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Comparison of Microwave-Assisted Hydrodistillation and Hydrodistillation Methods for the Analysis of Volatile Secondary Metabolites

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Abstract

Microwave-assisted hydrodistillation (MWHD) and hydrodistillation (HD) were carried out for the analysis of volatile components in whole and ground fruits of *Anethum graveolens* L. (dill seed) and *Coriandrum sativum* L. (coriander seed). Fruits were distilled using a microwave oven modified to fit a Clevenger apparatus. The effect of microwave energy on the yield and composition of the essential oil was investigated against the classical hydrodistillation. Essential oils of all samples were analyzed by GC-FID and gas chromatography-mass spectrometry (GC-MS). In the whole dillseed oil, the amounts of *cis*-isodihydrocarvone (from 7.5% to 10.9%) and carvone (from 45.7% to 69.3%) were increased by microwave energy while limonene (from 17.7% to 4.7%), myristicin (from 8.7% to 5.7%) and dill apiole (from 14.1% to 6.1%) were decreased. Grinding of the material also increased the amounts of main components except for myristicin and dill apiole. A decrease in the linalool content of the coriander oil (from 80.0% to 75.5%) was observed in the microwave-assisted hydrodistilled ground fruits. Microwave-assisted distillation appeared to increase the amounts of fatty acids, for example, tetradecanoic acid (from 2.8% to 8.8%) and hexadecanoic acid (from 1.9% to 6.0%) in coriander oil.

Keywords: *Anethum graveolens*, *Coriandrum sativum*, microwave-assisted hydrodistillation.

Introduction

The fruits of *Anethum graveolens* L. (dill) and *Coriandrum sativum* L. (coriander) (Apiaceae) are used as a spice in Europe; northern Africa, western, central, and southern Asia; as well as in Turkey. Dill and coriander fruits are used as appetizer, digestive, sedative, and for colic (Baytop, 1999). The fruits contain oils, and there are several reports on the composition (Shatar & Altantsetseg, 2000; Lazutka et al., 2001; Bouwmeester et al., 1995; Carrubba et al., 2002; Delaquis et al., 2002; Jirovetz et al., 2003; Mazza, 2002). Conventional hydrodistillation (HD) with a modified Clevenger apparatus is widely used to obtain the essential oil from plants for scientific investigations. In this technique, plant material was distilled in water for at least 3 h in a closed vessel. Microwave-assisted methods have been used increasingly in the past few years, especially for extraction (Tomaniova et al., 1998; Pino et al., 2000; Simoneau et al., 2000; Szentmihalyi et al., 2002; Criado et al., 2003; Shu et al., 2003), but the microwave-assisted hydrodistillation (MWHD) method is rarely used to recover volatile components (Ganzler et al., 1986; Craveiro et al., 1989; Pare, 1994; Xiong et al., 2003; Lucchesi et al., 2004). In this method, plant material placed in a Clevenger apparatus was heated inside a microwave oven for a short period of time to take out the essential oil. Heat is produced by microwave energy so the sample reaches its boiling point very rapidly, leading to very short extraction or distillation times with fresh materials (Ganzler et al., 1986; Craveiro et al., 1989; Pare, 1994; Tomaniova et al., 1998; Pino et al., 2000; Simoneau et al., 2000;

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Szentmihalyi et al., 2002; Criado et al., 2003; Shu et al., 2003; Xiong et al., 2003; Lucchesi et al., 2004;). It is possible to achieve distillation with the indigenous water of the material.

The aim of this study was to provide a rigorous comparison between microwave-assisted hydrodistillation and classical hydrodistillation techniques to obtain essential oil from Apiaceae fruits. Both whole and ground fruits were evaluated from the point-of-view of the effect of microwave energy on oil composition.

Materials and Methods

Plant material and reagents

Fruits of *Anethum graveolens* L. and *Coriandrum sativum* L. were obtained from Türer Ltd. Sti. (Izmir, Turkey). Distilled water was used in the distillation.

Hydrodistillation

Plant material (100 g) and 1000 ml distilled water placed in a 2000 ml round-bottom flask and connected to a Clevenger-type apparatus. Hydrodistillation was performed for 3 h after boiling. Oil yields of the samples were calculated on a moisture free basis.

Table 1. The yields of essential oils of fruits of *Anethum graveolens* and *Coriandrum sativum*.

	Classical hydrodistillation		Microwave-assisted hydrodistillation	
Sample	Whole fruit	Ground fruit	Whole fruit	Ground fruit
Anethum graveolens	2.1	2.1	2.0	2.5
Coriandrum sativum	0.4	0.4	0.4	0.5

Microwave-assisted hydrodistillation

The oils were obtained from the fruits of dill and coriander by hydrodistillation for 60 min using a Clevenger-type apparatus placed in a modified microwave oven (Milestone ETHOS E Microwave Labstation). During distillation, time, temperature, pressure, and power were monitored and controlled with the "easy-CONTROL" software package of the system. Microwave power applied to the plant material was controlled by a shielded thermocouple inserted directly into the flask. The oven was operated for 10 min at 800 W up to 100°C, and then kept at 100°C for 50 min at 500 W followed by 5 min of ventilation. Oil yields of the samples were calculated on moisture-free basis.

Table 2. The composition of essential oils of *Anethum graveolens* obtained from hydrodistillation and microwave-assisted hydrodistillation.

		Classical hydrodistillation		Microwave-assisted hydrodistillation	
RRI	Compounds	Whole fruit	Ground fruit	Whole fruit	Ground fruit
1176	α-Phellandrene	0.3	0.3	0.2	0.3
1203	Limonene	17.9	20.5	4.7	17.6
1218	β-Phellandrene	tr	tr	0.1	0.1
1224	*o*-Mentha-1(7),5,8-triene	0.5	0.4	0.2	0.3
1280	*p*-Cymene	0.1	0.2	0.2	0.2
1452	α,*p*-Dimethylstyrene	0.1	0.1	0.1	0.1
1458	*cis*-1,2-Limonene epoxide	0.1	0.1	0.1	0.1
1468	*trans*-1,2-Limonene epoxide	0.1	0.1	0.1	0.1
1529	Dill ether	tr	0.1	0.1	0.1
1624	*trans*-Dihydrocarvone	1.9	1.3	1.1	1.0
1645	*cis*-Isodihydrocarvone	7.5	10.1	10.9	9.1
1751	Carvone	45.7	52.2	69.3	54.3
1760	Isodihydrocarveol	0.3	0.3	0.3	0.2
1783	*neo*-Isodihydrocarveol	0.3	0.2	0.3	0.3
1845	*trans*-Carveol	tr	tr	0.2	0.1
1856	Carvone-1,2-epoxide	0.1	0.1	0.1	0.1
1865	Isopiperitenone	0.1	0.1	0.1	0.1
1882	*cis*-Carveol	0.1	0.1	0.1	0.1
2245	Elemicin	0.1	tr	tr	0.1
2296	Myristicin	8.7	5.5	5.6	5.9
2384	Dill apiole	14.1	8.1	6.2	9.8
TOTAL		98.0	99.8	100	100

tr: <0.1. RRI, relative retention indices.

Table 3. The composition of essential oils of *Coriandrum sativum* obtained from hydrodistillation and microwave-assisted hydrodistillation.

		Classical hydrodistillation		Microwave-assisted hydrodistillation	
RRI	Compounds	Whole fruit	Ground fruit	Whole fruit	Ground fruit
1032	α-Pinene	2.6	2.1	0.1	1.0
1118	β-Pinene	0.3	0.3	—	0.2
1132	Sabinene	0.2	0.1	—	0.1
1174	Myrcene	—	0.2	—	0.2
1203	Limonene	0.2	0.3	—	0.2
1255	γ-Terpinene	3.3	—	0.5	3.0
1280	*p*-Cymene	2.1	2.1	0.3	1.0
1290	Terpinolene	tr	0.1	—	0.1
1400	Nonanal	0.1	0.1	0.1	0.1
1450	*trans*-Linalool oxide	0.1	0.1	0.1	0.1
1474	*trans*-Sabinene hydrate	tr	—	0.1	0.1
1478	*cis*-Linalool oxide	0.1	0.1	0.1	—
1487	Citronellal	0.1	0.1	0.1	0.1
1506	Decanal	0.1	0.1	0.2	0.1
1532	Camphor	0.4	0.6	—	0.7
1553	Linalool	80.0	79.6	75.5	81.2
1562	Octanol	0.3	0.3	0.5	0.4
1611	Terpinen-4-ol	0.3	0.3	0.3	0.4
1655	(*E*)-2-Decenal	tr	0.1	0.1	0.1
1668	Citronellyl acetate	tr	0.1	0.1	0.1
1704	Myrtenyl acetate	tr	0.1	—	tr
1706	α-Terpineol	0.2	0.3	0.3	0.3
1719	Borneol	0.1	0.1	—	0.1
1733	Neryl acetate	tr	0.1	—	0.1
1741	β-Bisabolene	tr	—	0.1	—
1751	Carvone	0.2	0.2	—	0.2
1765	Geranyl acetate	1.7	2.8	1.5	4.1
1772	Citronellol	0.2	—	—	—
1830	Tridecanal	tr	—	0.1	—
1849	(*E*)-2-Dodecenal	0.2	0.4	0.2	0.5
1857	Geraniol	0.9	1.0	1.0	1.1
2008	Caryophyllene oxide	tr	—	0.2	0.1
2030	Methyl eugenol	tr	—	0.1	0.1
2296	Myristicin	—	—	0.1	—
2298	Decanoic acid	—	—	0.1	—
2400	Undecanoic acid	—	—	0.2	—
2503	Dodecanoic acid	—	—	1.5	—
2670	Tetradecanoic acid	2.8	2.3	8.8	2.7
2822	Pentadecanoic acid	—	0.2	0.6	0.2
2931	Hexadecanoic acid	1.9	2.5	6.0	1.3
TOTAL		98.4	96.7	98.9	100

tr: <0.1. RRI, relative retention indices.

Gas chromatography

All the oils were analyzed by gas chromatography (GC) using a Hewlett Packard HP6890 system with Innowax FSC column (60 m × 0.25-mm Ø, with 0.25-μm film thickness). Nitrogen (from 1.2 to 0.9 ml/min ramp flow) was used as carrier gas. The GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min and then kept constant at 220°C for 10 min and programmed to 240°C at a rate of 1°C/min. Split flow was adjusted at 12 ml/min with 10:1 split ratio. The injector and FID detector temperatures were adjusted at 250°C. The relative percentage amounts of the separated compounds were calculated from FID chromatograms.

Gas chromatography-mass spectrometry

The essential oils were analysed using a Hewlett Packard G1800A GCD system with Innowax FSC column

(60 m × 0.25-mm Ø, with 0.25-μm film thickness). Helium (0.8 ml/min) was used as carrier gas. The GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min and then kept constant at 220°C for 10 min and programmed to 240°C at a rate of 1°C/min. The mass range was recorded from m/z 35 to 425. The split flow was adjusted at 50 ml/min with 50:1 slit ratio. The injector temperature was adjusted at 250°C. MS are recorded at 70 eV. Alkanes were used as reference points in the calculation of relative retention indices (RRI).

Identification of compounds

The components of essential oils were identified by comparison of their mass spectra with those of Baser Library of essential oil constituents, Wiley GC/MS Library, Adams Library, Mass Finder.3 Library, and confirmed by comparison of their retention indices.

Results and discussion

The whole or ground fruits of dill and coriander samples were distilled both by HD and MWHD methods. All the samples were distilled using a Clevenger-type apparatus for 3 h in a heating mantle and for 60 min in a microwave oven, respectively. The yields of essential oils calculated on a moisture-free basis are shown in Table 1. The oil yields of whole or ground fruits were found to be similar in HD. Dill fruit yielded more essential oil (2.1%) than coriander fruit (0.4%). Microwave energy appeared to slightly increase the yield of essential oil in both ground dill (2.5%) and ground coriander (0.5%) samples. In microwave-assisted hydrodistillation, distillation time was shorter than classical hydrodistillation, and also the sample reached boiling stage more rapidly. This is an advantage of MWHD if more samples are to be distilled in a shorter time period.

All the oils were analyzed using GC-FID and GC-MS. Relative percentages of the characterized compounds calculated from FID integrator are shown in Tables 2 and 3. Carvone, limonene, and dill apiole were found as main compounds in dillseed oils. Grinding appeared to increase the amount of carvone in the oil obtained by HD (from 45.7% to 52.2%), whereas its amount was found to decrease in the oil obtained by MWHD (from 69.3% to 54.3%). However, microwave energy resulted in the production of carvone-rich oils from the fruits of *A. graveolens*. On the other hand, grinding resulted in a decrease in the amount of dill apiole (from 14.1% to 8.1%) in HD. Its amount rose from 6.2% to 9.8% in MWHD oil. As seen in Table 2, MWHD gave the oil with less limonene. MWHD afforted slight changes in the amounts of carvone derivatives such as *trans*-dihydrocarvone and *cis*-isodihydrocarvone (Table 2).

Coriander fruits yielded linalool-rich oils by both distillation techniques. No significant difference was observed in the linalool content (80%) and ground fruits (79.6%) subjected to HD; MWHD, however, appeared to extract more linalool from ground dillseed. Monoterpene hydrocarbon content of the MWHD oils were less than HD-oils (Table 3). As shown in Table 3, grinding of the material also increased the content of geranyl acetate in MWHD coriander oil. Fatty acid content appeared to increase in coriander oils obtained by microwave energy (Table 3).

HD takes 3 h to complete, whereas 1 h is enough for a complete distillation by the microwave technique. The results have shown that there is no significant difference in oil yields by both techniques, and similar oil profiles are obtained. In the same cases, MWHD appeared to yield more of oxygenated components than terpenic hydrocarbons. This is an advantage in the production of olfactorily more appealing oils. MWHD is still in its infancy, as there are only a few papers published. More research may prove it to be an advantageous technique over HD even for industrial applications.

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