

Chemical composition of the dill essential oils (*Anethum graveolens* L.) from Bulgaria

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The oil of dill (*Anethum graveolens* L.) from Bulgaria harvested during various growth stages of the plant (flower, herb and fruits) was investigated by GC and GC/MS. The yields of flower, herb and fruit oils were 0.36 % v/w, 0.90 % v/w and 3.61 % v/w, respectively. The main compounds (over 3 %) in flower oil were: myristicin (23.24 %), carvacrol (22.04 %), carvone (18.93 %), limonene (11.20 %), 3,9-oxy-*p*-menth-1-ene (7.59 %), α -phellandrene (6.50 %), and dihydrocarvone (4.63 %). The major constituents (over 3 %) in herb oil were: α -phellandrene (21.83 %), carvacrol (20.85 %), limonene (18.96 %), 3,9-oxy-*p*-menth-1-ene (12.31 %), carvone (8.40 %), myristicin (7.11 %) and *p*-cymene (3.34 %). The main components (over 3 %) in fruit oil were: carvone (33.57 %), myristicin (24.21 %), limonene (15.02 %), dihydrocarvone (13.13 %) and carvacrol (4.92 %).

Keywords: *Anethum graveolens* L., essential oils, chemical composition

INTRODUCTION

Dill (*Anethum graveolens* L.) is an annual aromatic plant of the Apiaceae family. The plant is native to Europe and commercially produced in a number of European, American, and Asian countries [1, 2].

Dill seed oil is prepared by distillation from the crushed ripe fruits. Its main constituents are limonene (over 40 %) and (+)-carvone (over 60 %) [1–13].

Dill weed oil is obtained by distillation from dill weed (herb) before the fruit become mature. The typical flavor of the oil is due to α -phellandrene (10 – 20 %), limonene (30 – 40 %); (+)-carvone (30 – 40 %) and dill ether (over 10%) [1, 2, 6, 12–18].

Dill oils are used as flavoring in different foods [1, 2, 12, 19, 20].

The most important medicinal effects of dill oils are due to its antimicrobial [7, 11–13] and antioxidant [12, 13] activities, and pharmacological [12, 18] properties. Some of these activities are related to the major compound of the oils (+)-carvone.

The aim of present investigated is to examine the oil and its chemical composition of different parts (flowers, herb, and fruits) of dill grown in Bulgaria.

EXPERIMENTAL

Plant material

The plant parts of dill (*Anethum graveolens* L.) were harvested in the vicinity of the town of Yambol, Bulgaria of 2017.

The plant parts were air-dried immediately after harvesting in a shady site for 10 days, packed in paper bags and kept in a dark, dry and cool place.

The moisture content of the fresh raw materials was determined by drying to constant weight, at 105 °C [21].

Essential oil isolation

The air-herbs were cut in pieces (1 cm long) and the air-fruits were ground in laboratory mill to a size of 0.7 – 1.0 cm. The oil content in the plant parts was determined for 3 h in laboratory glass apparatus according to the British Pharmacopoeia, modified by Balinova and Diakov [22]. The oil obtained was dried over anhydrous sodium sulfate and stored in tightly closed dark vials at 4°C until analysis.

Chemical composition of the essential oil

Gas chromatography (GC) analysis was performed using an Agilent 7890A gas chromatograph, an HP-5 ms (30 m×250 μ m ×0.25 μ m) column, a temperature of 35 °C/3 min, 5 °C/min to 250 °C for 3 min, 49 min in total; helium gas as carrier at 1mL/min constant speed; split ratio 30:1.

GC/MS analysis was carried out on an Agilent 5975C mass spectrometer, with helium gas as a carrier, the column and temperature being the same as the GC analysis.

The identification of chemical compounds was made by comparison to their relative retention time and library data. The components identified were arranged according to the retention time and their quantity was given in percentage.

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All experiments were carried out in threefold repetition and the mean values with the respective error have been presented in the tables and figures below.

RESULTS AND DISCUSSION

The moisture of the flowers was 70.27 %, of herb was 79.71 %, and of fruits was 10.64 %.

The essential oil yield has been shown in Table 1. All essential oils were light yellow liquids and had a specific odor.

The data in the Table 1 shown that the oil yield during vegetative stage was different with those reported in literature, for example for flower oil (0.08 – 0.32 %) [9, 10], for herb oil (0.3 – 1.0 %) [6, 10, 16 – 18], and for fruit oil (1.75 – 4.0 %) [6, 8 – 10]. The differences in the oil quantities with those reported in literature were probably due to the climatic conditions in the respective place where the plant grows and the part of the plant processed.

The changes in the oil quality have been shown in Table 1.

The essential oil from the different plant organs contained the same compounds, but the quantitative differences between all main compounds were quite large.

As seen 14 components representing 98.11 % of the total content were identified in the flower oil. Nine of them were in concentrations over 1 % and the rest 5 constituents were in concentrations under 1 %. As seen the major constituents (over 3 %) of the

oil are as follows: myristicin (23.24 %), carvacrol (22.04 %), carvone (18.93 %), limonene (11.20 %), 3,9-oxy-*p*-menth-1-ene (7.59 %), α -phellandrene (6.50 %) and dihydrocarvone (4.63 %).

Seven compounds representing 92.88 % of the total content identified in the herb oil. As seen the major constituents (over 3 %) of the oil are as follows: α -phellandrene (21.83 %), carvacrol (20.85 %), limonene (18.96 %), 3,9-oxy-*p*-menth-1-ene (12.31 %), carvone (8.40 %), myristicin (7.11 %) and *p*-cymene (3.34 %).

As seen nine components representing 92.01 % of the total content were identified in the fruit oil. Five of them were in concentrations over 1 % and the rest four constituents were in concentrations under 1 %. As seen the major constituents (over 3 %) of the oil are as follows: carvone (33.57 %), myristicin (24.21 %), limonene (15.02 %), dihydrocarvone (13.13 %) and carvacrol (4.92 %).

The data shown that the highest percentage for myristicin and carvacrol is in the flowering stage, limonene and α -phellandrene in the vegetative stage, and carvone and myristicin in the fruiting stage. We also find that carvone percentage has reverse behavior, where carvone and myristicin percentage increase with the vegetative stage.

The difference in chemical composition of our investigations and the reported data may be due to environmental conditions under which the plant has grown as well as the variation in conditions of analysis.

Table 1. Percent composition of dill essential oils.

№	Components	RI*	Content, %		
			Flower oil	Herb oil	Fruit oil
1	α -Pinene	939	0.19±0.00	nd**	nd
2	β -Pinene	979	0.14±0.00	nd	nd
3	α -Phellandrene	998	6.50±0.02	21.83±0.08	0.19±0.00
4	<i>p</i> -Cymene	1024	2.05±0.00	3.34±0.01	0.40±0.00
5	Limonene	1030	11.20±0.04	18.96±0.06	15.02±0.05
6	Terpinolene	1088	0.15±0.00	nd	nd
7	3,9-oxy-1-menth-1-ene	1073	7.59±0.03	12.31±0.05	0.32±0.00
8	Dihydrocarvone	1179	4.63±0.01	nd	13.13±0.05
9	Carvone	1205	18.93±0.06	8.40±0.03	33.57±0.11
10	Thymol	1266	1.15±0.00	nd	0.25±0.00
11	Carvacrol	1277	22.04±0.08	20.85±0.07	4.92±0.02
12	β -Caryophyllene	1419	0.17±0.00	nd	nd
13	β -Bisabolene	1496	0.13±0.00	nd	nd
14	Myristicin	1502	23.24±0.09	7.19±0.03	24.21±0.09
Yield of essential oils, % (v/w)			0.36±0.00	0.90±0.02	3.61±0.01

* The retention index was calculated for all volatile constituents using a homologous series of *n*-alkanes C₈ – C₁₆, ** nd - not determined.

The classification of the identified compounds, based on functional groups, is summarized in Figure 1.

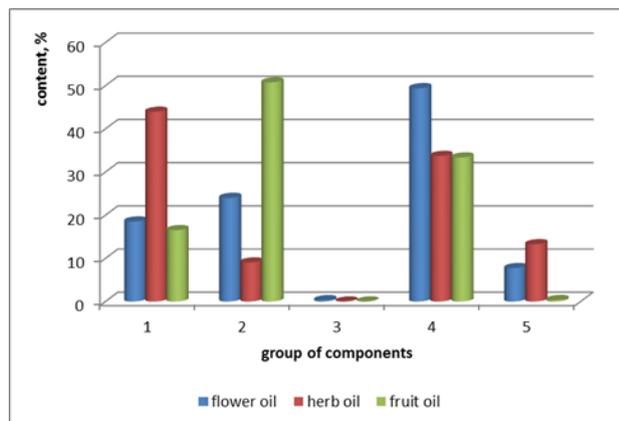


Fig. 1. Group of components in dill oils, %:
1 – monoterpene hydrocarbons; 2 – oxygenated monoterpenes; 3 – sesquiterpene hydrocarbons; 4 – phenyl propanoids; 5 – others (benzofurans)

Phenyl propanoids (49.41 %) are the dominant group in the flower oil, followed by oxygenated monoterpenes (24.01 %), monoterpene hydrocarbons (18.53 %), others (7.74 %) and sesquiterpene hydrocarbons (0.31 %).

Monoterpene hydrocarbons (43.95 %) are the dominant group in herb oil, followed by phenyl propanoids (33.73 %), others (13.27 %) and oxygenated monoterpenes (9.05 %).

Oxygenated monoterpenes (50.76 %) are the dominant group in the fruit oil, followed by phenyl propanoids (33.37 %), monoterpene hydrocarbons (16.53 %) and others (0.34 %).

CONCLUSIONS

Significant qualitative and quantitative differences in chemical composition of dill oils were detected. The main components in the flower oil are the phenyl propanoids myristicin (23.24 %) and carvacrol (22.04 %), oxygenated monoterpene carvone (18.93 %) and monoterpene hydrocarbon limonene (11.20 %), in the herb oil dominated the phenyl propanoid carvacrol (20.85 %) and monoterpene hydrocarbons α -phellandrene (21.83 %) and limonene (18.96 %), while in the fruit oil dominated oxygenated monoterpene carvone (33.57 %) and phenyl propanoid myristicin (24.21 %).

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