

COMPOSITION OF ESSENTIAL OIL FROM *Artemisia glauca* FROM WESTERN SIBERIA

E. V. Polyanskaya,¹ E. A. Korolyuk,²
and A. V. Tkachev³

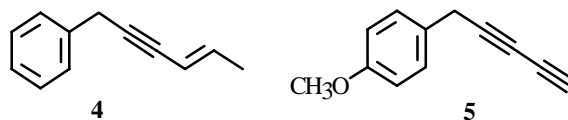
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The composition of essential oil from *Artemisia glauca* (Asteraceae) growing in southern Siberia was studied. More than 60 oil components consisting of 99.0-99.7% of the total volatile components were identified by GC-MS by comparison of full mass spectra and retention times. The main components of the essential oil were acetylene derivatives of capillene (11-60%) and benzyldiacetylene (1-31%). Other acetylene derivatives such as capillin, (*E*)-hex-4-en-2-ynylbenzene, 1-(4-methoxyphenyl)-2,4-pentadiyne, and capillarin were also identified in the oil.

Key words: *Artemisia glauca*, Asteraceae, gray wormwood, essential oil, natural acetylenes.

Herein we describe essential oil from freshly collected *Artemisia glauca* Pall. ex Willd. from various points of its distribution over southern Western Siberia. Table 1 lists the component composition and yield.

Table 1 shows that the yield of essential oil from freshly collected raw material is rather high (0.29-0.69%). A characteristic feature of essential oil from *A. glauca* is the high content of total known natural acetylene compounds such as benzyldiacetylene (demethylcapillene) (**1**), capillene (**2**), and capillin (**3**). In addition, we identified another two related acetylene derivatives in the oil, (*E*)-hex-4-en-2-ynylbenzene (**4**) [1] and 1-(4-methoxyphenyl)-2,4-pentadiyne (**5**) [2]. Both these compounds are known as synthetic products and have not previously been isolated from plants.



The total content of acetylene derivatives (**1-5**) was 41-63%. Capillene (**2**) dominated in all samples. The studied samples could be divided into two groups. The first (samples No. 1, 3, 4, 5, 8) had the maximum yield (0.29-0.69%) of essential oil that was slightly yellowish, the highest content (48-60%) of capillene (**2**), and a significantly lower content (1-9%) of benzyldiacetylene (**1**). The second group (samples No. 2, 6, 7) had a lower yield (0.31-0.35%) of essential oil that was more brightly colored, a lower content (11-17%) of **2**, and an elevated content (22-31%) of **1**.

Our results for the composition of essential oil from *A. glauca* differ markedly from previous data [3]. Thus, in contrast with the previous work, the samples obtained and studied by us lacked completely camphene, artemisiaketone, thujone, calamenene, calacorene, and 2-(hex-2,4-diynyl)phenol. We observed trace quantities of 3-carene and 1,8-cineol and only insignificant amounts of *ar*-curcumene. Such differences may be due to erroneous identification of components in the previous study [3] because only retention times were used to determine them. The fact that "*cis*-methyleugenol" and "*trans*-methyleugenol" were indicated as main components with a total content up to 13% [3] indicates that errors are highly probable because *cis*- and *trans*-isomers of methyleugenol do not exist.

1) Novosibirsk State Pedagogical University, ul. Vilyuiskaya, 28, Novosibirsk, 630126, Russian Federation; 2) Central Siberian Botanical Garden, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090, Russian Federation; 3) N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akad. Lavrent'eva, 9, Novosibirsk, 630090, Russian Federation, fax (383) 330 97 52, e-mail: atkachev@nioch.nsc.ru. Translated from *Khimiya Prirodnykh Soedinenii*, No. 5, pp. 446-449, September-October, 2007. Original article submitted March 27, 2007.

TABLE 1. Yield and Component Composition of Essential Oil from the Aerial Part of *Artemisia glauca* Pall. ex Willd. Collected in 1999-2005 in Various Regions of Western Siberia*

Component	RI	Percent of whole oil**							
		1	2	3	4	5	6	7	8
α -Pinene	932	0.7	1.2	1.1	0.8	0.3	2.3	0.8	0.7
α -Fenchene	945	+	0.2	+	-	0.1	0.1	0.1	0.1
Benzaldehyde	958	+	-	-	+	0.1	-	+	0.1
Sabinene	973	0.1	0.1	0.1	0.1	+	0.2	0.1	0.1
β -Pinene	975	0.1	0.1	0.6	0.1	0.1	1.7	0.1	0.1
β -Myrcene	991	4.7	6.1	0.9	1.7	6.8	4.7	8.1	5.6
α -Phellandrene	1004	0.3	0.4	1.0	1.0	0.3	0.6	0.4	0.3
(Z)-3-Hexen-1-ylacetate	1007	0.1	0.1	+	+	-	+	+	+
3-Carene	1009	+	+	0.1	0.1	+	+	+	+
α -Terpinene	1017	0.1	0.1	0.4	0.3	0.1	0.1	0.1	0.1
<i>p</i> -Cymene	1024	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Limonene	1027	1.3	1.4	2.3	1.9	0.6	4.1	1.0	0.8
β -Phellandrene	1027	1.4	6.8	0.7	0.3	3.3	4.2	4.7	4.9
1,8-Cineol	1031	-	+	+	0.2	-	+	-	+
(Z)- β -Ocimene	1038	2.7	1.7	6.7	10.7	1.4	3.6	2.2	3.4
(E)- β -Ocimene	1048	14.8	18.9	4.8	8.6	14.9	10.6	15.1	13.8
γ -Terpinene	1058	0.1	0.1	0.1	0.1	0.1	0.1	0.1	+
Artemisia-alcohol	1084	-	-	-	0.1	-	-	-	-
Terpinolene	1088	5.0	6.4	16.5	14.5	6.4	10.8	7.3	5.8
Linalool	1100	0.1	0.1	-	0.2	+	0.1	0.1	+
<i>allo</i> -Ocimene	1129	+	-	0.1	2.3	-	+	-	+
<i>neo-allo</i> -Ocimene	1141	-	-	-	0.1	-	+	-	-
Camphor	1144	-	-	-	0.1	-	-	-	-
4,7-Epoxyterpinolene	1145	+	-	+	+	+	+	0.1	+
Cryptone	1186	-	-	-	-	+	-	0.1	0.1
Methylchavicol	1199	-	-	-	-	-	2.0	-	-
Benzylacetylene	1284	2.8	23.1	2.9	0.7	0.3	21.5	31.4	8.9
Bornylacetate	1287	+	-	+	+	0.2	+	+	+
<i>trans</i> -Sabinylacetate	1295	-	-	-	0.3	-	-	-	-
δ -Elemene	1338	-	-	-	-	-	0.1	-	-
Bicycloelemene	1339	-	-	-	0.5	-	-	-	-
(E)-Hex-4-en-2-ynylbenzene	1388	0.6	0.4	0.5	0.6	2.8	0.8	0.4	0.6
β -Elemene	1394	-	-	-	-	-	0.2	-	-
Methyleugenol	1406	-	-	-	-	-	0.5	1.0	-
Caryophyllene	1422	0.9	1.4	0.1	0.1	0.8	1.4	0.9	0.7
(Z)- β -Farnesene	1444	-	0.1	-	-	+	+	0.1	+
α -Humulene	1456	0.1	0.4	-	+	0.3	0.3	0.3	0.2
(E)- β -Farnesene	1458	+	0.1	-	+	+	0.1	0.1	0.1
γ -Decalactone	1470	-	-	0.3	0.5	-	0.2	-	-
γ -Curcumene	1782	2.2	7.0	-	0.1	1.9	1.5	5.8	1.1
Germacrene D	1484	1.4	1.6	0.4	0.3	2.3	3.4	0.4	0.6
<i>ar</i> -Curcumene	1485	+	0.8	-	-	+	+	-	0.1
α -Zingiberene	1496	+	-	-	-	+	+	0.5	-
(Z,E)- α -Farnesene	1496	+	-	-	-	+	+	0.6	+
Capillene	1498	59.5	16.9	59.6	52.6	51.2	11.2	15.2	47.8
Germacrene A	1507	-	-	-	-	-	0.2	-	-
β -Curcumene	1513	-	0.1	-	-	+	+	0.1	-
δ -Cadinene	1527	+	0.1	-	0.1	0.1	0.5	0.1	+
1-(4-Methoxyphenyl)-2,4-pentadiyne	1546	-	0.5	-	-	+	7.3	0.1	2.7

TABLE 1. (continued)

Component	RI	Percent of whole oil**							
		1	2	3	4	5	6	7	8
Elemicine	1559	-	0.1	-	-	-	0.3	-	-
(<i>E</i>)-Nerolidol	1565	+	+	-	-	+	0.1	+	0.1
Spatulenol	1580	0.2	0.2	0.1	+	0.2	0.2	0.3	0.2
Caryophyllene oxide	1586	+	+	-	+	+	+	0.1	+
Capillin	1640	0.1	-	-	-	0.2	-	0.1	0.3
(<i>E</i>)-Isoelemicine	1655	-	0.4	-	-	-	1.7	0.1	0.2
β -Bisabolol	1673	+	0.2	-	-	+	+	0.1	-
<i>epi</i> - α -Bisabolol	1686	+	+	-	-	+	+	0.1	-
α -Bisabolol	1688	+	+	-	0.1	+	+	0.1	-
(<i>E</i>)-Artemidine	1820	-	0.6	-	-	0.4	0.2	0.3	-
(<i>Z</i>)-Artemidine	1880	-	0.8	-	-	3.7	0.2	0.4	-
Capillarin	1885	-	0.6	-	-	-	0.1	0.6	-
Σ Unident.		99.3	99.2	99.4	99.2	99.0	97.3	99.7	99.6

*1) Altai Krai, Troitsk Region (vegetative/start of budding, 0.42); 2) Altai Krai, Khabarsk Region (flowering, 0.34); 3) Altai Republic, Kosh-Agachsk Region (flowering, 0.55); 4) Altai Republic, Kosh-Agachsk Region (flowering, 0.69); 5) Altai Krai, Ust'-Pristansk Region (budding/start of flowering, 0.29); 6) Khakasiya Republic, Bogradsk Region (flowering, 0.31); 7) Altai Krai, Burlinsk Region (flowering, 0.35); 8) Novosibirsk District (flowering, 0.37).

**Only components for which the content in at least one sample was greater than 0.1% are shown; the sign "+" means that the corresponding component was present in trace quantities (<0.1%) but its content could not be measured.

EXPERIMENTAL

General Comments. All solvents were freshly distilled. TLC was carried out on Sorbfil PTLC-AF-V-UF plates with a fixed SiO₂ layer. Compounds were developed by spraying with alcoholic vanillin (2 g vanillin + 5 mL conc. H₂SO₄ in 150 mL EtOH) and heating. Preparative column chromatography used Merck silica gel (0.063-0.100 mm). GC-MS was performed in a Hewlett-Packard 5890/II gas chromatograph with a Hewlett-Packard 5972A mass-selective detector [30 m quartz capillary column HP-5ms, 30 m length, 0.25 mm internal diameter, 0.25 μ m stationary phase thickness (copolymer 5% diphenyl-95% dimethylsiloxane), He carrier gas (1 mL/min), vaporizer temperature 280°C, column 50°C (2 min)-4°C/min-280°C; ion source 173°C, interface between GC and mass-selective detector 280°C, ionizing electron energy 70 eV, data collection 1.2 scan/s for mass range 30-650 amu]. The percent composition of essential oil was calculated from areas of GC peaks without using correction coefficients. The qualitative analysis was based on a comparison of retention times and full mass spectra with data in a specialized library [4].

High-resolution mass spectra were obtained in a Finnigan MAT-8200 mass spectrometer (electron impact, 70 eV). PMR and ¹³C NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13 MHz for ¹H; 125.75 MHz for ¹³C) for solutions in CCl₄ and benzene-d₆ (4:1 v/v) at 25°C with the benzene-d₆ signal as an internal standard (δ_C 128.00 ppm; δ_H 7.19 ppm). IR spectra were recorded on a Bruker Vector-22 instrument for CHCl₃ solutions (*c* 1%). Indices of refraction were measured on an IRF-454B refractometer; densities, by a calibrated pycnometer. Rotation angles were determined for pure oils on a Polamat A instrument at λ 578 nm.

Preparative GC was carried out in a Chrom-5 instrument with a flame-ionization detector that was refurbished for use with a preparative column and N₂ carrier gas, steel column (4 m \times 5 mm), 15% OV-101 on Chromosorb-N-AW-PMCS support, particle size 0.315-0.400 mm, column temperature 200°C, N₂ carrier gas, injector and detector temperature 250°C. Samples (100 μ L) were injected as solutions (10%) in ether. Fractions were collected in glass traps cooled on the outside by ice.

Essential Oil Samples. Samples of essential oil collected during expeditions in 1999-2005 under field conditions from freshly collected raw materials by steam distillation in a stainless-steel apparatus were used for the investigation. Herbarium samples of plants that were used as raw material for each sample of essential oil are preserved in collections of the Central

Siberian Botanical Garden of the SD RAS in the main collections and in a special section of the "Essential-oil flora of South Western Siberia."

Essential Oil Analysis. Low-boiling components were distilled from samples (2-10 mL) of oil by heating a flask to 100°C at 5-7 mm Hg. A portion (100 µL) of the bottoms was dissolved in hexane (0.5 mL) and chromatographed over a SiO₂ column (1-15 cm × 0.8 cm diameter) with elution of hydrocarbons by hexane; slightly polar *O*-containing derivatives, hexane:diethylether (20:1 v/v); and polar derivatives; diethylether.

Six GC—MS chromatograms were recorded for each oil sample in order to ensure reliable identification of minor components. This included whole oil, the low-boiling fraction, bottoms from the distillation, and hydrocarbon, slightly polar, and polar fractions obtained from separation of the bottoms.

The analyzed sample (10 µL for whole oil or 5 µL for fractions) was mixed with acetone (500 µL) and treated with a solution of a mixture of *n*-alkanes (C₇, C₈, ..., C₂₀, 0.1%). The resulting solution containing 0.9-2.0 wt % of the studied mixture and ~0.001% of each of the *n*-alkanes that were used as internal standards for calculating retention times was injected directly into the instrument for GC—MS analysis.

(*E*)-Hex-4-en-2-ynylbenzene (4). A sample (10 mL) of oil No. 5 was distilled in vacuo to afford a low-boiling fraction (3 mL) and bottoms (7 mL). Column chromatography of the bottoms (200 mg) isolated the hydrocarbon fraction (170 mg), from which preparative GC isolated **4** (3 mg).

PMR spectrum (CCl₄ + CDCl₃, δ, ppm, J/Hz): 1.75 (3H, ddt, J = 6.8, 2.0, 0.7), 3.68 (2H, dq, J = 2.0, 0.7), 5.51 (1H, dtq, J = 15.8, 2.0, 2.0), 6.11 (1H, dq, J = 15.8, 6.8), 7.25 (1H, m), 7.27-7.34 (4H, m). ¹³C NMR spectrum (CCl₄ + CDCl₃, δ, ppm): 13.99 (q), 25.59 (t), 81.18 (s), 85.48 (s), 110.8 (d), 126.41 (d), 127.80 (d), 128.37 (d), 136.95 (s), 138.59 (d).

High-resolution mass spectrum: found *m/z* 156.0930; calc. for C₁₂H₁₂, [M]⁺ 156.0939. Mass spectrum (*m/z*, *I*_{rel.}, %): 157 (10) [M + 1]⁺, 156 (83) [M]⁺, 155 (61), 154 (17), 153 (30), 152 (16), 142 (11), 141 (100), 139 (9), 129 (24), 128 (49), 127 (17), 126 (5), 116 (10), 115 (85), 91 (16), 89 (6), 78 (11), 77 (18), 76 (9), 63 (9).

1-(4-Methoxyphenyl)-2,4-pentadiyne (5). A sample (10 mL) of oil No. 6 was distilled in vacuo to afford a low-boiling fraction (4 mL) and bottoms (6 mL). Column chromatography of the bottoms (200 mg) separated the hydrocarbon fraction (160 mg, hexane eluent) and isolated a slightly polar fraction (27 mg, hexane:diethylether, 20:1), repeated column chromatography of which isolated **5** (12 mg). IR spectrum (CCl₄, cm⁻¹): 3313 (≡C-H), 2221 (—C≡C—), 2064 (R—C≡CH).

PMR spectrum (CCl₄ + CDCl₃, δ, ppm, J/Hz): 7.13 (2H, d, J = 8.5), 6.76 (2H, d, J = 8.5), 3.73 (3H, s), 3.55 (2H, d, J = 1.3), 1.94 (1H, t, J = 1.3).

¹³C NMR spectrum (CCl₄ + CDCl₃, δ, ppm, J/Hz): 158.58 (s), 128.75 (d, ¹J_{C-H} = 157.6, ²J_{C-H} = 7.2, ³J_{C-H} = 2 × 3.8), 126.64 (s, ⁿJ_{C-H} = 4 × 7.4), 114.00 (d, ¹J_{C-H} = 159.3, ²J_{C-H} = 4.9), 75.44 (s, ³J_{C-H} = 2 × 11.9), 68.47 (s, ³J_{C-H} = 51.7, 2 × 3.2), 66.70 (s, ²J_{C-H} = 6.6, ⁴J_{C-H} = 2 × 4.3), 65.39 (d, ¹J_{C-H} = 257.0, ⁵J_{C-H} = 2 × 2.2), 54.90 (q, ¹J_{C-H} = 3 × 143.5), 24.47 (t, ¹J_{C-H} = 2 × 131.5, ³J_{C-H} = 2 × 4.5).

High-resolution mass spectrum: found, *m/z* 170.0736; calc. for C₁₂H₁₀O, [M]⁺ = 170.0732. Mass spectrum (*m/z*, *I*_{rel.}, %): 171 (13) [M + 1]⁺, 170 (100) [M]⁺, 169 (15), 156 (7), 155 (59), 154 (8), 140 (6), 139 (18), 128 (7), 127 (66), 126 (30), 77 (11), 75 (7), 74 (7), 63 (7).

ACKNOWLEDGMENT

We thank NIOC SD RAS staff members A. M. Agafontsev, O. N. Burchak, D. V. Domrachev, T. N. Komarova, E. V. Malykhin, A. M. Chibiryaev, M. S. Yusubov (Tomsk Medical University), and A. A. Alekseev (IKhKiG SD RAS) for help with collection and processing of plant material. The work was supported financially by the SD RAS program of research expeditions (1998-2005).

REFERENCES

1. W. R. Roth and T. Bastigkeit, *Liebigs Ann. Org. Bioorg. Chem.*, No. 12, 2171 (1996).
2. a) K. Schulze and M. Muehlstaedt, *J. Prakt. Chem.*, **33**, No. 1-2, 84 (1966); b) K. Schulze, A. Hiller and M. Muhlstadt, *J. Prakt. Chem.*, **318**, No. 3, 381 (1976).
3. L. A. Zarubina, G. I. Kalinkina, and A. D. Dembitskii, *Rastit. Resur.*, **29**, No. 3, 70 (1993).
4. A. V. Tkachev, *Library of GC—MS Spectrometric Data of Volatile Compounds of Plant Origin* [in Russian], N. N. Vorozhtsov Novosibirsk Inst. Org. Khim., Sib. Div., Russ. Acad. Sci., (2006).