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Chemical composition of essential oils of *Glechoma hederacea* L. growing wild in Vilnius district

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Wild plants of *Glechoma hederacea* L. were collected at full flowering in four localities of Vilnius district. Essential oils produced by hydrodistillation were analysed using GC and GC / MS methods. Germacrene D (15.6–18.8%) was the dominant compound in the oils. The other major constituents were γ-elemene (9.7–16.0%), β-elemene (9.8–11.1%), iso-phytol + phytol (4.7–15.6%) and (Z)-β-ocimene (4.7–5.6%). Sesquiterpene hydrocarbons comprised the largest (55.0–66.2%) part of the essential oils. Sesquiterpenoids with germacrane and elemane carbon skeletons formed about a half of the samples. Forty-two identified constituents made up 87.5–94.0% of the oils.

Key words: *Glechoma hederacea* L., *Labiatae*, essential oil composition, germacrene D, γ-elemene, β-elemene, phytols, (Z)-β-ocimene

INTRODUCTION

Two species of *Glechoma* L., *Glechoma hederacea* and *Glechoma chirsuta*, grow in Lithuania [1]. The first species is widespread, but the second was found only in Vilnius district. The overground parts collected during flowering are used for healing different diseases and as a spice [2–6]. A review on the chemical composition of *Labiatae* essential oils included some data on the oil of *Glechoma hederacea* L. growing in North America in New Brunswick [7]. The oil yield in the plants was 0.01%. The dominant constituents were germacrene D (19.4%) and germacrene B (13.9%). The marked amounts of (Z)-β-ocimene (9.2%), β-elemene (8.9%) and 1.8-cineole (6.2%) were determined in the oil [7]. Germacrenes A, B and C are less stable than germacrene D and may be sometimes converted into β-, γ- and δ-elemenes under GC conditions [8].

The properties of the main compounds were investigated. Germacrenes are used by different insects as synomones (producing natural enemies in a situation of plants infested with herbivores), sex and alarm pheromones (attractants) [9]. β-Elemene also influences the behaviour of insects [10]. The above compounds are used for synthesis of anticancer drugs [11, 12].

The present study deals with the composition of *Glechoma hederacea* L. essential oils from four different localities in Vilnius district.

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MATERIALS AND METHODS

Samples of *Glechoma hederacea* L. were collected at full flowering in four localities of Vilnius district (in 2005): A – Þolyno, B – Salininkai, C – Antakalnis, D – Nemenèinë. Voucher specimens were deposited in the Herbarium of the Institute of Botany (BILAS), Vilnius, Lithuania (Numbers: A–268767, B–268766, C–268771, D–268770).

G. hederacea L. plants were dried at room temperature (20–25 °C). The essential oils were prepared by hydrodistillation for 3 h using a mixture of hexane and ethyl ether (1:1) as a collecting organic solvent. The yield of essential oils was ~0.02–0.03%.

An HP 5890 II chromatograph equipped with a FID and an HP-FFAP capillary column (30 m × 0.25 mm i. d, film thickness 0.3 μm) was used for quantitative analysis. The GC oven temperature was set at 70 °C for 10 min and then programmed at a rate of 3 °C min^{-1} to 210 °C, using He as a carrier gas (0.7 ml min^{-1}). The injector and detector temperatures were 200 and 250 °C, respectively.

GC/MS analyses were performed using a chromatograph interfaced with an HP 5971 mass spectrometer (ionisation voltage 70 eV) and equipped with a CP-Sil 8 CB capillary column (50 m × 0.32 mm i. d., film thickness 0.25 μm). The oven temperature was held at 60 °C for 2 min, then programmed from 60 to 160 °C at a rate of 5 °C min^{-1}, held for 1 min and then programmed to 250 °C at the rate of 10 °C min^{-1} and isothermal for 5 min, using

Table. **Chemical composition (%) of essential oils of *Glechoma hederacea* L. collected in Vilnius district (2005).**

Compound	**RI**	**A**	**B**	**C**	**D**
1,3-trans, 5-cis-Octatriene	920	0.3	t	0.5	t
α-Pinene	939	t	0.1	0.2	t
β-Pinene	979	0.3	0.2	0.7	1.7
3-Octanone	984	0.6	0.3	0.5	1.0
Myrcene	991	0.6	0.4	1.3	1.7
1,8-Cineole	1033	2.0	1.9	2.4	3.5
Z-β-Ocimene	1037	2.5	1.9	4.7	5.6
E-β-Ocimene	1050	1.5	0.7	0.9	0.7
p-Mentha-2,4(8)-diene	1088	t		0.1	t
n-Nonanal	1101	0.5	0.2	0.2	0.2
1-Octen-3-yl acetate	1113	t	0.1	0.4	0.6
allo-Ocimene	1132	1.2	0.8	2.4	2.5
dihydro-Pinocarvone	1160		1.2	1.6	8.5
Myrtenal	1196		t	0.1	0.4
n-Decanal	1202	0.2	t	0.1	0.3
δ-Elemene	1338	2.4	2.1	1.9	2.2
Eugenol	1359	t			t
α-Copaene	1377	0.5	0.6	0.9	0.2
β-Bourbonene	1388	2.0	1.6	1.5	1.7
β-Elemene	1391	**10.2**	**9.8**	**10.2**	**11.1**
β-Ylangene	1421	3.9	3.6	3.9	2.7
β-Gurjunene	1434	1.2	1.2	2.0	1.0
γ-Elemene	1437	**16.0**	**16.0**	**10.3**	**9.7**
Aromadendrene	1441	1.5		1.1	0.8
α-Humulene	1455	0.2	1.6	1.9	1.5
γ-Muurolene	1480	0.6	0.5	0.6	t
Germacrene D	1485	**17.2**	**17.8**	**18.8**	**15.6**
α-Zingiberene	1494		t		3.4
Bicyclogermacrene	1500	2.0	2.5	2.0	t
(E,E)-α-Farnesene	1506	1.8	1.0	1.3	1.9
γ-Cadinene	1514	0.6	0.4	0.6	t
d-Cadinene	1523	1.1	1.3	1.0	0.8
trans-Cadina-1(2),4-diene	1535			0.5	
α-Cadinene	1539	1.1	t		
cis-Sesquisabinene hydrate	1544	t		0.5	
Germacrene B	1561	3.9	3.4	2.9	2.4
Germacrene D-4-ol	1576	1.8	2.0	1.8	1.4
γ-Eudesmol	1632	0.6			t
Cubenol	1647		1.0		t
α-Cadinol	1654	1.2	1.3	2.3	1.1
6,10,14-trimethyl-2-Pentadecanone	1860	1.0	2.9	0.7	t
iso-Phytol + Phytol	1945	**10.0**	**15.6**	**4.7**	**5.9**
Total		90.5	94.0	87.5	90.1
Monoterpene hydrocarbons		6.4	4.1	10.8	12.2
Oxygenated monoterpenes		2.0	3.1	4.1	12.4
Sesquiterpene hydrocarbons		66.2	63.4	61.4	55.0
Oxygenated sesquiterpenes		3.6	4.3	4.6	2.5
Germacrane skeleton		22.9	23.2	23.5	19.4
Elemane skeleton		28.6	27.9	22.4	23.0

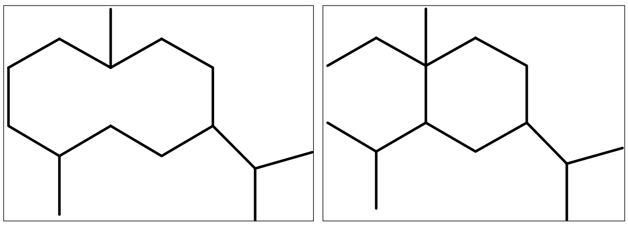
RI- Retention index on nonpolar column CP-Sil 8CB, t-traces.

He as a carrier gas (1.0 ml min^{-1}). The injector and detector temperatures were 250 °C.

The percentage composition of the essential oils was computed from GC peak areas without correction factors [13]. Qualitative analysis was based on the comparison of retention times and mass spectra with the corresponding data in the literature [14] and the computer mass spectra libraries (Wiley and NBS 54K).

RESULTS AND DISCUSSION

Fresh and dried ground ivy (*Glechoma hederacea* L.) has a strong odour, but the amount of the essential oil reaches only 0.02–0.03%. B. M. Lawrence has concluded that oil-poor species of the family *Labiatae* produce essential oils rich in sesquiterpene hydrocarbons, with germacrene D often being one of the predominant compounds [7]. Germacrene D (15.6–18.8%) dominated in the oils from all investigated habitats of Vilnius district (Table). The close content of the above compound contained a corresponding American oil (19.4%) [7]. The constituents with germacrane carbon skeleton (germacrene D + germacrene B + germacrene D-4-ol, Figure) comprised 19.4–23.5% in the study samples. The second and third positions in the essential oils were occupied mostly by γ-elemene (Table, 9.7–16.0%) and β-elemene (9.8–11.1%) which was characteristic of American oil (8.9%) [7]. The samples A and B included larger amounts of constituents with the elemane carbon skeleton (Figure, Table, 27.9–28.6%, three elemenes: β, γ and δ) than with germacrane (22.9–23.2%). Nearly the same correlation was found in the oil D, but the content of compounds with both carbon skeletons was lower: 19.4% with germacrane and 23.0% with elemane.



1 2

Fig. Germacrane (1) and elemane (2) carbon skeletons

The essential oil of sample C contained close amounts of constituents with both main carbon skeletons: 23.5 % and 22.4%. The same chromatographic conditions of analysis of the oils under study allowed to compare the data. The amounts of compounds with elemane carbon skeleton might be elevated during analysis while some molecules of germacrenes (A, B, C) might transformed to elemenes [8]. The sum of compounds with both main carbon skeletons will be constant. The compounds with germacrane and elemane skeletons comprised more than a half of the essential oils A and B (51.1–51.5%), while the samples C and D included lower amounts of these compounds (42.4–45.9%). The major constituents were mostly sesquiterpene hydrocarbons which comprised 55.5–66.2% of the essential oils (Table). The notable levels of iso-phytol and phytol mixture (4.7–15.6%) were determined. The oils A and B included 10.0–15.6% of the above mixture. The samples C and D contained lower quantities of the phytol mixture (Table, 4.7–5.9%) and nearly the same amounts of (Z)-β-ocimene (4.7–5.6%) which was characteristic (9.2%) of the American *Glechoma hederacea* L. essential oil [7]. The amount of germacrene B, which might be converted into γ-elemene [8] during analysis, was lower in the essential oils under study (Table, 2.4–3.9%) than in the earlier investigated oil (13.9%) [7]. An opposite correlation was observed for γ-elemene: the oils under study included 9.7–16.0% and 1.1% contained a corresponding American oil.

The amounts of monoterpenoids comprised 7.2–24.6% and were markedly lower than those of sesquiterpenoids (57.5–69.8%). The main way of volatile compound biosynthesis was formation of sesquiterpenoids. The 42 identified constituents made up 87.5–94.0% of the A–D essential oils. Thirty one compounds from the identified constituents were found in all study oils.

CONCLUSIONS

The major constituents of the essential oils of wild *Glechoma hederacea* L. from Vilnius district were mostly germacrene D (15.6–18.8%), γ-elemene (9.7–16.0%) and β-elemene (9.8–11.1%). The 42 identified constituents made up 87.5–94.0% of the oils. Sesquiterpene hydrocarbons comprised 55.0–66.2% and sesquiterpenoids 57.5–69.8% of the samples. About a half of the study essential oils of ground ivy were made of compounds with germacrane and elemane carbon skeletons. The above data allowed to conclude that the main way of volatile compounds biosynthesis was formation of sesquiterpenoids.

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VILNIAUS APSKRITYJE AUGANÈIØ ÐLIAUÞIANÈIØJØ TRAMAÞOLIØ (*GLECHOMA HEDERACEA* L.) ETERINIØ ALIEJØ CHEMINË SUDËTIS

S a n t r a u k a

Tirta paprastoji ðliauþianèioji þydinti tramaþolë, surinkta keturiose augavietëse Vilniaus apskrityje. Eteriniai aliejai, iðgauti hidrodistiliacijos bûdu, buvo analizuojami dujø chromatografijos ir dujø chromatografijos–masiø spektrometrijos metodais. Germakrenas D (15,6–18,8%) yra vyraujantis komponentas ðiuose eteriniuose aliejuose. Kiti junginiai, kuriø nustatyti nemaþi kiekiai, yra: γ-elemenas (9,7–16,0%), β elemenas (9,8–11,1%), izofitolis + fitolis (4,7–15,6%) ir (Z)-β-ocimenas (4,7–5,6%). Seskviterpeniniai angliavandeniliai sudarë didþiausià eteriniø aliejø dalá. Nustatyta, kad apie pusë visø junginiø yra seskviterpenoidai su germakrano ir elemano skeletais. Keturiasdeðimt du identifikuoti komponentai sudarë 87,5–94,0% tramaþolës eterinio aliejaus.