Changes in the chemical composition of essential oil of *Angelica archangelica* L. roots during storage

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Essential oils obtained from *Angelica archangelica* L. roots immediately and after storage about 2.5 months after crushing were analyzed by GC and GC–MS. The dominant component in the oils from roots crushed before analysis was α-pinene (15.7–19.4%), the other major compounds being δ-3-carene (15.4–16.0%) and limonene (8.1–8.8 %) or β-phellandrene (15.4%) and δ-3-carene (14.2%), depending on the growing localities. The dominating constituent of the crushed and stored root oils was 15-pentadecanolide (7.2–14.9%). The other main constituents were coumarine osthol (5.3–8.8%) and macrocyclic lactone 13-tridecanolide (5.4–6.1%). A large part (about 70%) of monoterpene hydrocarbons was evaporated during storage from small particles of roots, while the fraction of macrocyclic lactones (14.3–25.2%) and the amounts of coumarin osthol (5.3–8.8%) increased relatively 2–5 times.

Key words: *Angelica archangelica* L., chemical composition of essential oil, α-pinene, β-phellandrene, δ-3-carene, limonene, 15-pentadecanolide, 13-tridecanolide, osthol

INTRODUCTION

Roots of *Angelica archangelica* L. have been used for healing since antiquity for strengthening the heart, stimulating the circulation and the immune system in general [1–4]. Angelica roots have been used for centuries in Europe for bronchial ailments, coughs, colds, indigestion and as a urinary antiseptic. Chinese employed at least ten kinds of angelica, well know for promoting fertility, fortifying the spirit and for treating female disorders generally. Different compounds in the plant might cause the healing of different diseases.

The healing power of the roots may by attributed to the essential oils, organic acids, steroides, coumarins and flavonoids biosynthesized by *A. archangelica* L. [5]. Essential oils of *A. archangelica* L. roots were used in healing (including aromatherapy) of the same diseases as the other forms of the root drugs [1, 6–8].

The odour of the essential oil is warm, aromatic with a green-spicy top note and a pleasant musky dry-out. The oil of roots was used in confectionary, drinks, cosmetics, soaps and perfumes [1].

Monoterpene (> 60%) hydrocarbons made up the largest part of essential oils of *A. archangelica* L. [9–18]. The dominant constituent was α-pinene in more than half of the essential oils studied and the second one in all the others. Limonene, α-and β-pinenes, δ-3-carene, p-cymene, α-and β-phellandrenes were frequent among the five main constituents of the oils. The content of monoterpene hydrocarbons in pentane/ether extracts or in liquid CO_2 extracts of the roots depended on the extraction conditions [19, 20].

The macrolide fraction containing different amounts of 13-tridecanolide, 12-methyl-tridecanolide, 15-tridecanolide, 16-hexadecanolide and 17-heptadecanolide was found both in the essential oils [9–15, 21] and in extracts [19, 20] of *A. archangelica* L. roots. The compounds of macrolide fraction determined the musk odour of the essential oil of *A. archangelica* L.

The essential oils or pentane/ether extracts of *A. archangelica* L. roots contained coumarins such as osthol (12.4–12.6%), psarolen (0.3–1.3%) [16, 17, 19], bergaptene, angelicin and imperatorin [1].

The chemical composition of essential oils depended on the experimental conditions [15, 18]. The content of compounds with a higher boiling temperature increased with the longer time of distillation. The quantities of constituents in the oils depended on the ratio of plant material/water mass, still load, drying and storage conditions of the roots [15, 18]. The composition of essential oils of *A. archangelica* L. determined their medicinal and flavouring quality.

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The aim of the study was to investigate the effects of storage condition on the chemical composition of essential oil of the roots.

EXPERIMENTAL

The roots of *A. archangelica* L. were collected in September from two habitats: in Švenčionys district (A, 1997, 2000) and Prienai district (B, 2000). Air-dried roots were crushed up and stored for about 2.5 months and crushed before analysis. Essential oils (0.2–0.6%) were prepared by hydrodistillation of 100 g of roots with a plant : water ratio of 1:4.

Gas chromatography (GC) analyses were carried out on a HP 5890 (Hewlett Packard) gas chromatograph equipped with a flame ionisation detector. The separation was performed on a silica capillary column, CP-Sil 8CB (50 m × 0.32 mm i.d., film thickness 0.25 μm). The GC oven temperature was programmed as follows: from 60 °C (isothermal for 1 min) then 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.

The same capillary column and temperature program as in the GC analysis was used in GC–MS. Mass spectra in electron mode were generated at 70 eV. Qualitative analysis was based on a comparison with mass spectral libraries and retention index (22–24). The percentage composition of the essential oil was computed from GC peak areas without using correction factors.

RESULTS AND DISCUSSION

The chemical composition of essential oil of *A. archangelica* L. roots depended on storage form. Part of monoterpene hydrocarbons evaporated from small particles of crushed up roots after 4 days of storage [18].

The amount of monoterpene hydrocarbons in the essential oil from powder of *A. archangelica* L. roots (Table, A 2000 P) decreased markedly in compari-

Table. **Chemical composition of the essential oils of *Angelica archangelica* L. roots**

No.	Compounds	RI	Percentage					
			A*			B*		
			1997	1997 S*	2000	2000 P*	2000	2000 S
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
1	α-Thujene	931	0.2	t*	t	t	0.1	t
2	**α-Pinene**	**939**	**19.1**	**4.4**	**15.7**	**3.8**	**19.4**	**4.5**
3	Camphene	953	1.5	0.3	1.1	0.2	0.8	0.2
4	Sabinene	976	7.5	3.8	6.2	3.3	3.6	2.1
5	β-Pinene	980	0.7	0.2	1.4	0.3	3.1	1.1
6	*trans*-p-Mentha-2.8-diene	981	0.9	0.4	1.5	0.4	0.0	0.0
7	Myrcene	991	3.0	0.6	2.0	0.6	2.3	0.4
8	α-Phellandrene	1005	2.9	0.7	2.1	0.9	9.1	2.8
9	**δ-3-Carene**	**1011**	**16.0**	**4.2**	**15.4**	**4.8**	**14.2**	**3.4**
10	α-Terpinene	1018	2.0	0.3	1.4	0.4	0.2	0.1
11	p-Cymene	1018	3.4	2.0	3.9	0.6	1.5	0.9
12	**Limonene**	**1026**	**8.1**	**3.4**	**8.8**	**2.1**		
13	**β-Phellandrene**	**1031**	1.0	t	2.0	t	**15.4**	**5.4**
14	*trans*-β-Ocimene	1050	0.4	0.2	0.5	0.2	0.1	0.1
15	γ-Terpinene	1062	1.9	0.9	2.4	0.4	0.9	0.4
16	α-Terpinolene	1088	1.8	1.3	1.9	0.8	1.8	0.5
17	*p*-Cymenene	1089	0.9	4.6	0.4	2.5		
18	*cis*-Menth-2-en-1-ol	1121	0.2	0.3	0.3	0.5		
19	*trans*-Menth-2-en-1-ol	1140	0.1	0.2	0.3	0.4		
20	*cis*-Verbenol	1140	0.3	0.8	0.3	0.4	0.2	0.3
21	*trans*-Verbenol	1144	0.3	1.1	0.4	0.7	0.4	0.6
22	Mentha-1.5-dien-8-ol	1166	0.1	1.3	0.1	0.8	0.2	2.6
23	Menthol	1173	0.1	0.2	0.1	0.2	0.2	0.3
24	Terpinen-4-ol	1177	1.1	5.1	1.0	2.9	0.9	2.4
25	p-Cymen-8-ol	1183	0.1	1.1	0.2	0.3	0.3	0.5
26	α-Terpineol	1189	0.1	0.7	0.1	0.6	0.1	0.2
27	*cis*-Piperitol	1193	0.1	t	0.1	t		
28	Myrtenal	1193	0.1	0.4	0.1	0.5	0.1	0.2
29	Myrtenol	1194	t	0.3	0.1	0.4	0.1	0.2

Table (continued)

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
30	*trans*-Chrysantenyl acetate	1235	0.3	1.1	0.3	0.8	0.1	0.3
31	Myrtenyl acetate	1235	0.1	0.4	0.1	0.3		t
32	*cis*-Chrysantenyl acetate	1262	0.2	0.6	0.1	0.4	0.2	0.5
33	Bornyl acetate	1285	3.2	3.9	2.4	4.2	3.1	3.5
34	p-Cymen-7-ol	1287	0.1	0.6	0.1	0.5	0.1	0.7
35	Sabinyl acetate	1291	0.2	0.5	0.1	0.3	0.4	0.5
36	Isoamylbenzyl ester	1310	0.3	0.3	0.1	0.1	0.2	0.2
37	Carvyl acetate	1337	0.1	0.1	t	0.1		
38	δ-Elemene	1339	t	0.2	t	0.1	0.1	0.2
39	*Cis*-Carvyl acetate	1362	t	0.2	t	0.1	t	
40	α-Copaene	1376	0.4	0.6	0.1	0.4	0.4	0.5
41	β-Cubebene	1390	t	0.3			0.3	0.4
42	β-Elemene	1391	0.1	0.2	0.1	0.2	0.5	0.6
43	γ-Caryophyllene	1404	0.1	0.2	0.1	0.3	0.2	0.7
44	β-Cedrene	1418	0.2	0.3	0.1	0.2	0.2	0.4
45	β-Caryophyllene	1418	0.1	0.2	tr	0.2	0.2	0.3
46	γ-Elemene	1433	0.7	0.8	0.6	0.8	0.8	2.2
47	Aromadendrene ??	1439	0.4	0.5	0.2	0.7		
48	α-Humulene	1454	0.6	1.4	0.4	1.1	1.3	1.4
49	β-Farnesene	1458	0.3	0.5	0.1	0.3	0.3	0.7
50	γ-Muurolene	1477	0.2	0.3	0.2	0.3	0.2	0.4
51	Germacrene D	1480	0.2	0.3	0.2	0.3	0.6	1.0
52	β-Selinene	1485	t	t	t	t	t	t
53	Bicyclogermacrene	1494	0.1	0.2	0.1	0.2	0.3	0.6
54	Zingiberene	1495	0.1	0.2	0.1	0.2	0.2	0.5
55	α-Muurolene	1499	0.4	0.7	0.2	0.5	0.3	1.1
56	α-Cuparene	1502	0.2	0.4	0.2	0.4	0.1	0.3
57	β-Bisabolene	1509	0.3	0.6	0.3	0.6	0.5	1.3
58	γ-Cadinene	1513	0.3	0.3	0.1	0.4		
59	δ-Cadinene	1524	0.2	0.6	0.3	0.7	0.4	0.9
60	Cadinadiene-1.4	1532	t	0.2	0.2	0.4	0.2	0.5
61	α-Copaen-11-ol	1537	1.7	3.3	1.8	4.5	0.3	1.3
62	Elemol	1549	0.3	1.5	0.5	1.7	1.0	2.9
63	Germacrene B	1556	0.1	0.4	0.1	0.2	0.2	0.6
64	α-Copaen-8-ol	1561	0.7	2.0	0.7	2.5	0.1	0.4
65	Longipinanol ? m/z 109	1566	1.3	1.9	1.4	4.2	0.4	1.9
66	Spathulenol	1576	0.4	0.6	0.2	0.4	0.1	0.2
67	Caryophyllene oxide	1581	0.3	0.4	0.3	0.4	0.2	0.3
68	Copaen-4-α-ol ?	1584	t	0.2	0.1	0.3	0.1	0.2
69	**13-Tridecanolide**	**1590**	**1.5**	**5.4**	**2.2**	**5.9**	**1.5**	**6.1**
70	Humulene epoxide	1606	0.2	0.3	0.2	0.5	0.3	0.4
71	γ-Eudesmol	1630	0.1	0.2	0.1	0.3	0.2	1.2
72	α-Muurolol	1645	0.2	0.4	0.1	0.3	0.3	0.4
73	β-Eudesmol	1649	0.4	1.8	1.1	1.7	0.5	1.3
74	α-Eudesmol	1652	0.1	1.0	0.2	1.1	0.1	0.8
75	Tridecanolide. 12-methyl	1654	0.1	0.7	0.2	0.8	0.1	0.9
76	7-epi-g-Eudesmol	1658	0.1	0.4	0.2	0.7	0.1	0.5
78	Bisabolone	1744	0.3	0.5	0.2	0.5		
79	**15-Pentadecanolide**	**1828**	**2.0**	**7.2**	**3.3**	**10.8**	**2.8**	**14.9**
80	16-Hexadecanolide	1928	0.1	0.3	0.1	0.4	0.1	0.5
81	17-Heptadecanolide	2028	0.2	0.7	0.5	1.6	0.2	2.9
82	**Osthol**	**2138**	**3.6**	**5.3**	**2.7**	**8.8**	**1.5**	**7.9**
	Total		96.7	90.0	92.8	91.7	95.3	94.5
	Monoterpene hydrocarbons		**71.3**	**27.3**	**66.7**	**21.3**	**72.5**	**21.9**
	Oxygenated monoterpenes		7.1	19.2	6.3	14.5	6.6	13.0
	Sesquiterpenes hydrocarbons		5.0	9.4	3.7	8.5	7.3	14.6
	Oxygenated sesquiterpenes		7.3	19.4	9.1	24.5	4.2	17.9
	Macrocyclic lactones		**3.9**	**14.3**	**6.3**	**19.5**	**4.7**	**25.3**

Note.*A (Švenčionys), B (Prienai) – habitats,
S – small crushed roots, P – powder of roots, t – traces

son with the oil from roots crushed up before analysis (Table, A 2000). The content of the main constituents of the essential oil of stored uncrushed roots – (α-pinene, δ-3-carene and limonene) decreased 3.5–4.0 times during the storage of pulverized roots. Nearly the same differences were found in essential oils from crushed up and stored roots after about 2.5 months (Table, A 1997 S, B 2000 S) in comparison with the essential oil of the stored uncrushed roots oils (Table, A 1997, B 2000). α-Pinene was the dominant constituent in the oil of roots crushed immediately before analysis, with the other main constituents, δ-3-carene and limonene, in A samples and β-phellandrene and δ-3-carene in B sample. The chemical compositions of the above essential oils (Table, A 1997, A 2000, B 2000) were similar to the composition of the oils from plants collected in Finland [9,17], Norway [11], France [13, 15] and commercial [13, 18]. The 82 compounds identified make up 90.0–96.7% of essential oils. The largest part (66.7–72.5%) of oil comprised monoterpene hydrocarbons. The other groups of compounds (oxygenated monoterpenes, sesquiterpene hydrocarbons, oxygenated sesquiterpenes, macrocyclic lactones and coumarin) did not exceed 9.1% each.

The main constituents of essential oils from stored pulverized or crushed up roots was macrocyclic lactone 15-pentadecanolide (7.2–14.9%), coumarin osthol (5.3–8.8%) and macrocyclic lactone 13-tridecanolide (5.4–6.1%). The musky odour of the essential oil depended on the content of macrocyclic lactones. The total amount of macroclide fraction and coumarine osthol in essential oils from stored crushed roots of *A. archangelica* L. increased relatively 3.5–5 and 2–5.5 times, respectively (Table).

Coumarin osthol was the strongest bioactive compound in the volatile oils of *A. archangelica* L. roots [8]. The healing power of the oils was attributed to coumarins [1, 6, 8]. The essential oil of *A. archangelica* L. growing in Lithuania contained 1.5–8.8% of coumarin osthol (Table). Nearly all constituents of the essential oils are bioactive [1, 6]. The main constituent, α-pinene, which has antioxidative properties [25] and affects 25 different bacteria [26], was found in the samples of A and B localities (15.7–19.4%). Limonene (3.4–8.8%, A locality) exhibits antioxidative properties [25], inhibits acetylcholinesterase activity [27] and cancer cell proliferation [28] and is an effective anticarcinogen tested with chemical carcinogens [29]. Menthol, α- and γ-terpinenes and terpinene-4-ol inhibits also acetylcholinesterase activity [27]. δ-Cadinene and β-caryophyllene exhibited *in vitro* cytotoxicity against two tumor cells and enhanced the activity of indole and indole-3-carbinol in the same process [30]. These data on the bioactivity of some terpenoids show that changes in the chemical composition of the oils might influence some aspects of their healing power.

CONCLUSIONS

The volatile components isolated from of *A. archangelica* L. roots crushed up before analysis were compared with those of the roots stored for about 2.5 moths pulverized or crushed up. GC determined more than 95 compounds, and 82 were identified by GC–MS. The relative content of the compounds varied greatly. The largest part (66.7–72.5%) of the oil from roots crushed before analysis consisted of monoterpene hydrocarbons (with α-pinene as the dominant constituent). The composition of the oil from stored crushed roots was distinctly different: the main constituent was 15-pentadecanolide (7.2–15.9%), the fraction of macrocyclic lactones (14.3–25.3%), and the content of coumarin osthol increased relatively 2.0–5.0 times, whereas the content of monoterpene hydrocarbons decreased about 3 times (21.3–27.3%). The percentage of the volatile substances determined the differences in odour and in the healing power.

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ETERINIŲ ALIEJŲ CHEMINĖS SUDĖTIES POKYČIAI SAUGOJANT ŠVENTAGARŠVĖS (*ANGELICA ARCHANGELICA* L.) ŠAKNIS

S a n t r a u k a

Susmulkintos arba natūralios šventagaršvės šaknys buvo saugomos ~2,5 mėn. Išskirti eteriniai aliejai buvo analizuojami dujų chromatografu su masių detektoriumi. Prieš analizę susmulkintų šaknų eterinio aliejaus pagrindinis komponentas – α-pinenas, o priklausomai nuo augavietės kiti svarbūs junginiai buvo δ-3-karenas (15,4–16,0%) ir limonenas (8,1–8,8%) arba β-felandrenas (15,4%) ir δ-3-karenas (14,2%). Prieš saugojant susmulkintų šaknų eterinio aliejaus pagrindinis komponentas – 15-pentadekanolidas (7,2–14,9%). Kiti svarbūs komponentai buvo kumarinas ostolis (5,3–8,8%) ir makrociklinis laktonas 13-tridekanolidas (5,4–6,1%). Saugant susmulkintas šaknis, dauguma monoterpeninių angliavandenilių (~70%) išgaravo, tuo tarpu makrociklinių laktonų (14,3–25,2%) ir kumarino ostolio kiekiai (5,3–8,8%) santykinai padidėjo 2–5 kartus.