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TERPENOIDS AND AROMATIC COMPOUNDS IN ESSENTIAL OILS OF THE HERBS *Galium hercynicum* AND *G. humifusum*

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Representatives of the genus *Galium* L. are widely used in the folk medicine of many countries and are of interest to researchers. The lipophilic substances include mainly iridoids and terpenoids of several types [1–3]. We have previously studied the essential oil constituents of *G. verum* L. flowers [1]. In continuation of work on species of the genus *Galium*, we established the composition of essential oils from the herbs *G. hercynicum* Weigel. and *G. humifusum* Bieb. The raw material for obtaining essential oils was ground upper parts of the stems with leaves and flowers that were collected during flowering in June 2009 in Ivano-Frankovsk Oblast and in July 2009 in Kherson Oblast of Ukraine (herbarium specimens No. 7/09 and No. 9/09 are preserved in the Herbarium of the Pharmacognosy Department, NPU).

Essential oil was obtained by steam distillation followed by treatment of the distillate with hexane in order to isolate the essential oil occurring in the plant raw material in minor or trace quantities [4]. The constituent composition of the herb essential oil of the studied species was established on an Agilent Technology 6890 N chromatograph with a 5973 N mass-spectrometric detector. The analytical conditions were capillary quartz chromatographic column HP-5MS, length 30 m, inner diameter 0.25 mm; He carrier gas at flow rate 1 mL/min; sample volume 0.1–0.5 μL. Injected samples were divided 1/50. Thermostat temperature was 50°C with programming to 220°C at 4°/min. The detector and vaporizer temperatures were 250°C. Compounds were identified by comparison of the chromatographic mass spectral results with data in the NIST02 mass spectra library.

The essential oil content in air-dried *G. hercynicum* herb was 0.01%. A total of 47 compounds was found, of which 35 were identified. Of these, 15 were terpenoids; 7, higher hydrocarbons; 7, fatty acids; and 6, alcohols, aldehydes, and ketones. The monoterpenoids included acyclic linalool, geraniol, nerol, geranylacetone; monocyclic, α-terpineol, β-ionone; bicyclic, borneol; monocyclic aromatic, thymol and carvacrol; bicyclic sesquiterpenoids, α- and β-eudesmol, hexahydrofarnesylacetone, farnesylacetone; the diterpenoid phytol, and the triterpenoid squalene.

The essential oil content in air-dried *G. humifusum* herb was 0.01%. A total of 75 compounds was found, of which 38 were identified. Of these, 14 were terpenoids and aromatic compounds; 21, higher hydrocarbons; 3, fatty acids. The monoterpenoids included acyclic, myrcene, geranylacetone; monocyclic, α-terpinene, γ-terpinene, α-terpineol; monocyclic aromatic, thymol, carvacrol, *p*-cymene; triterpene squalene; aromatic compounds, 2-methylbenzaldehyde, 1-methylnaphthalene; phenolic compounds, β-phenylethyl alcohol, phenylacetaldehyde, 2-methoxy-4-vinylphenol. Table 1 presents the results.

A comparison of the essential oil constituents of *G. hercynicum*, *G. humifusum*, and *G. verum* [1] showed that α-terpineol and squalene were common to these *Galium* species.

The characteristic constituents of essential oils of *G. hercynicum* and *G. verum* were the terpenoids α-terpineol, linalool, borneol, and squalene; common to *G. humifusum* and *G. verum*, α-terpineol, squalene, and 2-methoxy-4-vinylphenol.

It is interesting that the aromatic monoterpenoids thymol (12.39 and 9.11%) and carvacrol (10.22 and 1.14%) dominated essential oils of *G. hercynicum* and *G. humifusum*, respectively. Common to them in addition to α-terpineol and squalene was geranylacetone. It is noteworthy that bicyclic monoterpenoids and sesquiterpenoids were not found in *G. humifusum*.

The compositions of these essential oils were studied for the first time.

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Table 1. Terpenoids and Aromatic Compounds in Essential Oils of *G. hercynicum*, *G. humifusum*, and *G. verum*

Compounr	RI	*G. hercynicum,* herb		*G. humifusum,* herb		*G. verum,* flowers [1]	
		T, min	%	T, min	%	T, min	%
Myrcene	994			7.35	1.8		
α-Terpinene	1018			8.1	1.74		
p-Cymene	1026			8.35	5.93		
Benzyl alcohol	1055					9.28	7.85
γ-Terpinene	1060			9.43	8.62		
cis-Linalooloxide	1095					10.55	0.65
Linalool	1102	10.78	0.93			11.44	0.79
trans-Linalooloxide	1110					11.07	0.90
β-Phenylethyl alcohol	1117			11.28	0.36		
2-Methylbenzaldehyde	1156			12.58	10.72		
Camphor	1167					12.95	0.61
Borneol	1169	13.03	1.61			13.68	0.38
Phenylacetaldehyde	1178			13.33	4.75		
cis-Epoxylinalool	1192					13.8	0.45
α-Terpineol	1193	13.84	3.08	13.83	0.21	14.52	
trans-Epoxylinalool	1197					13.96	0.45
Nerol	1236	15.13	1.06				1.31
4-Vinylphenol	1247					15.47	
Geraniol	1265	16.02	2.91				
1-Methylnaphthalene	1303			17.14	0.22		0.59
Thymol	1313	17.44	12.39	17.38	9.11		
Carvacrol	1323	17.75	10.22	17.66	1.14		
2-Methoxy-4-vinylphenol	1352			17.94	1.21	18.63	1.58
Geranylacetone	1458	22.29	1.38	22.26	0.39		
β-Eudesmol	1491	27.53	0.90				
β-Ionone	1494	23.32	2.22				
α-Eudesmol	1497	27.58	1.35				
Hexahydrofarnesylacetone	1803	30.41	2.87				
Farnesylacetone	1900	31.31	1.1				
Phytol	2123	33.37	1.86				
Squalene	2837	39.14	2.18	39.15	5.04	39.96	20.82

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