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Volatile Constituents Obtained by the Extraction with Alcohol-Water Mixture and by Steam Distillation of Coriander Fruit

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The composition of the volatile oil of Coriander fruit *(Coriandrum sativum* L.) isolated by distillation with steam and by extraction and distillation with an alcohol-water mixture was investigated by means of gas chromatography, column chromatography, infra red spectrophotometry and mass spectrometry. 45 compounds were identified including 19 hydrocarbons, 10 alcohols, 7 aldehydes and, in the alcoholic distillate only, 6 ethyl esters of long chain fatty acids.

Coriander is an annual herb originating in the Mediterranean countries, and is nowadays mostly grown in Italy, Morocco, India and Eastern Europe. Two types of coriander are distinguished according to the size of the fruit, *Coriandrum sativum* L. var. *vulgare* Alef. (fruit diameter 3-5 mm) and *Coriandrum vulgare* L. var. *microcarpum* DC. (fruit diameter 1.5 – 3 mm). Steam distillation of the fruit yields 0.15 – 1.7 % of volatile oil,[1] which is used in food industry, perfumery and pharmacy. The alcoholic extracts and distillates of dried fruits are used extensively for flavouring liquors.

The examination of the chemical composition of Coriander oil started at the end of the last century and in 1893 Barbier [2] identified its main component as *d*-linalool. In 1909 Walbaum and Müller [3] published quite a detailed study of the oil. They found the amount of linalool to be 60 – 70 % and identified 16 additional compounds.

Since 1960 gas chromatographic studies of the composition of coriander oil have been made by Ikeda *et al.*,[4] Schratz and Qadry,[5] Akimov and Voronin,[6] Paukov *et al.*,[7] Karlsen *et al.*[8] and Rasmussen *et al.*[9] The identification of most of the 31 compounds reported in these studies are based on the gas chromatographic retention times. In all, the following compounds have been found in coriander oils of various origin: α-pinene, β-pinene, camphene, sabinene, 3-carene, myrcene, α-terpinene, γ-terpinene, α-phellandrene, β-phellandrene, limonene, α-thujene, *cis*-ocimene, *trans*-ocimene, terpinolene, *p*-cymene, linalool, borneol, geraniol, nerol, citronellol, α-terpineol, terpinenol-4, linalyl acetate, geranyl acetate, bornyl acetate, camphor, decanal, 2-tridecenal, thymol, anethol, acetic acid, and decanoic acid.

It is obvious that the method of separation may have some effect on the composition of an essential oil. In the present study the chemical composition of both steam distilled oil and an alcoholic coriander distillate was investigated.

EXPERIMENTAL

Apparatus. A Hewlett-Packard 7620 A with FI detector was used for the analytical gas chromatography. The packed columns used were 5 % LAC-2R-446 on 70/80 mesh Chromosorb G AW DMCS, 15 % Apiezon L on 60/80 mesh Chromosorb W AW and 5 % SE-30 on 60/80 mesh Chromosorb G all in 6 mm O.D. × 3 m stainless steel tubes. A 0.28 mm I.D. × 25 m SP 1000 glass capillary column was also used in the same gas chromatograph fitted with a glass inlet splitter of S.G.E. The detector temperature was maintained at 290 °C and the injector temperature at 240 °C. Helium flow was 80 ml/min with packed columns and 0.7 ml/min with the capillary column. Peak areas were measured with an Infotronics CRS-11 HSB/42 integrator.

For the preparative gas chromatography the same packed columns and the same instrument were used with TC detector at 240 °C. The fractions eluting from the gas chromatograph

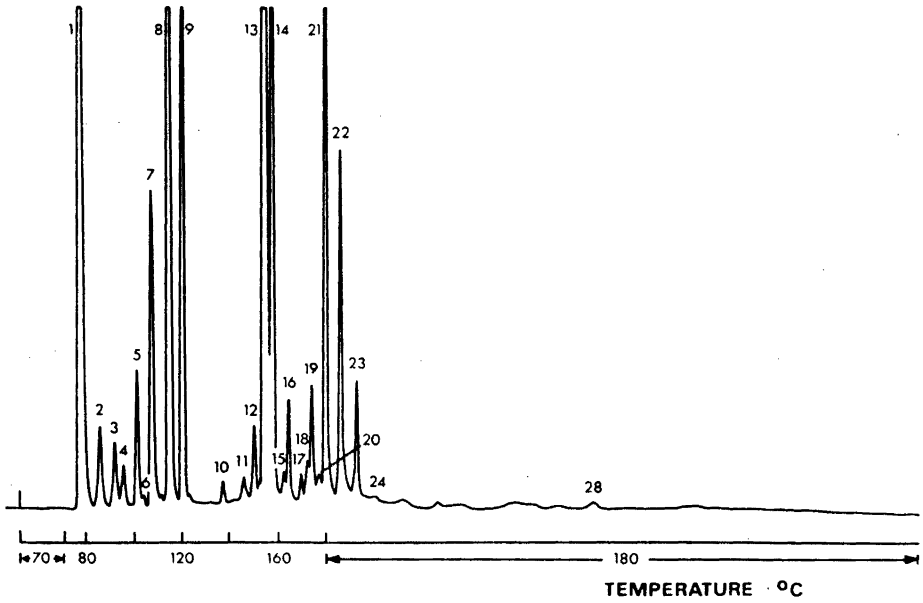

Fig. 1. Gas chromatogram of steam distilled coriander oil on 6 mm × 3 m LAC-2R-446 column.

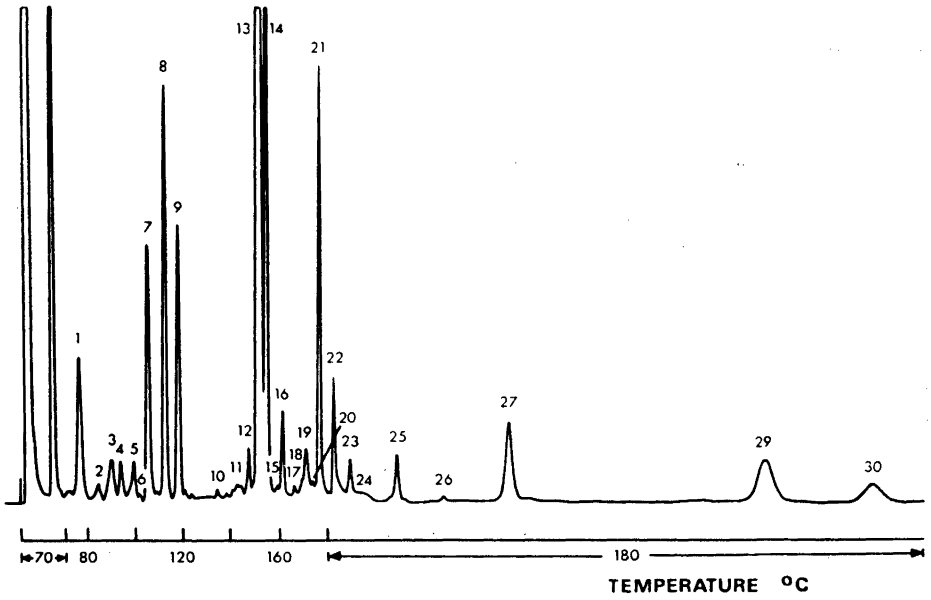

Fig. 2. Gas chromatogram of the pentane extract of the alcoholic coriander distillate on 6 mm × 3 m LAC-2R-446 column.

Table 1. Compounds identified in the steam distilled oil and the alcoholic distillate of coriander fruit.

Peak No.	Compound	Percentage		Evidence for identification
		Steam distilled oil	Extract of the alcoholic distillate	
1	α-Pinene	6.5	2.1	GLC, IR,[a] MS[a]
	α-Thujene	+	+	GLC
2	Camphene	0.39	0.11	GLC, MS[a]
3	β-Pinene	0.27	0.30	GLC, MS[a]
4	Sabinene	0.15	0.32	GLC, MS[a]
5	Myrcene	0.65	0.32	GLC, MS[a]
	α-Phellandrene	+	+	GLC
	3-Carene	+	+	GLC
6	α-Terpinene	0.05	0.02	GLC, MS[a]
7	Limonene	1.7	3.1	GLC, MS,[a] IR[a]
	β-Phellandrene	0.05	0.02	GLC, MS[a]
8	γ-Terpinene	10.1	4.5	GLC, MS,[a] IR[a]
	cis-Ocimene	+	+	GLC
	trans-Ocimene	+	+	GLC
9	*p*-Cymene	3.7	2.8	GLC, MS,[a] IR[a]
	Terpinolene	0.1	0.02	GLC, MS[a]
10	Nonanal	0.07	0.04	MS [12]
11	Linalool oxide	0.08	0.05	MS [13]
12	Decanal	0.31	0.38	GLC, MS [12]
13	Linalool	65	66	GLC, MS,[a] IR[a]
14	Camphor	5.0	6.7	GLC, MS,[a] IR[a]
15	Caryophyllene	0.06	0.01	GLC, MS[a]
	Undecanal			MS [12]
16	Terpinenol-4	0.31	0.67	GLC, MS[a], IR[a]
17	*trans*-2-Decenal	0.07	0.03	MS,[11] IR
18	Borneol	0.13	0.05	GLC, MS,[14] IR[15]
19	α-Terpineol	0.46	0.70	GLC, MS,[a] IR[a]
	Decanol			GLC, MS.[16] IR[a]
	Dodecanal			MS [12]
	Ethyl undecanoate			MS
	Heptadecane	+		MS [17]
20	Citronellol	0.02	0.03	GLC, MS, IR[a]
21	Geranyl acetate	2.6	3.8	GLC, MS, IR[a]
	Nerol	+	+	GLC, MS [14]
	trans-Citral	+	+	GLC, MS [18]
22	Geraniol	1.7	1.3	GLC, MS,[14] IR[a]
	Octadecane	+	+	MS [17]
23	*trans*-2-Dodecenal	0.44	0.25	MS, IR
24	Dodecanol	+	+	GLC, MS
25	Ethyl myristate		0.59	GLC, MS, IR[a]
26	Ethyl pentadecanoate		0.02	MS
27	Ethyl palmitate		2.3	GLC, MS,[17] IR[a]
28	Myristicin	0.05		MS,[19] IR[19]
29	Ethyl stearate		2.1	GLC, MS, IR[a]
30	Ethyl linoleate		0.64	GLC, MS, IR[a]

[a] = spectrum of an authentic sample.

were collected in 1 mm I.D. × 20 cm glass tubes cooled with dry ice.

The IR spectra were measured between KBr plates using a Perkin-Elmer 521 spectrophotometer fitted with a beam condenser.

The mass spectra were run on a Perkin-Elmer GLC-MS model 270 using a 15 m FFAP SCOT column or on a Varian CH7 GLC-MS using a 2 mm I.D. × 2 m SE-30 glass column in the gas chromatograph. A Spectro-System 100 MS computer was coupled to the Varian mass spectrometer.

Materials and procedure. The alcoholic distillate studied in this work was produced in Alko's flavour distillery from Moroccan coriander (fruit diameter 3 – 5 mm). The distillate is prepared by percolating the spice with 43 % alcohol-water mixture for two weeks and by distilling the percolate under reduced pressure. In the distillate the essential oil of coriander is present as a dilute alcoholic solution and for analyses it was concentrated by extracting with pentane as described previously.[10]

Another sample of coriander oil was obtained by three hours' steam distillation of 500 g of pulverized coriander fruit (from the same batch of herb as used for the alcoholic distillate.) The distillate was extracted with pentane, the extract dried over Na_2SO_4 and the pentane evaporated to leave about 2 g of oil.

The percentage composition of the samples was determined with LAC-2R-446 column from peak areas without using response factors. The composition of some unresolved monoterpene hydrocarbon peaks was determined with the capillary column.

The initial preparative fractionation of the steam distilled oil and the pentane extract of the alcoholic distillate was performed with an LAC-2R-446 column. The fractions obtained were further chromatographed on the SE-30 column to collect pure compounds. The GLC-MS analyses were made from the initial fractions using the SE-30 column.

The hydrocarbons were also analysed after separation from the oxygenated compounds in a silica gel column as described previously.[10] GLC-MS analysis was made directly from this fraction using an FFAP SCOT column.

RESULTS AND DISCUSSION

The gas chromatograms of steam distilled coriander oil and the pentane extract of the alcoholic distillate obtained with the LAC-2R-446 column are shown in Figs. 1 and 2. For the most part the numbered peaks correspond to the preparative fractions. The compounds identified, with their approximate percentage contribution and identification methods, are presented in Table 1.

Peaks 1 – 9 in Figs. 1 and 2 represent monoterpene hydrocarbons. These constitute about 24 % of the steam distilled oil and about 14 % of the aroma compounds of the alcoholic distillate. The same 16 compounds were found in both samples: α-pinene, β-pinene, camphene, sabinene, myrcene, limonene, β-phellandrene, α-terpinene, γ-terpinene, *p*-cymene, terpinolene, α-thujene, 3-carene, α-phellandrene, *cis*-ocimene, and *trans*-ocimene. The last five compounds were present in trace amount and were identified by gas chromatographic retention times only.

Some higher boiling compounds were isolated from the hydrocarbon fraction of the steam distilled oil. The largest of these (about 0.03 % of the oil) was identified as caryophyllene. Three other unidentified sesquiterpene hydrocarbons were detected by GLC-MS analysis. Sesquiterpenes have not previously been reported as constituents of coriander oil. Also found in this fraction were non-terpenic compounds heptadecane and octadecane, and two other saturated hydrocarbons, which according to IR and MS analyses would be bicycloalkanes of molecular weight 180 and 208.

The most important group of compounds in the aroma of coriander are the oxygen containing monoterpenes, which are distributed from peak 13 to 22 in the gas chromatograms. Linalool was found to form about 65 % of both samples. The other monoterpene alcohols, geraniol, α-terpineol, borneol, terpinenol-4, citronellol, and nerol, constituted together about 3 %, camphor 5 – 7 %, and geranyl acetate 3 – 4 %. *trans*-Citral and linalool oxide were also identified as minor components. Linalyl acetate and bornyl acetate, which are reported in many earlier papers,[3,6–8] could not be found in the samples studied.

Several non-terpenic oxygenated compounds were found as minor constituents of coriander oil. Four saturated aldehydes, nonanal, decanal, undecanal, and dodecanal, were identified. In addition, two unsaturated aldehydes, *trans*-2-decenal and *trans*-2-dodecenal, represented by peaks 17 and 23, were found. The IR spectrum of compound 17 exhibited a strong absorption band at 1690 cm^{-1} typical for α,β-unsaturated aldehyde and absorptions at 1630 and 970 cm^{-1} characteristic for a *trans*-disubstituted double bond. The mass spectrum matched well with the spectrum published for *trans*-2-decenal.[11]

The IR spectrum of compound 23 also had absorption bands (at 3020, 2810, 2720, 1688, 1632, 970 cm^{-1}) implying the presence of an aldehyde carbonyl group conjugated with a *trans*-disubstituted double bond. The mass spectrum showed the molecular peak at *m/e* 182 and the fragmentation pattern closely resembled that of *trans*-2-decenal. Accordingly, compound 23 was identified as *trans*-2-dodecenal. Two further aliphatic compounds, decanol and dodecanol, were found in trace amounts. Of these compounds decanal has been reported earlier,[3,5,7] while Schratz and Qadry [5] have shown the presence of *trans*-2-tridecenal in a sample of bulgarian oil.

Besides *p*-cymene, myristicin was the only aromatic compound identified. Neither thymol, found by Schratz and Qadry [5] in Indian coriander oil, nor anethol reported by Rasmussen *et al.*[9] were detected.

The ethyl esters of undecanoic, myristic, pentadecanoic, palmitic, stearic, and linoleic acids were found in the alcoholic distillate of coriander fruit. Together they constituted about 6 % of the aroma fraction. These compounds were absent from the steam distilled oil and are obviously formed during the preparation of the alcoholic distillate. Other qualitative differences between the two samples investigated proved to be small.

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