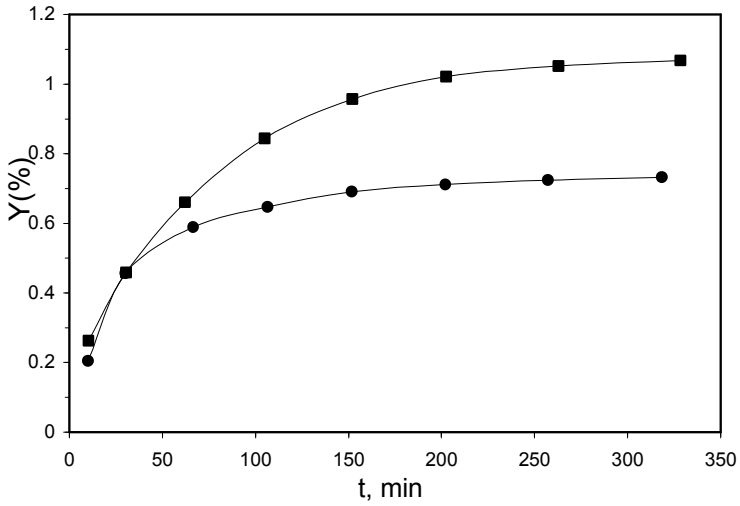

Figure 1: Yield of extracted volatile oil from coriander at mean particle size 0.6 mm. ■ -150 bar and 40°C; ● - 90 bar and 40° C.

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