Chemistry of Natural Compounds, Vol. 39, No. 4, 2003

COMPOSITION OF VOLATILES OBTAINED FROM SPICES BY MICRODISTILLATION

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UDC 547.915

*Organic volatiles obtained by microdistillation from five common spices (*Coriandrum sativum *L.*, Foeniculum vulgare *Miller*, Piper nigrum *L.*, Anethum graveolens *L.*, Pimpinella anisum *L.*) *using an Eppendorf Micro-Distiller were analyzed by GC/MS. The results are presented in a comparative manner with conventional water distillation.*

Key words: microdistillation, hydrodistillation, GC/MS, *Coriandrum sativum* L., *Foeniculum vulgare* Miller, *Piper nigrum* L., *Anethum graveolens* L., *Pimpinella anisum* L.

The following common species were used in this study: *Coriandrum sativum* L., *Foeniculum vulgare* Miller, *Anethum graveolens* L., *Pimpinella anisum* L., Piper nigrum L.

Coriander fruits *C. sativum* yield 1.8% essential oil by steam distillation. Linalool and geraniol have been reported as the main constituents of coriander oil [1, 2, 4].

Our results demonstate (Table 1) that linalool, camphor, geraniol, and geranyl acetate were the main components of the fruit oil of *Coriandrum sativum*. This is consistent with the information available in the literature for the oil [7]. However, some notable differences were further observed in the microdistilled oils as compared to the hydrodistilled oil. Linalool was present in the microdistilled oils. Likewise, there was a drastic decrease in the amount of geraniol in the microdistilled oils from 5.1 to 1.8%. Prolongation of the microdistillation time resulted in the detection of only four main components (Table 1).

Anise fruits (*P. anisum*) yield 2–3% of volatile oil. This oil contains about 80–90% of *trans*-anethole [1–5].

Hydrodistilled and microdistilled oils gave different compositions. The results were not at all comparable, as seen in the table (Table 1). Therefore, in this case hydrodistillation cannot be replaced by microdistillation [7].

The fruits of *F. vulgare* contain 1–4% of volatile oil. Higher yields have been recorded. The principal constituents have been reported as *trans*-anethole (about 60%) and fenchone (10–30%). Minor constituents include limonene, anisaldehyde, and estragole (methyl chavicol) [1–6].

As in the case of aniseeds, for fennel, too, microdistillation cannot replace hydrodistillation since the results obtained by the two techniques were not comparable. Hydrodistilled oil gives the typical composition for sweet fennel oil (Table 1). However, high amounts of anisaldehyde in the microdistilled oils do not qualify this technique as suitable for fennel oil analysis under the tested conditions.

Black pepper (*P. nigrum*) contains 1–3% of volatile oil, which consists largely of terpenes, α- and β-pinene, phellandrene, diterpene and sesquiterpenes [1–4].

A short distillation period (55 min) in the microdistiller gave an oil composition quite similar to that obtained by hydrodistilation, as seen in Table 1. However, prolongation of the distillation time resulted in an increase in the amounts of sesquiterpenes and a marked decrease in the amounts of monoterpenes. Our results agree with the previously reported compositions of the oil of Piper nigrum with α-pinene (5–22%), β-pinene (5–36%), sabinene (7–42%), myrcene (3–10%), limonene (11–31%), δ-3-carene (9–10%), β-caryophyllene (10–22%), and α-humulene (2–6%) as the main constituents, and only exception being the lower content of sabinene in our oils [8].

Medicinal and Aromatic Plant and Drug Research Centre (TBAM) and Department of Pharmacognosy, Faculty of Pharmacy, Anadolu University, 26470 Eskisehir, Turkey. Published from Kimiya Prirodnykh Soedinenii, No. 4, pp 286-288, July-August, 2003. Original article submitted July 9, 2003.

0009-3130/03/3904-0355$25.00

TABLE 1. Composition of the Essential Oil, %

Compound	RI*	Hydrodistillation	Microdistillation, (55 min)	Microdistillation, (124 min)
		Coriandrum sativum L.		
α-Pinene	928	1.2	2.8	Tr.
γ-Terpinene	1043	2.8	3.5	Tr.
Linalool	**1051**	**68.8**	**81.1**	**89.0**
Camphor	1112	4.8	3.9	3.7
Terpinen-4-ol	1154	1.2	Tr.	-
Geraniol	1225	5.1	1.8	2.2
Geranyl acetate	1350	5.9	3.5	5.2
Tetradecanoic acid	1737	1.1	-	-
Hexadecanoic acid	1938	1.8	-	-
		Pimpinella anisum L.		
Methyl chavicol (estragole)	1167	3.9	7.7	2.0
Anisaldehyde	1215	1.4	3.9	0.4
(E)-Anethole	**1221**	**80.3**	**71.7**	**94.6**
α-Himachalene	1438	1.2	Tr.	0.5
Germacrene D	1464	2.4	Tr.	1.0
trans-Pseudoisoeugenyl-2-methylbutyrate	1802	4.8	-	0.8
		Foeniculum vulgare Miller		
Limonene	1013	8.8	5.5	5.0
Fenchone	1028	4.3	5.9	2.4
Methyl chavicol (estragole)	1163	7.9	7.0	4.9
Anisaldehyde	1204	1.6	11.4	6.9
(E)-Anethole	**1253**	**71.1**	**59.5**	**80.3**
		Piper nigrum L.		
α-Pinene	931	5.2	4.1	2.3
β-Pinene	969	9.1	8.3	4.4
Myrcene	977	3.7	3.0	1.6
α-Phellandrene	994	7.3	5.9	3.6
δ-3-Carene	1005	19.7	20.4	14.7
p-Cymene	1009	1.4	1.4	0.8
Limonene	1021	14.5	14.8	8.1
Terpinolene	1069	3.1	1.2	0.3
Linalool	1078	1.3	1.5	1.4
δ-Elemene	1328	1.0	1.0	1.3
β-Caryophyllene	1418	20.9	26.5	39.9
α-Guaiene	1429	0.8	0.8	1.1
α-Humulene	1445	2.1	2.2	3.5
β-Selinene	1476	2.2	2.0	4.0
α-Selinene	1485	1.7	1.6	3.1
β-Bisabolene	1494	0.8	0.8	1.5
Caryophyllene oxide	1563	0.7	0.5	1.1
		Anethum graveolens L.		
Limonene	1020	23.5	23.0	6.9
cis-Dihydrocarvone	1162	1.1	1.8	1.6
trans-Dihydrocarvone	1171	12.6	14.6	14.5
Carvone	**1219**	**40.4**	**46.2**	**53.9**
Myristicine	1480	1.3	0.5	1.0
Dillapiole	1589	18.6	9.8	21.7

*Retention index on a non-polar column. Tr.: trace (< 0.1%).

Dill seeds (*A. graveolens*) have been reported to contain 3–4% volatile oil, with carvone and limonene as the main constituents [1, 2, 4].

Except for a slightly higher content of carvone and 10–50% lower content of dillapiole and myristicine, the results of microdistilled oils are comparable with those of the hydrodistilled oil (Table 1). However, via some manipulation with the distillation program the conditions can be adjusted to get an oil composition at par with the hydrodistilled oil [7].

EXPEREMINTAL

The species were purchased from a local store in Eskisehir. Drugs were crushed and hydrodistilled for 3 hours using a Clevenger-type apparatus.

The crushed spices were subjected to microdistillation for 55 and 124 minutes.

Microdistillation Conditions. Crushed plant material was added to sample vial containing 10 ml distilled water. NaCl (2.5 g) and water (0.5 ml) were placed in the collecting vial. *n*-Hexane (300 ml) was added into the collecting vial to trap the volatile components. The sample vial was heated to 108°C at a rate of 20°C/min and kept at this temparature for 90 min, then heated to 112°C at a rate of 20°C/min and kept at this temperature for 30 minutes. Finally the sample was subjected to post-run for 2 min under the same conditions. The collecting vial was cooled to –5°C during distillation. After the distillation was completed the organic layer in the collection vial was separated and injected in – to the GC/MS system [9, 10].

The same sample was heated to 100°C at a rate of 20°C/min and kept at 100°C for 15 min, then heated to 112°C at a rate of 20°C/min and kept at this temperature for 35 min. Finally the sample was subjected to post-run for 2 min under the same conditions [9, 10].

The oils obtained by both techniques were analyzed by GC/MS

GC-MS Conditions. The oils was analyzed by GC/MS using a Shimadzu GC-MS QP5050A system. A CPSil5CB column (25m × 0.25 mm i.d., 0.4 mm film thickness) was used with helium as a carrier gas. The GC oven temperature was kept at 60°C and programmed to 260°C at a rate of 5°C/min, then kept constant at 260°C for 40 min. Split flow was adjusted at 50 mL/min. The injector temperature was at 250°C. MS were taken at 70 eV. Mass range was between *m/z* 30 to 425. A library search was carried out using the Wiley GC-MS Library and the inhouse TBAM Library of Essential Oil Constituents. The MSs were also compared with those of reference compounds and confirmed with the aid of retention indices from published sources.

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