# Chemical composition of the essential oils of *Achillea millefolium* L. ssp. *millefolium* (yarrow) growing wild in Vilnius

# Danutė Mockutė and Asta Judžentienė\*

Institute of Chemistry, A. Goštauto 9, LT-2600, Vilnius, Lithuania Fax: 370-2 617 018; e-mail: judzent@ktl.mii.lt Eighteen samples of the inflorescences and leaves of *Achillea millefolium* L. ssp. *millefolium* with white flowers were collected at 9 habitats (1999 and 2000) in Vilnius. Essential oils were analyzed by GC and GC–MS. The volatile oils were divided into 3 groups containing the same two or three major constituents: I (9 samples) – β-pinene (11.8–31.1%) + 1,8-cineole (8.1–17.0%), II (5 samples) – chamazulene (9.8–23.2%) + β-pinene (9.7–30.2%) + 1,8-cineole (5.3–16.0%) and III (4 samples) – *trans*-nerolidol (8.2–13.5%) + β-pinene (5.5–21.3%). According to the first major component the oils can be distributed into four chemotypes such as β-pinene, 1,8-cineole, chamazulene and nerolidol. The essential oil of nerolidol chemotype has not been found in formerly investigated plants of yarrow. The inflorescences and the leaves formed the same chemotype of essential oils only in 3 habitats from the 9 investigated. Two samples of oils did not contain chamazulene, 11 samples contained 0.1–6.8% and 5 samples – 9.8–23.2% of this component. The 56 constituents found in the essential oils made up 78.7–98.7%.

Key words: Compositae, Achillea millefolium L. ssp. millefolium, chemical composition of essential oil, chemotype, inflorescences, leaves,  $\beta$ -pinene, 1,8-cineole, chamazulene, nerolidol

# INTRODUCTION

Three forms of the genus Achillea of Millefoliatae section are growing wild in Lithuania [1]. Achillea millefolium L. ssp. millefolium with white flowers is widely spread all over the country. The plants with rosy flowers (f. rosea Desf.) are rarer, and the plants with the purple colour of inflorescence (f. purpurea Schinz et Thellung) were found only in one habitat (Birštonas). Some hairy plants of Achillea millefolium L. ssp. millefolium var. lanata Koch. were found near Vilnius.

Grass, flowers, leaves and essential oils of yarrow have been widely used in healing since ancient times [2–5]. The above drugs help in healing wounds, sores, rashes, fever, respiratory infection, nervous tention and digestive diseases. Yarrow drugs in China are issued for menstrual problems and hemorrhoids, in Norway – for rheumatism. Differences in the healing power in some countries may be caused by different chemotypes of the essential oils. A large number of investigators connected the healing abili-

Several scientists took interest only in azulenes and proazulenes (sesquiterpenic lactones) in A. millefolium plants. The papers related to these problems were reviewed by Jaskonis [6], Ustiuzhanin et al. [7], Konovalov et al. [2], Figueiredo et al. [3] and Michler and Arnold [8]. The highest content of proazulenes was found in buds or inflorescence at the beginning of flowering. Leaves produced the largest amount of proazulenes at the same stages, but their quantity was several times as low as that in flowers. Different amounts of azulenes were found in a large part of the essential oils of A. millefolium studied. GC/MS analysis of the essential oils has confirmed the above data. The essential oils mostly contained azulenes (from traces to 30%). Some of the oils did not contain azulenes. A large part of chemists analyzed essential oils of all aerial parts of the plants [3, 9–14], although some investigators studied only essential oils from flowers and buds [15, 16].

Chamazulene was the first, second or third major constituent in some of the essential oils studied [10, 14, 16]. The oils presented in the above

ties of yarrow with the presence of chamazulene in the oil

<sup>\*</sup>Corresponding author

papers can be distributed into the following chemotypes according to the first major constituents: chamazulene, sabinene,  $\beta$ -pinene, 1,8-cineole, linalool,  $\alpha(cis)$ -thujone,  $\beta(trans)$ -thujone, ocimene, camphor, ascaridole, caryophyllene oxide,  $\beta$ -eudesmol and  $\alpha$ -bisabolol.

The composition of essential oils from flowers and leaves of *A. millefolium* was compared by Figueiredo et al. [17], Rohloff et al. [18], Orav et al. [14] and Lawrence [10]. Oils of all parts of plants in Portugal, Norway and Estonia (one sample) were of the same chemotype, while oils of separate parts of plants from Estonia (another sample) and Canada were of different chemotypes.

Only azulenes were analysed in 2 samples of yarrow growing in Lithuania. The essential oil of inflorescences and leaves was obtained from plants growing in a botanical garden, and they contained significant amounts of azulenes [6]. The other sample of inflorescence oil contained only traces of chamazulene [7].

The essential oils under study were distributed into 3 groups and 4 chemotypes. The nerolidol chemotype has not been described earlier.

#### MATERIALS AND METHODS

The aerial parts (~35 cm) of plants (0.1–1 kg) growing wild in 9 localities of Vilnius (indicated here by alphabetic symbols, A–L) were collected in August 1999 (with b) and 2000: Af, Al, Bf, Bl, Ef, El – in different parts of Antakalnis; Cf, Cl, Kf, Kl – in the different parts of Rokantiškės; Df, Dl, Df (b), Dl (b), Jf – on the Taurakalnis hill; Ff, Fl – in Žirmūnai; Ll – near the AS Library. The inflorescence oil is indicated by the second letter f, that of leaf – by the second letter l.

Voucher specimens were deposited in the Herbarium of the Institute of Botany (BILAS), Vilnius, Lithuania (numbers: 59433–59436, 59440, 59442, 59443, 59449 and 55451).

All samples were collected at full flowering stage. The plants were dried at room temperature (20–25 °C): flowers and leaves were separated before drying. Essential oils were prepared by hydrodistillation of 15–50 g of air-dried plants.

Analyses of the essential oils were carried out by GC and GC–MS. An HP 5890 II chromatograph equipped with FID and the HP-FFAP capillary column (25 m  $\times$  0.22 mm i. d.) was used for quantitative analysis. The GC oven temperature was set at 60 °C for 2 min, then programmed at a rate of 5 °C min<sup>-1</sup> to 160 °C, kept for 1 min, then programmed from 160 to 230 °C at a rate of 10 °C min<sup>-1</sup> and finally isothermal at 230 °C for 12 min.

Analyses by GC-MS were performed using an HP 5890 chromatograph interfaced to an HP 5971 mass spectrometer (ionization voltage 70 eV) and equipped with a CP-Sil 8 CB capillary column (50 m × 0.32 mm). The oven temperature was kept at 60 °C for 2 min, then programmed from 60 to 160 °C at a rate of 5 °C min<sup>-1</sup>, kept for 1 min, then programmed from 160 to 250 °C at a rate of 10 °C min<sup>-1</sup> and isothermal at 250 °C for 2 min, using He as the carrier gas (2.0 ml min<sup>-1</sup>). The temperature of the injector and detector was 250°C and 280°C, respectively.

The percentage composition of essential oils was computed from GC peak areas without correction factors. Qualitative analysis was based on a comparison of retention times and indices on both columns and mass spectra with corresponding data in the literature [19, 20, 21 and 22] and computer mass spectra libraries (Wiley and NBS 54K).

The following mass spectral data of unknown components were recorded, m/z (relative intensity):

Unknown 1: 218 (3), 187 (7), 163 (7), 145 (11), 136 (100), 117 (25), 105 (40), 91 (79), 79 (68), 69 (54), 55 (50), 41 (79).

Unknown 2: 220 (16), 202 (14), 177 (13), 159 (79), 131 (32), 119 (64), 109 (75), 93 (79), 91 (100), 79 (65), 67 (50), 55 (58), 41 (78).

Unknown 3: 207 (3), 177 (3), 159 (7), 145 (3), 126 (29), 108 (75), 93 (58), 79 (36), 67 (32), 55 (36), 43 (100).

#### RESULTS AND DISCUSSION

The essential oils were distributed into three groups according to their major constituents.

#### *I.* β-Pinene and 1,8-cineole group

A half of the investigated essential oils (9 samples) studied contained β-pinene (Table 1, 10.2–31.1%) and 1,8-cineole (7.8–17.0%) as the main components. The first major constituent, β-pinene, was found in 8 volatile oils and 1,8-cineole only in one. This group contained only 2 chemotypes of essential oils of β-pinene and 1,8-cineole. The essential oils of this group can be divided into 3 parts according to the content of chamazulene: 5 samples (Af, Al, Bl, Bf and Dl (b)) contained 2.5–6.8% of this component, 2 samples (Ef, Jf) – 0.9–1.5% and 2 were without chamazulene (Fl, Lf).

The both parts of the plants contained essential oils of the same chemotype in 2 habitats (Table 1, A, E). The volatile oils from one part belonged to this group in 5 habitats (3 samples of inflorescence and 2 of leaf).

Compound	R.I. <sub>CP-Sil8 CB</sub>	R.I. <sub>FFAP</sub>	Af	Al	Bl	Cl	Df(b)	Ef	El	Ff	Jf	Interval	Mear
							` '		l				
α-Pinene	939	1045	4.6	3.8	6.9	7.4	3.3	6.3	3	6	3.1	3–7.4	4.9
Camphene	953	1097	1.4	1	1.6	2.7	1.7	1.9	1.1	1.8	tr.	tr2.7	1.5
Sabinene	976	1147	5.4	3.8	3.8	14	4.1	6.1	3.5	8.6	3.3	3.3–14	5.8
β-Pinene	980	1138	26	23.5	31.1	14.2	14	16	11.3	11.8	14.7	11.8–31.1	18.1
Myrcene	991	1180	1.4	1.6	2.1	1.2	1.2	1.3	0.8	0.8	1.3	0.8–2.1	1.3
α-Terpinene	1018	1208	1	tr.	0.7	0.7	0.3	1.2	tr.	0.6	0.5	tr1.2	0.6
p-Cymene	1026	1303	0.6	0.7	160	0.9	0.6	1.2	1.6	0.7	1.2	0–1.6	0.8
1,8-Cineole	1033	1243	9.2	13.1	16.8	8.5	8.1	14.5	9.2	9.5	17	8.1–17	11.8
γ-Terpinene	1062	1274	2.8	0.9	1.9	2.6	0.3	3.4	1.5	1.7	2.7	0.3–3.4	2.0
Terpinolene	1088	1315	0.5	2.4	0.6	0.5	0.3	0.2	20	2.2	0.4	0-0.6	0.3
Camphor	1143	1560	2.6	3.4	2.4	1.9	3.1	2.3	2.8	3.2	tr.	tr3.4	2.4
cis-Chrysanthenol	1162	4545	0.2	2.5	2.2		0.3	0.1		2.2	tr.	0-0.2	0.1
Borneol	1165	1747	1.7	2.5	2.3	4.1	4.1	3.2	1.5	2.2	tr.	tr4.1	2.4
Terpinen-4-ol	1177	1642	1.6	0.9	2.6	2.4	1.2	3.4	1.1	2.1	1.9	0.9–3.4	1.9
α-Terpineol	1189	1732	1.9	2.5	3	1.4	1.7	1.9	0.6	1.5	0.2	0.2–3	1.6
Bornyl acetate	1285	1621	0.8	0.6	0.3	2.3	1.3	2.3	3.7	4	0.2	0.2–4	1.7
α-Cubebene	1351	1520	0.6	0.2		0.1	0.2	0.3	0.4	0.3	0.1	0-0.6	0.2
β-Bourbonene	1384	1598	0.7	0.4	0.3	0.1	0.4	0.1	tr.	2.0	0.3	0-0.7	0.3
β-Caryophyllene	1418	1657	5.6	5.9	3.5	3.9	3.8	4.2	4.3	3.8	4	3.5–5.9	4.3
α-Humulene	1454	1732	1.5	tr.	0.5	0.6	0.8	0.9	0.8	0.9	0.8	tr1.5	0.8
Germacrene D	1480	1772	4.2	3.2	1.1	3.4	2.5	3	2.8	3.2	4.1	1.1–4.2	3.1
Bicyclogermacrene	1494	1780	1	0.3	0.4	0.4	0.3	0.7	0.3	0.6	0.5	0.3–1	0.5
α-Muurolene	1499	1783	0.2			0.4	0.1	0.2	tr.		0.2	0-0.4	0.1
β-Bisabolene	1509	1788	0.3			0.4	0.3	0.6	0.3	0.4	0.2	0-0.6	0.3
Sesquicineole	1514	1000	0.3	0.6	0.6	0.4	2.4	0.2	0.4	0.2	0.5	0-0.4	0.2
δ-Cadinene	1524	1808	1.1	0.6	0.6	0.6	2.4	1	1	1.7	0.8	0.6–2.4	1.1
trans-Nerolidol	1564	2055	3.7	0.8	0.5	4.4	1.1	2.7	2.5	6.8	7.8	0.5–7.8	3.4
Spathulenol	1576	2185	1	1.8	1	0.6	0.7	0.5	2.4	0.5	0.5	0.5–2.4	1.0
Caryophyllene oxide	1581	2038	2.1	3.5	1.6	2	6.3	1.4	8	3	1.9	1.4–8	3.3
Viridiflorol	1590	2152	0.6	1.6		0.3	5.1	0.3	0.9	1.2	0.2	0–5.1	1.1
Humulene epoxide	1606	2122	0.6	0.6	0.2	0.0	0.2	0.5	0.4	0.3	0.2	0-0.6	0.3
10-epi-γ-Eudesmol	1619	2245	1.5	4	0.3	0.8	1.2	1	2.5	1.4	11	0.3–11	2.6
1-epi-Cubenol ?	1627		1.5	0.5	0.3	0.8	1	0.3	1.9	1	0.2	0.3–1.9	0.8
Unknown 1	1635	2204	0.5	0.8	0.6	0.6	0.5	0.3	2.4	0.8	0.5	0-2.4	0.7
τ-Cadinol	1640	2204	0.5		0.6	0.8	0.4	0.3	0.9	0.9	1.2	0-1.2	0.6
Himachalol ?	1647		1.4	4	0.5	1.9	1.7	0.5	0.5	0.5	0.6	0-1.9	0.4
Selin-11-en-4-α-ol	1652	2210	1.4	1	0.5	2	1.7	1.4	3.8	3.9	0.6		1.8
14-Hydroxy-9-epi-	1664	2310	0.9	1.2	0.4	0.7	0.4	0.3	1.7	0.8	0.7	0.3-1.7	0.8
β-caryophyllene	1.602	2254					0.5		1.4	2.2	0.5	0.22	0.5
α-Bisabolene oxide	1682	2354	0.0	0.6	0.2		0.5	0.5	1.4	2.2	0.5	0-2.2	0.5
Unknown 2	1685		0.8	0.6	0.2	tr.	0.1	0.5	1.2	0.8	0.5	tr1.2	0.5
Unknown 3	1689	2412	0.6	0.5		1	0.4	0.2	tr.	0.2	0.9	0–1	0.4
E, E-Farnesol ?	1722	2412	0.8	tr.	6.0	0.4	0.2	0.2	0.6	1.7	0.8	0–1.7	0.5
Chamazulene	1725	2451	4.1	6.5	6.8	3.2	6.2	0.9			1.5	0–6.8	3.2
Total			96.7	92.3	94.7	94.6	82.4	87.6	83.5	91.6	87	82.4–96.7	90.0
Monoterpene hydrocarbons			43.7	35.3	48.7	44.2	25.8	37.6	22.8	32	27.2	22.8-48.7	35.3
Oxygenated monoterpenes			18	23	27.4	20.6	19.8	27.7	18.9	22.5	19.3	18-27.7	21.9
Sesquiterpene hydrocarbons			15.2	10.6	6.4	9.9	10.8	11	9.9	10.9	11	6.4–11	10.6
Oxygenated sesquiterpenes			15.7	16.9	5.4	16.7	19.8	10.4	31.5	26.2	28	5.4-31.5	19.0

The quantity of caryophyllene oxide (Table 1) in the plants containing the same chemotype of essential oil in both parts was markedly higher in the volatile oil of leaf (3.5–8.0%) in comparison with

that of inflorescence (1.0–2.9%). The above regularity held true for the content of spathulenol as well, but the opposite ratio was noted for the quantities of *trans*-nerolidol.

Beside the 43 compounds listed in Table 1, seven more constituents were found in some essential oils:  $\alpha$ -thujene (tr.–0.8%, Af, Cf, Ef,); *cis*-chrisanthenyl acetate (tr.–0.8%, Af, Al and Bl); myrtenol (0.8%, Ef); *trans*-carveol (tr.–2.1%, Af, Ef and El); geranyl acetate (tr.-0.7 %, Af, Cf);  $\beta$ -isocomene (tr.–2.1 %, Af, Ef) and  $\beta$ -ionone (tr.–0.4%, Bl, El). The total sum increased up to 98.9% in the presence of the above additional constituents.

## II. Chamazulene group

Five samples (3 habitats) of oils contained chamazulene (9.8–23.2%) as the major constituent (Table 2). Chamazulene was the third main component in inflorescence (Df) and leaves (Dl) in one habitat, the second in inflorescences in 2 habitats (B and D), and the first one from inflorescences in 1 habitat (C). The quantities of the constituents in the essential oils from the same habitats depended on

seasonal conditions. The amount of chamazulene in the inflorescence oils was approximately the same in both samples Df (2000) and Df (b) (1999), but the quantity of 1,8-cineole in the Df (b) was notably lower and chamazulene became the second major constituent, while it was the third in sample Df. The content of chamazulene in the volatile oils from the leaves was lower than in that from the inflorescence of the same plants as in the formerly investigated plants (see Introduction).

Only 5 compounds were identified in the essential oils of this group alongside those listed in Table 2 (Bf, Cl, Df, Dl and Dl (b)):  $\alpha$ -thujene (tr., Dl, Dl and Df (b)); myrtenol (tr.–0.4%, Df, Dl); trans-carveol (tr.–0.5% Df, Dl and Df (b));  $\beta$ -isocomene (0.4%, Cl) and  $\alpha$ -selinene (1.8%, Cl). The last compound was not found in the first  $\beta$ -pinene and 1,8-cineole group. The total sum induding the above compounds was a little larger in comparison with that presented in Table 2 (85.9–98.7%).

Table 2. Chemical composition of essential oils (%) containing the major constituents:  $\beta$ -pinene+chamazulene+1,8-cineole (Df, DI, Df (b), Bf and Cl) and trans-nerolidol+ $\beta$ -pinene (Kf, Kf (b), FI and Lf) of Achillea millefolium growing wild in Vilnius<sup>a</sup>

Compound	R.I. <sub>CP-Sil8 CB</sub>	R.I. FFAP	Df	Dl	Df (b)	Bf	Cf	Kf	Fl	Lf	Kf (b)
1	2	3	4	5	6	7	8	9	10	11	12
α-Pinene	939	1045	4.1	3.4	2.7	5.3	4.5	5.1	2.1	3.1	7.1
Camphene	953	1097	tr.	0.6	0.8		1.4	1.6	0.6	1	2.8
Sabinene	976	1147	3.6	4.2	4.1	3.4	5.2	2.2	2	8.5	5.4
β-Pinene	980	1138	27.8	30.2	14	26.5	9.7	12	5.5	10.1	21.3
Myrcene	991	1180	0.9	2.2	1	1.1	1.7	0.5	1.1	0.8	0.6
α-Terpinene	1018	1208	0.6		0.2	0.4	0.7	1.4	1.1	0.5	0.5
p-Cymene	1026	1303	tr.	0.2	0.1	tr.	1.9	1.3	1	0.7	0.9
1,8-Cineole	1033	1243	15.3	16	7.8	10.6	5.3	8	4.4	5.4	9
γ-Terpinene	1062	1274	1.6	1	0.2	1.4	1.7	3.8	1.1	1.7	1.8
Terpinolene	1088	1315	tr.				tr.	0.9		0.4	
trans-Pinocarveol	1139		0.7	0.4	0.3			0.4			
Camphor	1143	1560	0.9	1.8	1.6	0.3	1.4	3.2	4.4	1.5	4.9
cis-Chrysanthenol	1162		1.5	1.3			0.4	0.4	0.2	0.3	0.2
Borneol	1165	1747	1.5	3.2	3	0.4	3.8	6.5	3.1	6.6	4.4
Terpinen-4-ol	1177	1642	3	1.3	1.6	1.2	2.1	5.5	1.2	1.9	2.4
α-Terpineol	1189	1732	2.8	2.2	2.2	1.7	0.6	1.2	tr.	1.3	1.1
cis-Crysanthenyl acetate	1262		1.6	1.7	tr.	tr.		3.8			
Bornyl acetate	1285	1621	tr.	tr.	1.2		tr.	1.1	4.9	0.3	2.2
α-Cubebene	1351	1520			0.2				0.4	0.1	
β-Bourbonene	1384	1598	tr.	0.2		0.2	0.2	tr.		0.2	
β-Caryophyllene	1418	1657	8.7	6.5	6.5	5.1	4.5	4.3	3.8	3.4	5
α-Humulene	1454	1732	1.4	1.1	1.2	0.3	0.8	0.9		0.2	0.7
Germacrene D	1480	1772	3.6	1.9	5	4.9	2.1	2.1	3.4	3.8	1.4
Bicyclogermacrene	1494	1780	0.9		0.4	1.2	0.6	0.3	0.7	0.7	0.3
α-Muurolene	1499	1783			0.2	0.2	0.7			0.4	
β-Bisabolene	1509	1788	tr.		0.3		0.5	tr.	0.4	0.3	
Sesquicineole	1514			tr.	tr.		0.4	tr.	0.5	1.8	0.2
δ-Cadinene	1524	1808	0.7	0.6	2.4	0.9	1	1.6	2.5	0.7	1.3
trans-Nerolidol	1564	2055	tr.		2.8	0.3	5.8	13.5	8.2	11.2	9.5
Spathulenol	1576	2185	0.5	1.3	0.6	0.7	1.5	0.6	1.8	1.1	0.3
Caryophyllene oxide	1581	2038	1.8	3.3	1.9	1.1	5.4	3.3	5.3	2.5	2.7

Table 2 (continue)											
1	2	3	4	5	6	7	8	9	10	11	12
Viridiflorol	1590	2152	tr.	tr.	6.5		1.5	1.6	3.1	1.2	0.9
Humulene epoxide	1606	2122	tr.	0.2	tr.		0.6	0.3	0.2	0.5	
10-epi-γ-Eudesmol	1619	2245	0.4	tr.	0.3		1.6	1.2	4.3	8.3	2.9
1-epi-Cubenol ?	1627		tr.		0.3	0.1	2.2	0.9	2.1	0.6	0.8
Unknown 1	1635		tr.		0.1	tr.	1.5	0.9	1.5	1.7	0.4
τ-Cadinol	1640	2204	tr.	tr.	0.4	1	0.8	0.6	1.4	0.7	0.7
Himachalol ?	1647			0.2	0.2	0.8	3.5		0.9	1.5	tr.
Selin-11-en-4-α-ol	1652		0.4	0.3	0.2	0.8	2.2	1.2	7	6.1	1.3
14-Hydroxy-9-epi-	1664	2310	0.4	0.8	0.5	0.8	1.3	0.9	1.7	1	0.4
β-caryophyllene											
α-Bisabolene oxide	1682	2354	tr.		0.3			0.3	3.1	1.5	2.3
Unknown 2	1685		tr.		0.3	0.4	2.4	0.9	1.3	0.7	0.3
Unknown 3	1682		tr.		0.5		1	0.7	1.4	0.7	
E, E-Farnesol ?	1722	2412	tr.	tr.	0.4		0.5	0.7	2.8	0.5	
Chamazulene	1725	2451	13.9	12.6	13.6	23.2	9.8	0.1			tr.
Total			98.6	98.7	85.9	94.3	92.8	95.8	90.5	95.5	96
Monoterpene hydrocarbons	S		38.6	41.3	23.1	38.1	26.8	28.8	14.5	26.8	40.4
Oxygenated monoterpenes			27.3	27.9	17.7	14.2	13.6	30.1	18.2	17.3	24.2
Sesquiterpene hydrocarbon	S		29.2*	23.4*	29.8*	36*	20.2*	9.2	11.2	9.8	8.7
Oxygenated sesquiterpenes			3.5	6.1	15.3	6	32.2	27.6	46.6	41.6	22.7

<sup>a</sup> A capital letter indicates the habitat, f – inflorescences, I – leaves, letter without b – plants collected in 2000, with b – in 1999, tr.–traces, \* including chamazulene.

# III. Nerolidol group

trans-Nerolidol (8.2-13.5%, Table 2) was the first major constituent in 3 samples of essential oils (Fl, Kf and Lf) and the second one in one sample (Kf (b)). The second or the first main component was β-pinene (5.5–21.3%), the third one was 1,8-cineole (8.0-9.0%) in 3 and oxygenated sesquiterpenes (7.0-8.3%) in 2 samples. The inflorescence essential oil of the same habitat collected in 1999 (Kf (b)) and in 2000 (Kf) contained trans-nerolidol (9.5 and 13.5%) and  $\beta$ -pinene as the major constituents, but their quantities were influenced by seasonal conditions. Samples of the volatile oils of this group were found only in one part of the plant. The leaf oil of these plants in 2 habitats (F and J) contained essential oils of the β-pinene + 1,8-cineole group containing 6.8-7.8% of trans-nerolidol and in other 2 habitats (K and L) it had no signs of a clear chemotype, but contained 3.4 and 5.7% of transnerolidol. One oil sample (Fl ) contained no chamazulene and the other 3 contained a small quantity of it (tr.-0.9%). The content of 1,8-cineole (4.4-9.0%) was markedly higher than that of chamazulene in all samples of this group.

In addition to the compounds listed in Table 2 (Fl, Kf, Kf (b) and Lf), 8 more constituents were identified as well: α-thujene (tr.–0.4 %, K, K (b)); myrtenol (tr.–0.9 %, K and L); *trans*-carveol (tr.–

0.3%, K and L); sabinyl acetate ( $\sim$ 0.2%, L);  $\beta$ -isocomene (tr. $\sim$ 0.4%, Fl, Kf, and Lf);  $\alpha$ -selinene (0.9% Kf (b)) and *trans*-arteannuic alcohol (0.2 $\sim$ 0.3%, F1, Kf(b)). The total sums of all components were 87.2 $\sim$ 97% in this group.

*trans*-Nerolidol as the main constituent was not found in the formerly investigated yarrow oils.

#### Variation of the constituent amounts

Some aspects of the healing power of yarrow are determined by chamazulene (see Introduction). This compound was found in 16 from the 18 essential oil samples studied (Tables 1 and 2), however, its content in 11 samples reached 0.9–6.8% and in 5 samples 9.8–23.2%.

Compounds of different bioactivity such as; 1,8-cineole (4.4–17%) [23–26],  $\beta$ -pinene (5.5–31.1%) [27],  $\alpha$ -pinene (2.1–7.4%) [26–28], camphor (tr.–4.9%), borneol (tr.–6.6%) [26],  $\beta$ -caryophyllene (3.4–8.7%) [25, 27, 29, 30] and caryophyllene oxide (1.1–8%) [30] were found in all samples (Tables 1 and 2). *trans*-Nerolidol (tr.–13.5%) [25, 29, 30] was not found only in one sample (DI).

The investigated groups of the essential oils studied could be assigned to different classes of compounds. The largest part of the volatile oils from the first,  $\beta$ -pinene + 1,8-cineole group consisted of monoterpene hydrocarbons (mean, 35.3%), from the

second, chamazulene group – monoterpene (26.8%) and sesquiterpene hydrocarbons with chamazulene (20.2%), and in the third, *trans*-nerolidol group – oxygenated sesquiterpenes (46.6%). Mono- and sesquiterpene hydrocarbons (45.9%) and the corresponding oxygenated compounds (40.9%) made up approximately equal amounts in the essential oils in the first group. The oils of group II were rich in hydrocarbons (61.3%), while those of group III (57%) were enriched in oxygenated terpenes.

#### **CONCLUSIONS**

Four chemotypes (β-pinene, 1,8-cineole, chamazulene and *trans*-nerolidol) of the essential oils of yarrow (*Achillea millefolium* L. ssp. *millefilium*) growing wild in Vilnius were identified according to the first major constituent. The volatile oils were divided into 3 groups containing the same two or three major constituents: I (9 samples) – β-pinene (11.8–31.1%), 1,8-cineole (8.1–17.0%); II (5) – chamazulene (9.8–23.2%), β-pinene (9.7–30.2%) and 1,8-cineole (5.3–16.0%); III (4) – *trans*-nerolidol (8.2–13.5%) and β-pinene (5.5–21.3%). The β-pinene chemotype was found in all groups beside the oils of the chamazulene (1 sample), *trans*-nerolidol (4 samples) and 1,8-cineole (1 sample) chemotypes.

Received 14 march 2002

#### References

- A. Lekavičius, In *Lietuvos TSR Flora* (Eds. M. Natkevičaitė-Ivanauskienė, R. Jankevičienė and A. Lekavičius), Vol. 6, 92, Mokslas, Vilnius (1980).
- 2. D. A. Konovalov, O. A. Konovalova, and V. A. Chelombitko, *Rast. Resur.*, **26**, 598 (1990).
- A. C. Figueiredo, M. S. S. Pais, and J. T. C. Scheffer, In *Biotechnology in Agriculture and Forestry*. (Ed. Y. P. S. Bajaj) Vol. 33, 1, Springer-Verlag, Berlin (1995).
- 4. R. Balz. *The Healing Power of Essential Oils*, Lotus Light, USA (1996).
- 5. J. Lawless. *The Illustrated Encyclopedia of Essential Oils*. Element Books, Singapore, 75 (1999).
- 6. J. A. Jaskonis. *Lietuvos TSR MA darbai* (in Russian), serija C, **1** (**54**), 81 (1971).
- A. A. Ustiuzhanin, A. I. Konovalov, A. I. Shreter, K. C. Konovalova, and K. S. Ribalko. *Rast. Resur.*, 23 (3), 424 (1987).
- 8. B. Michler and C. G. Arnold. *Folia Geobot.*, **34**, 143 (1999).
- 9. R. M. Mata and N. A. Velasco. 1 Jornadas Iber. plantas med., arom y aceites esenc. (in Spanish), 243 (1992).
- 10. B. M. Lawrence. Perf. Flavor., 22 (3), 68 (1997).
- 11. J. A. Pino, A. Rosado, and V. Fuentes. *J. Essent. Oil Res.*, **10**, 427 (1998).
- J. C. Chalchat, M. S. Gorunovic, and S. D. Petrovic.
  J. Essent. Oil Res., 11, 306 (1999).

- 13. M. Orth, F. C. Czygan, and V. P. Dedkov. *J. Essent. Oil Res.*, **11**, 681 (1999).
- 14. A. Orav, T. Kailas, and K. Ivask. *J. Essent. Oil Res.*, **13**, 290 (2001).
- 15. J. G. Barroso, A. C. Figueiredo, M. S. S. Pais, and J. T. C. Scheffer. *J. Chrom. Sc.*, **30**, 392 (1992).
- R. V. Polej, V. V. Plemenkov, N. P. Artemova, J. V. Chugunov, and M. G. Fazlyieva. *Rast. Resur.*, 32 (4), 37 (1996).
- A. C. Figueiredo, J. G. Barroso, M. S. S. Pais, and J. T. C. Scheffer. *Flav. Fragr. J.*, 7, 219 (1992).
- J. Rohloff, E. B. Skagen, A. H. Steen, and T. H. Iversen. J. Agric. Food Chem., 48, 6205 (2000).
- R. Adams. *Identification of Essential Oil Components* by Gas Chromatography/Mass Spectrometry. Allured Publishing Corp., Carol Stream, IL (1995).
- 20. T. Y. Chung, J. P. Eiserich, and T. Shibamoto. *J. Agric. Food Chem.*, **41**, 1693 (1993).
- 21. I. G. Zenkevich. Rast. Resur. 32 (1-2), 48 (1996).
- 22. I. G. Zenkevich. Rast. Resur. 33 (1), 16 (1997).
- 23. M. Miyazawa, H. Watanabe, and H. Kameoka. *J. Agric. Food Chem.*, **45**, 677 (1997).
- 24. G. C. Cameron and S. M. D. Easton. *Perf. Flavor.*, **25** (3), 6 (2000).
- A. Valentin, Y. Pelissier, F. Benoit, Ch. Marion, D. Kone, M. Mallie, J. M. Bastide, and J. M. Bessiere. *Phytochem.*, 40, 1439 (1995).
- T. Hiroi, Y. Miyazaki, and Y. Kobayashi. *Xenobiot.*,
  457 (1995).
- Z. Recsan, G. Pogliuca, M. Piretti, L. Penzes, A. Yoydim-Kuresh, R. Nolde, and S. Deans. *J. Essent. Oil Res.*, 9, 53 (1997).
- 28. M. Lis-Balchin, R. J. Ochocka, S. G. Deans, M. Asztemborska, and S. Hart. *J. Essent. Oil Res.*, 11, 393 (1999).
- 29. I. Kubo and Y. Morimitsu. *J. Agric. Food Chem.*, **43**, 1626 (1995).
- B. F. Binder and J. C. Robbins. J. Agric. Food Chem.,
  45, 980 (1997).

# Danutė Mockutė, Asta Judžentienė

# LAUKINIŲ KRAUJAŽOLIŲ *ACHILLEA MILLEFOLIUM* L. SSP. *MILLEFOLIUM*, AUGANČIŲ VILNIUJE, ETERINIŲ ALIEJŲ CHEMINĖ SUDĖTIS

# Santrauka

Buvo tiriami baltai žydinčių kraujažolių, surinktų 9 augimvietėse, žiedynų ir lapų eteriniai aliejai. Aliejai pagal pirmąjį pagrindinį komponentą priskirti 4 chemotipams: β-pineno, chamazuleno, 1,8-cineolio ir nerolidolio. Pirmieji trys chemotipai buvo rasti ir kitose šalyse, o ketvirtasis, nerolidolio, būdingas tik kai kurioms Vilniuje augančioms kraujažolėms. Pagal du ar tris pagrindinius komponentus eteriniai aliejai buvo suskirstyti į tris grupes: I (9 bandiniai) – β-pineno (11,8–31,1%) ir 1,8-cineolio (8,1–17,0%); II (5 bandiniai) – chamazuleno (9,8–23,2%), β-pineno (9,7–30,2%) ir 1,8-cineolio (5,3–16,0%), taip pat III (4 bandiniai) – *trans*-nerolidolio (8,2–13,5%) ir β-pineno (5,5–21,3%).

Skirtinga eterinių aliejų cheminė sudėtis sąlygoja nevienodą tiriamų augalų ir jų aliejų bioaktyvumą bei jų gydomasias savybes.