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Composition of the essential oil of dill, celery, and parsley from Estonia

Anne Orav*, Tiiu Kailas, and Anna Jegorova

Institute of Chemistry, Tallinn Technical University, Ehitajate tee 5, 19086 Tallinn, Estonia

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Abstract. The qualitative and quantitative composition of the essential oil of dill, celery, and parsley growing in Estonia was studied using the simultaneous distillation/extraction micro-method for oil isolation and capillary gas chromatography for analysing the extracts. The yields of the oils from dried aromatic plants after two hours distillation were 2.9–4.3 mg/g. Forty-eight compounds were identified representing over 96% of the total oil. α-Phellandrene (75.1–75.8%), β-phellandrene (7.4–7.9%), dill ether (2.2–3.9%), and limonene (2.8–2.9%) were the principal components of dill oil. *p*-1,3,8-Menthatriene (40.0–44.6%), β-phellandrene (15.1–16.9%), myristicin (13.0–13.1%), and myrcene (6.5–7.0%) were characteristic constituents in oil from parsley leaves, but apiole (34.5%), myristicin (28.8%), and terpinolene (13.2%) predominated in parsley root oil. Celery oil contained in high quantities limonene (62.4–70.3%), (Z)-β-ocimene (10.1–10.5%), and phthalide isomers (total 13.4–16.6%). Drying of aromatic plants for four weeks at room temperature did not significantly change the chemical composition of their essential oil.

Key words: *Anethum graveolens*, *Petroselinum crispum*, *Apium graveolens*, Apiaceae, essential oil composition, effect of drying.

INTRODUCTION

Aromatic plants include a broad range of species that are used for their aroma characteristics as flavoring in foods and beverages and as fragrances in pharmaceutical and industrial products. They are marketed fresh, which is best, frozen and dried, which makes them available year round. Today aromatic plants are incredibly popular and the volume of their production is increasing for both processing and fresh markets.

* Corresponding author, aorav@chemnet.ee

The chemical composition of essential oil of aromatic herbs has been the subject of several studies [1–21]. The content of the main components of oils has been found to vary according to the geographical origin, harvesting time, growth conditions, isolation method, and so on. The essential oils of aromatic plants growing in Estonia have not been studied by capillary gas chromatography earlier.

The aim of the present work was to identify the compounds that constitute the essential oils of aromatic plants growing in Estonia and to determine the effect of drying process of plant material on the chemical composition of their oils. Dill, celery, and parsley as the most widely used aromatic plants in Estonia were chosen as objects for this research.

EXPERIMENTAL

Materials

Commercial plant material of Estonian origin was used. Each plant species was bought fresh. All fresh material was divided into two parts, and essential oils were directly isolated from one part. The other part of the material was dried during 4 weeks at room temperature in accordance with all requirements of an air drying method. Characterization of the plant material and the yields of essential oils are given in Table 1.

It is a fact that the water content in fresh plant material is very variable. Carefully dried plant material consists practically only of dry matter. Therefore the yields of oil calculated for dry material are more accurate and more suitable for comparison than those for fresh material. The highest oil yield from dried plants was obtained from dill (4.3 mg/g) and the lowest from parsley leaves (2.9 mg/g).

Table 1. Characterization of the aromatic plant samples

Material	Plant part	Oil yield, mg/g	
		Fresh	Dried
Dill, *Anethum graveolens* L. (collected before flower formation)	Leaves with stems	0.80	4.3
Parsley, *Petroselinum crispum* (Mill.) Nyman	Leaves with stems	0.52	2.9
	Roots	0.42	–
Celery, *Apium graveolens* L.	Leaves with stems	0.37	3.8

Isolation of essential oil

The simultaneous distillation and extraction (SDE) method was chosen for essential oil isolation using Marcusson's type micro-apparatus with *n*-hexane (500 µL) as solvent and *n*-tetradecane (2 µL) as internal standard. Distillation time was 2 h. For the isolation procedure 10–20 g of plant material was used.

Capillary gas chromatography

n-Hexane extracts (1–5 µL) of the essential oils were analysed using a Chrom-5 gas chromatograph with FID on two fused silica capillary columns (50 m × 0.20 mm i.d.) with bonded stationary phases (OV-101, film thickness 0.50 µm and SW-10, film thickness 0.25 µm). Helium with a flow rate 0.4–0.6 mL/min was used as the carrier gas with the split ratio of 1 : 150. The column temperature was programmed from 50 to 250 °C (OV-101) and from 70 to 230 °C (SW-10) at 2 °C/min. The injector temperature was 200 °C.

The identification of the oil components was based on the comparison of their retention indices RI on two columns with the corresponding data of our RI data bank and with RI data presented in the literature. The results obtained were confirmed by GC/MS.

The quantitative composition of the essential oils was calculated using the internal normalization method. The yields of the oil isolated by the SDE method from aromatic plants were calculated by the internal standard method using pure *n*-tetradecane (>99.9%) as internal standard.

Gas chromatography–mass spectrometry

The mass spectra of the compounds were recorded at 70 eV on a Hewlett Packard GC/MS 5988A instrument, the mass number (m/z) range 30–350. The fused silica capillary column (10 m × 0.20 mm) with HP-17 as stationary phase was used. The oven temperature program was from 50 to 250 °C at 8 °C/min. The injector temperature was 280 °C.

RESULTS AND DISCUSSION

Common dill oil

The components of dill oil are listed in Table 2 together with their RI data on two columns and with their percentage amounts. We identified 29 compounds. Analysis indicated that the principal aroma compounds in Estonian dill oil were α-phellandrene (75.1–75.8%), β-phellandrene (7.4–7.9%), dill ether (2.2–3.9%), and limonene (2.8–2.9%). α-Pinene, (E)-β-ocimene, myrcene, and *p*-cymene were found in the oils in quantities from 0.6 to 2.0% and the other oil components constituted below 0.5%.

Table 2. Identification data and percentage composition of essential oils of aromatic plants. The components identified in the highest yields are in bold

Compound	RI		Concentration, %						
	OV-101	PEG 20M	Dill leaves		Celery leaves		Parsley leaves		Parsley roots
			Fresh	Dried	Fresh	Dried	Fresh	Dried	Fresh
α-Thujene	921	1029	0.3	0.4	–	–	–	–	–
α-Pinene	928	1029	1.6	2.0	0.2	0.2	1.0	2.8	0.2
Camphene	940	1074	tr.	tr.	–	–	0.1	tr.	0.1
Sabinene	964	1125	0.1	0.1	0.2	0.2	0.2	0.2	0.1
β-Pinene	967	1116	0.1	0.1	0.4	0.4	0.6	1.2	2.9
Myrcene	982	1161	0.6	0.6	1.3	1.3	**7.0**	**6.5**	0.9
α-Phellandrene	995	1167	**75.1**	**75.8**	0.1	0.4	**2.2**	**4.1**	0.3
α-Terpinene	1008	1180	–	–	–	–	0.1	0.1	–
p-Cymene	1010	1273	0.6	1.2	0.1	0.1	0.1	0.3	–
Limonene	1020	1204	**2.8**	**2.9**	**70.3**	**62.4**	**2.8**	**3.2**	0.5
β-Phellandrene	1020	1213	**7.9**	**7.4**	0.1	0.3	**16.9**	**15.1**	**4.6**
(Z)-β-Ocimene	1028	1232	0.1	0.1	**10.1**	**10.5**	0.1	tr.	0.1
(E)-β-Ocimene	1038	1250	1.3	1.2	0.3	0.2	0.2	0.2	–
γ-Terpinene	1048	1246	–	–	2.3	1.6	0.1	0.1	0.2
α-*p*-Dimethyl-styrene	1070		0.4	0.4	–	–	–	–	–
1-Methyl-4-isopropenylbenzene	1074	1428					**2.4**	**4.2**	0.1
Terpinolene	1077	1282	0.4	0.5	–	–	**2.9**	**2.6**	**13.2**
***p*-1,3,8-Menthatriene**	1096	1387	–	–	tr.	tr.	**44.6**	**40.0**	0.4
1-Phenyl-2-butene	1152	1414	–	–	0.3	0.3	0.4	0.3	tr.
Dill ether	1164	1506	**3.9**	**2.2**	–	–	–	–	–
Myrtenal	1166	1617	–	–	–	–	0.5	0.4	–
α-Terpineol	1174	1693	–	–	–	–	0.2	0.3	0.1
Carvone	1215	1725	tr.	tr.	–	–	0.1	tr.	–
Bornyl acetate	1268	1574	tr.	0.1	–	–	0.2	0.1	–
(E)-β-Caryophyllene	1412	1589	–	–	0.1	0.2	0.3	0.2	–
β-Farnesene	1450	1662	0.2	0.2	0.1	tr.	0.1	0.1	0.2
Sesquiterpene	1465	1675	–	–	–	–	0.8	0.6	1.5
Germacrene D	1467	1690	0.3	0.4	–	–	–	–	–
Bergaptene	1477	1910	–	–	–	–	0.3	0.2	1.8
Myristicin	1500	2246	0.5	0.3	–	–	**13.0**	**13.1**	**28.8**
β-Bisabolene	1504	1737	0.1	0.1	–	–	0.5	0.2	0.9
δ-Cadinene	1512	1749	–	–	–	–	0.1	0.1	–
γ-Selinene	1517	1755	–	–	–	–	tr.	tr.	2.1
Elimicin	1526	2215	–	–	–	–	–	–	1.1
Germacrene B	1549	1813	–	–	–	–	tr.	0.1	0.1
Viridiflorol	1575	2069	–	–	0.1	0.1	–	–	–
Phthalide isomer*	1585		0.2	0.3	tr.	0.1	–	–	–
Phthalide isomer*	1600		–	–	0.3	0.8	–	–	–
Phthalide isomer*	1605		–	–	0.7	1.7	0.1	tr.	0.3
T-Cadinol	1624	2156	0.2	0.1	–	–	0.1	0.1	0.1
Apiole	1645	2460	0.3	0.5	0.1	0.7	0.2	0.5	**34.5**
Farnesol*	1652	2275	0.1	0.3	0.1	0.1	0.1	0.1	0.1
Phthalide isomer*	1674		–	–	**2.9**	**4.9**	–	–	0.7

Table 2. *Continued*

Compound	RI		Concentration, %						
	OV-101	PEG 20M	Dill leaves		Celery leaves		Parsley leaves		Parsley roots
			Fresh	Dried	Fresh	Dried	Fresh	Dried	Fresh
Phthalide isomer*	1684		0.1	0.1	**9.4**	**8.4**	–	–	0.2
Phthalide isomer*	1691		–	–	0.1	0.7	–	–	–
n-Heptadecane	1700	1700	0.1	0.2	0.1	0.3	tr.	tr.	0.1
n-Octadecane	1800	1800	0.2	0.2	0.1	0.3	tr.	tr.	tr.
n-Nonadecane	1900	1900	0.1	0.1	–	–	–	–	0.2
COMPONENT GROUPS:									
Monoterpenes			90.3	91.1	85.3	77.5	78.8	76.1	23.5
Oxygenated monoterpenes			3.9	2.3	–	–	1.0	0.8	0.1
Sesquiterpenes			0.6	0.7	0.2	0.2	1.8	1.5	6.6
Oxygenated sesquiterpenes			0.3	0.4	0.2	0.2	0.2	0.2	0.2
Aromatic compounds			1.8	2.4	0.5	1.1	16.1	18.4	64.5
Phthalides			0.3	0.4	13.4	16.6	0.1	tr.	1.2
n-Alkanes			0.4	0.5	0.2	0.6	tr.	tr.	0.3
Total, %			97.6	97.8	99.8	96.2	98.3	97.0	96.4

– not found;
tr. – traces (<0.05%);
* Specific isomer not identified.

The concentration of α-phellandrene, the principal component of Estonian dill oil, was too high compared to those reported by other investigators [4–7]. Carvone (14–58%), found to be one of the main components in Cuban [5, 6], Romanian and Kazakhstan [4], and Hungarian [7] dill oils, occurred in trace amounts in the Estonian dill oil analysed. Such a divergence can be explained by differences in growth stages of plants used for analysis. Dill herb tested in the present work was harvested before flower formation, but the other studied dill samples [4–7] were harvested at the time of flowering or during the fruit formation period. In the essential oil of dill herb from Finland [3] harvested before bud formation large amounts of dill ether (37%) and α-phellandrene (32%) were found.

The chemical composition of essential oils obtained from fresh and dry materials was almost identical. Only the content of dill ether decreased from 3.9% to 2.2% on drying.

Celery oil

We identified 26 compounds in the celery oil (Table 2). The main group of compounds forming celery oil consisted of monoterpenoid hydrocarbons, among them limonene (62.4–70.3%), (Z)-β-ocimene (10.1–10.5%), γ-terpinene (1.6–2.3%), and myrcene (1.3%). The quantities of other monoterpenes and

sesquiterpenes in the celery oil were below 0.5%. Phthalide isomers (total 13.4–16.6%) were the second major group present in celery oil. These compounds appear to be most important in the aroma of celery [9–15]. The total amount of phthalides in Belgian celery oils was 6–11% [12]. By the data of Van Wassenhove et al. [11, 12] the main phthalide isomers in celery oils of Belgium are butylphthalide, trans-neocnidilide, and senkyunolide. MacLeod et al. [15] found 3-butylphthalide and sedanolide in high quantities in celery oil from Libya.

The analysis of oils obtained from fresh and dried materials indicated some changes in the oil composition. As it can be seen in Table 2, the percentage of limonene was reduced by the drying from 70.5% to 62.4% and the content of phthalides increased by 3.2%.

Parsley oil

In the essential oil of parsley leaves, stems, and roots 36 compounds were found (Table 2). These made up over 96% of the total oil. The oil from parsley leaves (with stems) contained mostly monoterpenes (76.1–78.8%). Aromatic compounds were found to form from 16.1% to 18.4% and oxygenated terpenes only from 1.0% to 1.2%. The oil from parsley roots contained a 3.3 times lower amount of monoterpenes (23.6%) and 2.7 times higher amount of aromatic compounds (64.5%) than the aboveground plant did.

Compounds present in greatest concentrations in parsley leave oil were *p*-1,3,8-menthatriene (40.0–44.6%), β-phellandrene (15.1–16.9%), myristicin (13.0–13.1%), and myrcene (6.5–7.0%). Terpinolene, α-phellandrene, limonene, 1-methyl-4-isopropenylbenzene, β- and α-pinene were found in quantities from 0.6% to 4.2% and the other constituents below 0.8%. The main compounds of parsley root oil were apiole (34.5%), myristicin (28.8%), terpinolene (13.2%), and β-phellandrene (4.6%).

The same compounds were found in the parsley leaves and roots as the main components by other investigators [16–21]. The intensity of odours was measured for each identified compound in oils from parsley leaves by researchers from Sweden [17]. No single compound was described as being uniquely parsley-like; however, the aromas of *p*-1,3,8-menthatriene, β-phellandrene, myristicin, and apiole were found to have very strong odour intensities. It was considered that the aroma of parsley leaves was caused by a mixture of at least these naturally occurring volatile compounds. Myrcene, terpinolene, and *p*-cymenene, reported to have strong intensities, could also influence the aroma of parsley [17–21].

The oils obtained from fresh and dried materials did not have great differences in their chemical composition. Decreasing of the amount of *p*-1,3,8-menthatriene by 4.6% and of the amount of β-phellandrene by 1.8% occurred in parsley leave oil by drying. The content of 1-methyl-4-isopropenylbenzene, α-phellandrene, and α- and β-pinene increased after drying by 0.6–1.8%. Variations in the amounts of other components were insignificant.

CONCLUSION

The analysis of the essential oils produced from aromatic plants growing in Estonia demonstrated good aroma characteristics of Estonian aromatic plants. Drying, which was carried out for four weeks at room temperature, did not change the chemical composition of essential oils from dill, parsley, and celery significantly.

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Eestis kasvatatud tilli, selleri ja peterselli eeterliku õli koostis

Anne Orav, Tiiu Kailas ja Anna Jegorova

Eestis kasvatatud tilli, selleri ja peterselli eeterlik õli eraldati samaaegse destillatsiooni ja ekstraktsiooni mikromeetodil ning analüüsiti kapillaargaasikromatograafilisel meetodil. Õli saagised kuiva taimmaterjali kohta jäid vahemikku 2,9–4,3 mg/g. Tilli õli põhikomponentideks olid alfa-fellandreen (75,1–75,8%), beeta-fellandreen (7,4–7,9%), limoneen (2,8–2,9%) ja tilli eeter (2,2–3,9%). Peterselli lehtede õlis domineerisid *p*-1,3,8-mentatrieen (40,0–44,6%), beeta-fellandreen (15,1–16,9%) ja müristitsiin (13,0–13,1%), peterselli juurikate õlis aga leiti rohkesti apiooli (34,5%), müristitsiini (28,8%) ja terpinoleeni (13,2%). Selleri õli iseloomustas suur limoneeni (62,4–70,3%), (Z)-beeta-otsimeeni (10,1–10,5%) ja ftaliidide (13,4–16,6%) sisaldus. Uuritud maitsetaimede kuivatamine ühe kuu jooksul toatemperatuuril ei avaldanud õli koostisele olulist mõju.