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Chemical composition of seed (fruit) essential oils of *Angelica archangelica* L. growing wild in Lithuania

Ona Nivinskienë*,

Rita Butkienë and

Danutë Mockutë

Institute of Chemistry,
A. Goštauto 9,
LT-01108 Vilnius, Lithuania

Seeds (fruits) of *Angelica archangelica* L. were collected in three habitats of Lithuania. The oils were analysed by GC and GC/MS. β-Phellandrene (33.6–63.4%) was the dominant constituent in all seed essential oils. α-Pinene (4.2–12.8%) was the second major compound. The third position among the main constituent of the essential oils was taken by germacrene D (3.0%), α-phellandrene (7.4%) and sabinene (3.3%). Monoterpene hydrocarbons (63.5–76.6%) comprised the largest part in the seed oils. Sixty seven identified compounds made up 83.9–93.0% of the essential oils.

Key words: *Angelica archangelica,* Apiaceae, angelica seed, essential oil composition, β-phellandrene, α-pinene

INTRODUCTION

Two species of the genus *Angelica* L., *Angelica archangelica* L. and *Angelica silvestris* L., are growing wild in Lithuania [1]. Essential oils of seeds (fruits) and roots of *A. archangelica* are used for healing [2, 3]. Both oils are non-toxic and non-irritant, however, the author of [2] proposed that the phototoxicity of root oil (not seed oil) is probably due to a higher level of coumarin bergapten.

β-Phellandrene (≤87.4%) or both phellandrenes prevailed in all earlier investigated seed essential oils and hexane extracts of *A. archangelica* [4–10]. The volatile constituents were investigated in different parts of plants (roots, stems, leaves, flowers and seeds) in Romania [4]. β-Phellandrene prevailed only in flower and seed oils.

The essential oil produced by seeds from the Central Station of Seed Production in Bydgoszcz (Poland) contained three monoterpenes (59.4% of β-phellandrene, 2.9% of α-pinene and 2.3% of α-phellandrene), ketone cryptone (2.6%) and sesquiterpene hydrocarbon α-copaene (3.3%) among the five major constituents [10]. The amounts of monoterpene hydrocarbons in the hexane extract of the above seed were close to those in the seed essential oil, but the content of α-copaene was markedly decreased. Hexane did not extract cryptone from angelica seeds [10]. Monoterpene hydrocarbons were the major constituents in the hexane extracts of plants growing wild in Finland [8]. β-Phellandrene prevailed in all the above extracts. The composition of the other four major constituents depended on growing locality. α-Pinene, α-phellandrene, myrcene and limonene were found in the extract of seeds from West Lapland. Sabinene, α-pinene, myrcene and α-phellandrene characterized the extract of seeds from East Lapland. Seeds from North Lapland produced α-pinene, sabinene, myrcene and α-phellandrene as the main constituents beside the dominant β-phellandrene [8]. The five major constituents in seeds from East and North Lapland were the same, but their amounts and possition among the main compounds varied markedly [8]. The essential oils from seeds collected in France [9] contained the above monoterpene hydrocarbons (except sabinene) as the major constituents.

β-Phellandrene was the dominant constituent in some root essential oils, but its content was far lower (≤28.2%) than in seed oils (≤87.4%) [4–13]. This compound was among the five major constituents in most of root essential oils studied [4–13]. Phellandrene was in the first possition among the main constituents in the books about the healing power of angelica essential oils [2, 14]. The above oils exhibited antispasmodic, carminative, digestive, diuretic, nervine, stimulant, tonic and some other activities [2, 3, 14]. The authors of [3] indicated that the alarm regarding the toxicity of angelica seeds and herbs was probably false or a case of contention.

The essential oil of angelica is used extensively as a flavoring agent in most food categories and in alcoholic and soft drinks, especially liquors [2]. This essential oil is highly valued as a fraqrance component in parfumery and cosmetics [2].

* Address for correspondence: Fax: +370 5 2649774 E-mail: vita_n@mail.lt

The present report deals with the composition of the seed essential oils of wild *A. archangelica* from three habitats of Lithuania.

MATERIALS AND METHODS

Angelica (*A. Archangelica* L.) samples were collected in three habitats: A (Švenèionys, 2000), B (Prienai, 2002), C (Vilnius, 2003). Voucher specimens have been deposited in the Herbarium of the Institute of Botany (BILAS numbers: A – 65213, B – 65212, and C – 65214). Essential oils were prepared by hydrodistillation (2 h) of 10 g air-dried ripe seeds (fruits). The ratio of seeds and water was 1:4. Essential oils were collected in 2 ml of a hexane: diethyl ether mixture (1:1). Yields of the essential oil of ripe seeds (0.8–1.4%) were obtained using 100 g of seeds and expressed in v/w% of dry weight.

Analysis of the essential oils was carried out by GC and GC/MS. The separation was performed on a CP-Sil 8CB silica capillary column (50 m × 0.32 mm; film thickness 0.25 μm) using a HP 5890II chromatograph equipped with FID. The GC oven temperature was programmed as follows: from 60 °C (isothermal for 1 min) increased to 160 °C at a rate of 5 °C/min and to 250 °C at a rate of 10 °C/min, and the final temperature was kept for 3 min. The temperatures of the injector and the detector were 250 °C and 280 °C, respectively. The flow rate of carrier gas (helium) was 1 ml/min. Analysis by GC/MS were carried out with a HP 5890 gas chromatograph equipped with an HP 5971 mass selective detector and HP 7673 split / splitless injector. Mass spectra in electron mode were generated at 70 eV.

The percentage composition of the essential oils was computed from GC peak areas without correction factors. Qualitative analysis was based on the comparison of retention times, retention indexes and the mass spectra with corresponding data in the literature

Table. **Chemical composition (%) of seed essential oils of *Angelica archangelica* L. growing wild in Lithuania**

Compounds	**RI**	**A**	**B**	**C**
α-Thujene	931	0.1	t	t
α-Pinene	939	9.1	12.8	4.2
Camphene	953	0.1	0.1	0.1
Sabinene	976	2.5	4.6	3.3
β-Pinene	980	2.4	3.7	0.7
Myrcene	991	2.5	2.0	2.0
α-Phellandrene	1005	2.7	7.4	2.6
δ-3-Carene	1011	0.3	0.5	t
p-Cymene	1018	0.1	0.1	0.1
β-Phellandrene	1031	43.8	33.6	63.4
trans-β-Ocimene	1050	0.6	0.4	t
γ-Terpinene	1062	t	t	t
α-Terpinolene	1088	0.3	0.4	0.2
Isopentyl 2-methylbutanoate	1100	t	0.5	0.2
Isopentyl isovalerate	1103	0.3	0.9	0.2
cis-Verbenol	1141	0.1	0.2	0.1
trans-Verbenol	1144	0.2	0.3	0.2
Mentha-1,5-dien-8-ol	1166	0.1	t	–
Menthol	1173	t	0.1	–
Terpinen-4-ol	1177	0.6	0.4	0.2
p-Cymen-8-ol	1183	t	–	t
Cryptone	1186	0.3	0.2	0.2
Hexyl isovalerate	1244	t	0.1	0.1
Bornyl acetate	1285	0.2	0.1	0.2
Sabinyl acetate	1291	t	0.1	t
Isoamylbenzyl ester	1310	0.1	0.6	t
δ-Elemene	1339	0.1	0.2	t
α-Longicyclene	1374	t	t	t
α-Ylangene	1375	0.2	0.2	0.1
α-Copaene	1376	0.2	t	t
β-Bourbonene	1388	0.4	0.1	0.2
β-Elemene	1391	0.3	0.1	0.3
Benzyl isovalerate	1399	t	t	0.1
Longifolene	1408	0.3	0.9	0.1
β-Caryophyllene	1418	0.1	0.4	0.2
β-Ylangene	1421	t	–	0.1
γ-Elemene	1433	1.4	0.8	0.6
α-Humulene	1454	1.5	3.4	1.0
β-Farnesene	1458	0.3	0.3	0.4
γ-Muurolene	1477	0.2	2.1	0.5
Germacrene D	1485	3.0	0.5	0.4
ar-Curcumene	1481	0.6	–	0.7
γ-Curcumene	1483	–	3.2	–
Phenyl ethyl 2-methylbutanoate	1487	0.1	–	0.2
Zingiberene	1495	1.3	–	1.9
α-Muurolene	1499	1.6	0.3	0.8
β-Bisabolene	1509	0.9	1.2	1.6
γ-Cadinene	1513	0.2	0.2	0.2
δ-Cadinene	1524	1.3	1.2	1.2
α-Cadinene	1539	t	0.1	0.1
Selina-3,7(11)-diene	1547	–	–	0.3
Elemol	1549	0.2	1.3	0.6
Germacrene B	1556	0.1	0.1	0.1

Compounds	RI	A	B	C
Longipinanol	1566	0.6	1.6	0.1
Spathulenol	1576	0.3	0.2	0.1
Caryophyllene oxide	1581	t	t	0.2
cis-β-Elemenone	1589	0.1	0.1	0.1
13-Tridecanolide	1590	0.6	1.0	1.3
Humulene epoxide	1606	0.1	0.5	t
α-Muurolol	1645	t	1.2	t
α-Bisabolol	1686	0.2	0.3	t
Bisabolone	1744	t	0.2	0.2
Farnesol*	1746	0.1	0.1	0.1
15-Pentadecanolide	1828	0.8	1.1	0.9
Methyl hexanoate	1922	0.1	0.1	0.2
Methyl octanoate	2125	0.2	0.2	0.1
Osthol	2138	0.1	0.2	t
Total		83.9	92.5	93.0
Monoterpene hydrocarbons		64.5	65.6	76.6
Oxygenated monoterpenes		1.6	2.1	1.0
Sesquiterpene hydrocarbons		12.8	15.1	10.9
Oxygenated sesquiterpenes		2.3	6.6	2.8
Macrocyclic lactones		1.4	2.1	2.2

Notes. RI – retention index on nonpolar column, A – Ðvenèionys district, B – Prienai district, C – Vilnius district, t – traces, * – correct isomeric form not identified.

[15] and the computer mass spectra libraries (Wiley and NBS 54K).

RESULTS AND DISCUSSION

The seed essential oils produced by *A. archangelica* growing wild in three habitats of Lithuania were of β-phellandrene chemotype (Table, 33.6–63.4%) as all earlier investigated appropriate oils [4–10]. α-Pinene (4.2–12.8%) was the second major constituent in the essential oils under study. This compound in the seed oils in some countries was also in the second position among the main constituents [6, 8–10]. Germacrene D was the third main compound only in habitat A (Table). Three first major constituents (Table: β-phellandrene, α-pinene and α-phellandrene) in the seed essential oil from habitat B were the same as in the seed oils from Poland [10] and West Lapland [8]. The seed essential oils of *A. archangelica* from habitats A and B contained β-phellandrene (Table, 33.6–43.8%) as the dominant constituent, while this position in the root essential oils from the same habitats was taken by α-pinene (15.5–20.0%) [16]. The root essential oil from habitat A contained only 2.0% of β-phellandrene and the corresponding oil from habitat B included 14.9% of this compound.

The growing locality influenced the composition of seed essential oils. The highest content of β-phellandrene (63.4%) was found in the seed essential oil from habitat C. The first and the second major constituents in seed and root essential oils from the above habitat were the same, but their levels differed markedly. The seed and root essential oils contained 63.4% and 16.2% of β-phellandrene, respectively. An opposite correlation was determined for α-pinene (4.2 and 13.7%) in the essential oils from habitat C. The position and the level of the main compounds (Table: β-phellandrene, α-pinene, sabinene, α-phellandrene and myrcene) in the oil C were the same as in the corresponding essential oil of *A. archangelica* growing wild in North Lapland [8].

The quantitative composition of the seed (Table) and root [16] essential oils of angelica plants from the same habitat differed markedly. The content of α-pinene (4.2–12.8%), δ-3-carene (t – 0.5%) and osthol (t – 0.2%) in seed oil was lower than that of the above constituents in the root essential oils (14.8–20.0%; 11.8–15.4% and 1.4–2.7%). The content of β-phellandrene (Table; 33.6–63.4%) in the seed oils several times exceeded that (2.0–18.5%) in root oils of the plants growing in the same habitat. The percentage of monoterpene hydrocarbons in both seed (Table) and root [16] essential oils was close and varied from 64.5 to 76.6%. The differences were determined for oxygenated monoterpenes (seed oils 1.0–2.1%, root oils 5.1–6.5%) and macrocyclic lactones (seed oils 1.4–2.2%, root oils 4.1–6.3%). Sixty identified compounds in seed essential oils made up 82.3–92.8%.

CONCLUSIONS

A. archangelica seed essential oils produced by plants growing wild in Lithuania were of β-phellandrene (33.6–63.4%) chemotype. α-Pinene (4.2–12.8%) was the second major constituent. Monoterpene hydrocarbons (63.5–76.6%) made up the largest part of the seed oils.

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Ona Nivinskienë, Rita Butkienë, Danutë Mockutë

LIETUVOJE AUGANÈIØ *ANGELICA ARCHANGELICA* L. SËKLØ (VAISIØ) ETERINIØ ALIEJØ CHEMINË SUDËTIS

S a n t r a u k a

Angelica archangelica L. (ðventagarðvës) sëklos surinktos trijose augavietëse. Hidrodistiliacijos bûdu gauti eteriniai sëklø aliejai buvo analizuoti dujø chromatografijos ir dujø chromatografijos/masiø spektrometrijos metodais. Visi sëklø eteriniai aliejai buvo β-felandreno (33,6–63,4%) chemotipo. Antrasis vyraujantis komponentas buvo α-pinenas (4,2–12,8%), o treèioje vietoje – germakrenas D (3,0%), α-felandrenas (7,4%) ir sabinenas (3,3%). Sëklø eteriniuose aliejuose daugiausia aptikta monoterpeniø angliavandeniliø (63,5–76,6%). Ðeðiasdeðimt septyni identifikuoti junginiai sudaro 83,9–93,0% eteriniø aliejø.