

## Chemical Composition of the Essential Oil from Two Wormwood Species *Artemisia frigida* and *Artemisia argyrophylla*

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**Abstract**—The composition of the essential oil from the wormwood sage (*Artemisia frigida* Willd., *Asteraceae*) of populations growing in the Altai Territory, the Altai Republic, the Khakass Republic, the Tuva Republic, and the East-Kazakhstan region of the Republic of Kazakhstan and the representative species of the silver-leaved wormwood *Artemisia argyrophylla* Ledeb. growing in the Republic Altai has been studied by chromatomass spectrometry. An analysis of 15 samples of the essential oil from *A. frigida* obtained over a period from 1999 to 2007 indicates that samples from different populations have similar sets of the main components:  $\alpha$ -pinene (0.2–7.8%), camphene (1.9–5.8%), 1,8-cineole (8.9–33.8%), camphor (6.7–40.0%), borneol (3.9–12.3%), terpine-4-ol (1.5–6.5%), bornyl acetate (1.4–22.0%), and germacrene D (1.4–14.6%). Some samples contain substantial amounts of  $\alpha$ - and  $\beta$ -thujones (in total up to 19.1%), which are completely absent in other samples. Some samples contain santolina alcohol (up to 13.8%) and its acetate (up to 4.8%). As differentiated from *A. frigida*, the essential oil of *A. argyrophylla* contains yomogi alcohol (1.2%), artemisia ketone (12.9%), artemisia alcohol (3.1%), artemisia alcohol acetate (3.9%), and small amounts of camphor (3.2%), borneol (0.3%), and bornyl acetate (0.2%).

**Key words:** wormwood sage, silver-leaved wormwood, *Artemisia frigida*, *Artemisia argyrophylla*, *Asteraceae*, essential oil, chemical composition, chromatomass spectrometry

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### INTRODUCTION

The wormwood sage *Artemisia frigida* Willd. [family *Asteraceae*, section *Abstinthium*, DC, subsection *Frigidae* (Rydb.) Korobkov.] is a xerophyte dominating in mountain and flatland steppes, fallow lands, on rocks, sandy soils of steppe pine forests in South Siberia, the land along the Volga, Middle Asia, and Mongolia; the species is also encountered in North America [1]. I.M. Krashennikov divided this species within western Siberia into three races with related intermediate forms in border zones; he did not indicate to which regions these races are confined [2]. The next monographers interpreted this species more broadly [3–5], and P.P. Polyakov, when describing the species on the territory of the former Soviet Union, also assigned the high-mountain species *Artemisia argyrophylla* Ledeb. to *A. frigida* [6].

*A. frigida* from the subsection *Frigidae* of the *Asteraceae* family has been studied chemically most extensively; most studies have been devoted to flavonoids [7, 8], sesquiterpene lactones [9, 10], and essential oils from different regions of the geographic range: Kha-

kass, Gornyi Altai, and the Transbaikal region. The presence of trace amounts of azulene in the oil has been reported [4, p. 56]. The composition of the oil of Mongolian populations has been described in a paper [11] and a book [12], and the composition of the oil from the plants of Kazakhstan is presented in [13]. The composition of the essential oil from the wormwood sage growing in Buryat and a detailed review of published data concerning the application of this species in folk and official medicine have been reported [14]. The biological activity of the essential oil is believed to be due to a high content of camphor and 1,8-cineole [15].

According to modern views, *A. frigida* and *A. argyrophylla* are representative species. *A. argyrophylla* is morphologically distinguished by larger calathides and internal leaves of the involucre colored dark red at the edges. In mountains, it grows in higher localities than *A. frigida* and is encountered on stone alluvial deposits, morains, and in arid regions of lichen tundra. The geographical range of this species covers Gornyi Altai, Tuva, and Northwest Mongolia. The data on the

essential oil from *A. argyrophylla* are unavailable in the literature.

Here we present a comparative analysis of the composition of the essential oil from two closely related wormwood species *A. frigida* Willd. and *A. argyrophylla* Ledeb., the flora of South Siberia.

## RESULTS AND DISCUSSION

It follows from a comparison of the data in Tables 1 and 2 that samples of essential oil from *A. frigida* growing in different loci of the geographical range (the Altai Territory, Khakass, Tuva, and the East Kazakhstan region of the Republic Kazakhstan) at altitudes from 110 to 1950 m, which is a dominant species in steppe communities, though similar, at the same time exhibit marked differences. The yields of essential oils also vary in rather wide ranges, from 0.07 to 0.27%.

The essential oil from *A. frigida* contains about 150 components. Some of them are present in samples in trace amounts; because of this, they show low-quality mass spectra in chromat-mass spectrometric experiments and, therefore, cannot be precisely determined. All basic components are readily identified from characteristic mass spectra and linear retention indices presented in the instruction [16] (Table 2). Comparing the chromatographic profiles of samples of essential oil from *A. frigida* growing in different localities of the geographical range (see figure) shows that all samples have one and the same set of dominant components:  $\alpha$ -pinene (0.2–7.8%), camphene (1.9–5.8%), 1,8-cineol (8.9–33.8%), camphor (6.7–40.0%), borneol (3.9–12.3%), terpine-4-ol (1.5–6.5%), bornyl acetate (1.4–22.0%), and germacrene D (1.4–14.6%). An exception is  $\alpha$ - and  $\beta$ -thujones; in some samples, they are present in considerable amounts (in total up to 19.1%), and in others there are even no traces of these compounds.

A curious thing is that four essential oil samples of *A. frigida* contain irregular monoterpene compounds of santolina alcohol and its derivatives: santolina triene (dehydration product) and the *O*-acyl derivative. The four samples represent two geographically isolated *A. frigida* cenopopulations: a population from flatland steppes adjacent to Bol'shoe Topol'noe Lake (extreme west end of the Altai Territory; samples nos. 4 and 10) and a high-altitude population of the Chuiskaya steppe (Kosh-Agachskii region of the Altai Republic; samples nos. 5 and 7). The four samples differ from the others in the content of the main components but include the above-mentioned santolina derivatives, which are completely absent (even in trace amounts) in other samples examined.

The essential oil from *A. argyrophylla* (sample no. 16) also contains santolina derivatives but differs

from *A. frigida* by the presence of irregular monoterpenoids of another type: yomogi alcohol (1.2%), artemisia ketone (12.9%), and artemisia alcohol (3.1%) as well as a low content of camphor (3.2%), borneol (0.3%), and bornyl acetate (0.2%).

## EXPERIMENTAL

### *Gathering and Preparation of Plant Material*

The raw material for obtaining the essential oil was collected during the expedition of 1999–2007 from different localities of the geographical range at different vegetation phases (Table 1). Herbarium samples are stored in collections of the Central Siberian Botanical Garden, Siberian Branch, Russian Academy of Sciences (NS).

### *Extraction of Essential Oil*

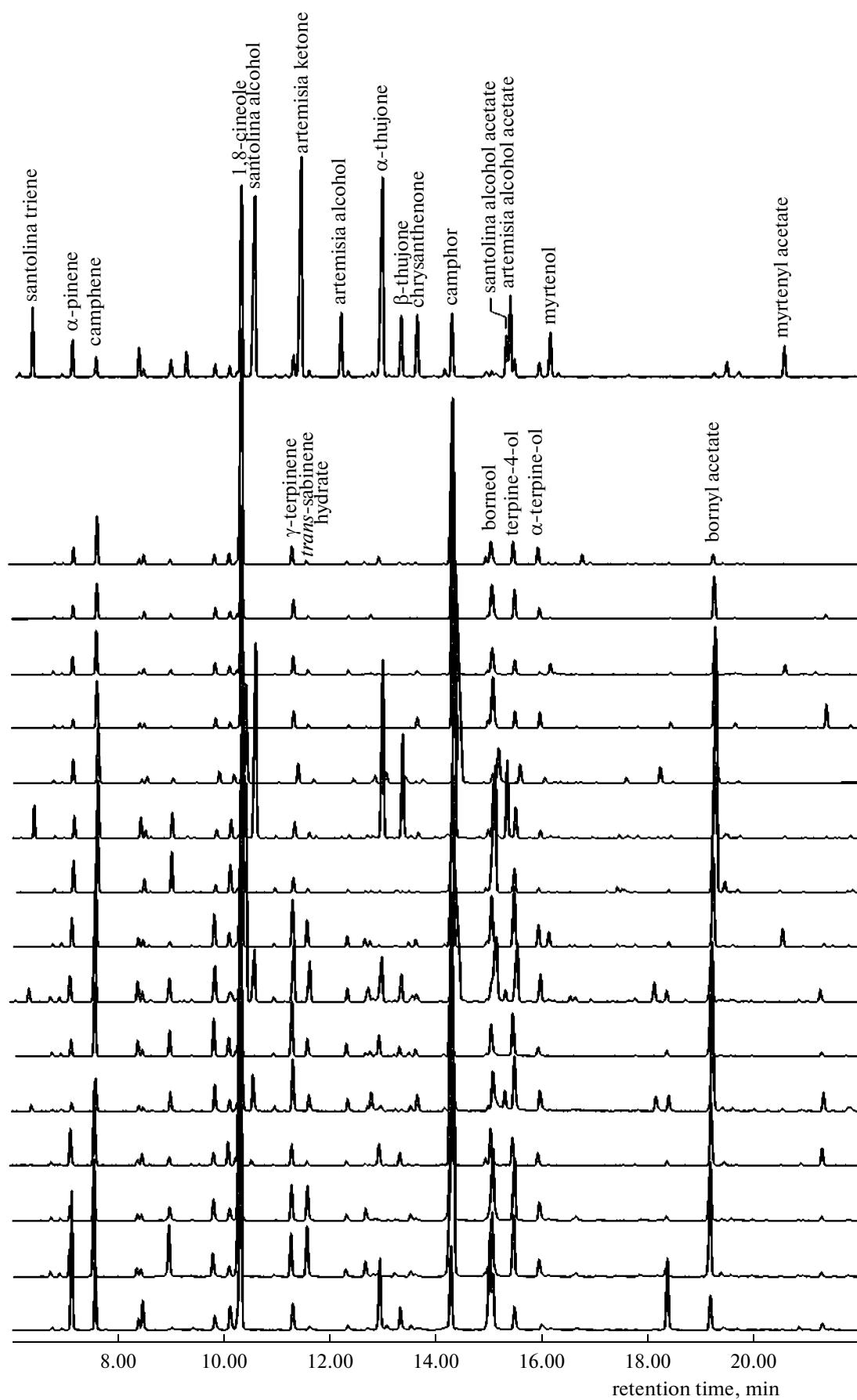
Samples of essential oil were obtained from freshly gathered raw material in field conditions by the method of steam distillation at atmospheric pressure (at an altitude of 110 to 2220 m above sea level) in a stainless steel apparatus. Five to seven kilograms of plant raw material was processed one time, the distillate was taken within 1.5 h, and essential oil was separated in a glass Florentine vial. Oil was dried by anhydrous sodium sulfate (shaking for 15–20 min), separated from the drying agent by decantation, and placed in glass ampoules, which were immediately sealed. The ampoules were stored in darkness at ordinary temperature under expedition conditions (from 0 to +39°C) and then in a refrigerator at +4–+8°C until used for analysis.

### *Chromato-Mass Spectrometric Examination*

**Preparation of samples for analysis.** The mixture being analyzed (1–10  $\mu$ l) was dissolved in acetone (500  $\mu$ l), and 100  $\mu$ l of a hexane solution of a mixture containing equal weight amounts of normal hydrocarbons  $C_8$ ,  $C_9$ , ...,  $C_{24}$  of a total concentration of 0.1% was added to the solution.

**Chromato-mass spectrometry.** Chromato-mass spectrograms were recorded on an Agilent 5973N device (Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences) and an Agilent 5973N EI/PCI device (Faculty of Natural Sciences, Novosibirsk State University). Essential oil components were separated on Agilent 6890 gas chromatographs incorporated in the above-indicated chromato-mass spectrometric systems. The separation was carried out on an HP-5ms quartz capillary column 30 m long with an internal diameter of 0.25 mm. The

Chromatographic profiles of essential oils of *A. frigida* and *A. argyrophylla* from the total ionic current in the range of 7.0–22.0 min (range of retention indices *J* from 900 to 1370). The figures to the right designate the numbers of oil samples (see Tables 1, 2).



**Table 1.** Characterization of *A. frigida* and *A. argyrophylla* samples

No.	Site of collection Ecological zone Geographical coordinates, altitude above sea-level, date of collection	Stage of plant development Characteristics of raw material Yield of oil (%)* Color of oil
<i>Artemisia frigida</i> Willd.		
1	Altai Territory, Kalmanskii region, exit from Ust'-Kalmanka village to the northeast Side of the road LAT 52°10' LON 83°20' H 190 m 17.07.1999	vegetation aboveground part 0.07 yellow
2	Republic Altai, Ongudaiskii region, 664 km along the Novosibirsk–Ashanta highway, the left bank of the Ursul River Stony outcrops LAT 50°45' LON 86°16' H 800 m 28.07.1999	budding aboveground part 0.26 slightly yellowish
3	Republic Altai, Ongudaiskii region, the left bank of the Bol. Yaloman River 6 km away from the Novosibirsk–Ashanta highway, the eastern hillside Arid fine-scrub steppes LAT 50°30' LON 86°28' H 9500 m 01.08.1999	budding aboveground part 0.28 light green
4	Altai Territory, Burlinskii region, surroundings of Petrovka settlement, the south extremity of Bol'shoe Topol'noe Lake Arid, small-scrub, thinned out wormwood steppe LAT 53°15' LON 78°04' H 110 m 23.07.2000	budding aboveground part 0.09 blue-green
5	Republic Altai, Kosh-Agachskii region, 12 km from Chagan-Uzun village, northern spurs of the North Chuiskii range Stony steppe of southern exposure LAT 50°03' LON 88°16' H 1950 m 23.07.2001	flowering aboveground part 0.13 blue-green
6	Republic of Altai, Kosh-Agachskii region, northern spurs of the North Chuiskii range, the left bank of the Korumdu River Stony steppe of southern exposure LAT 50°11' LON 87°45' H 1890 m 03.08.2001	flowering the entire plant 0.12 yellowish
7	Altai Republic, Kosh-Agachskii region, the surroundings of Ortolyk village, 874 km along the Novosibirsk–Ashanta highway The stony bed of a temporary water stream LAT 50°03' LON 86°27' H 1810 m 30.07.2002	flowering aboveground part 0.24 gray-blue
8	Altai Republic, Ust'-Kanskii region, the southern spurs of the Bashchelakskii range, the right bank of the Charysh River Steppe-covered slope with stony outcrops LAT 51°02' LON 84°35' H 930 m 21.07.2003	budding aboveground part 0.12 yellowish-greenish
9	Altai Territory, Ust'-Pristanskii region, environs of the village of Kamyshenka, outskirts of the pine forest Weakly turfed wormwood–feather grass–Chleistogenes genus steppe LAT 52°36' LON 83°45' H 160 m 04.08.2003	onset of flowering aboveground part 0.10 pale yellow
10	Altai Territory, Burlinskii region, the surroundings of Ust'yanka village, the northern bank of Khomutinoe Lake Cereal wormwood steppe LAT 50°25' LON 78°38' H 1200 m 21.07.2005	flowering aboveground part 0.12 pale yellow
11	Republic of Tuva, Tandinskii kozhuun, the environs of Chagytaï Lake Stony steppe LAT 51°02' LON 94°41' H 1040 m 18.07.2006	onset of budding the entire plant 0.04 pale yellow
12	Tuva Republic, Erzinskii kozhuun, the flood-lands of the Tes-Khem River Stony steppe LAT 50°27' LON 94°59' H 1010 m 24.07.2006	onset of budding the entire plant 0.09 emerald green

Table 1. (Contd.)

No.	Site of collection Ecological zone Geographical coordinates, altitude above sea-level, date of collection	Stage of plant development Characteristics of raw material Yield of oil (%)* Color of oil
13	Tuva Republic, Pii-Khemsii kozhuun, the valley of the river Bol'shoi Yenisei (Bii-Khem), the southwestern mountainside Hollows down the mountainside LAT 52°01' LON 94°24' H 670 m 28.07.2006	onset of budding the entire plant 0.06 sky-blue
14	Republic of Khakass, Bogradskii region, the environs of Ust'-Erba village, the left bank of the Krasnoyarsk water storage basin Abandoned stone quarry LAT 54°28' LON 91°11' H 310 m 03.08.2006	budding the entire plant 0.26 yellowish-greenish
15	Republic of Kazakhstan, East Kazakhstan region, UR, the surroundings of Targyn village, West Kalba Screes LAT 49°30' LON 82°48' H 800 m 03.08.2007	flowering aboveground part 0.27 bluish-greenish
<i>Artemisia argyrophylla</i> Ledeb.		
16	Altai Republic, Kosh-Agachskii region, the Chikhachev range, below the Buguzun pass, at the junction of the Buguzun and Akkayalu-Ozek rivers Wormwood degraded steppe LAT 50°07' LON 89°25' H 2220 m 22.07.2002	flowering aboveground part 0.10 yellowish-greenish

Notes: \* Yield is given in % of the weight of fresh raw material.

immobile phase was the copolymer 5% diphenyl–95% dimethylsiloxane; the thickness of the film of the immobile phase was 0.25  $\mu\text{m}$ . The temperature of evaporator was 280°C, the volume of a sample was 1  $\mu\text{l}$ , and the separation of the flow was 100 : 1. The temperature regime of the column was as follows:

50°C (2 min) – 50–240°C (4°/min) – 240–280°C (20°/min) – 280°C (5 min).

The carrier gas was helium with a constant flow rate of 1 ml/min. The temperature of the interface between the chromatograph and mass-selective detector was 280°C. Mass spectra were recorded on an HP MSD 5971 quadrupole mass spectrometer under ionization by electron impact with an energy of ionizing electrons of 70 eV. The data were retrieved with a rate of 1.9 scan/s in the range of 30–650 amu (Agilent 5973N) or 3 scan/s in the range of 29–500 amu (Agilent 5973N EI/PCI). The delay between the introduction of a sample into the evaporator of the chromatograph and the onset of the recording of chromatogram was 3.0 min.

The linear **retention index**  $J_x$  was calculated by the formula

$$J_x = J_n + 100k \frac{t_{Rx} - t_{Rn}}{t_{R(n+k)} - t_{Rn}}, \quad (1)$$

where  $J_n = 100n$  is the retention index for  $n$ -alkane whose molecule contains  $n$  carbon atoms;  $t_R$  are the absolute times of retention of components;  $t_x$  is the retention time for the substance being examined; and  $t_n$  and  $t_{n+k}$  are the times of retention for the nearest ref-

erence  $n$ -alkanes with the number of carbon atoms  $n$  and  $n+k$ , respectively; usually,  $t_n < t_x < t_{n+k}$ .

**Identification of components.** The components of the mixtures being examined were identified from complete mass spectra, linear retention indices given in the instruction [16], and our own library of chromatogram-mass spectrometric data.

**Quantitative analysis** was performed by the method of internal normalization from the areas of gas-chromatographic peaks without using correcting coefficients.

The results of chromatogram-mass spectrometric examination of essential oil samples are presented in Table 2. Chromatographic profiles of samples are shown in the figure.

## CONCLUSIONS

Taken together, the data on the macrocomponents of the essential oil from *A. frigida* are consistent with the data for the Transbaikal population of *A. frigida* [14]. Following the authors of the last paper, note again that the data on the composition of essential oils from *A. frigida* reported earlier in the 1960s–1980s are incomparable with the results obtained by using present-day instruments. Presumably, this is explained by both imperfect methods of identification used previously and possible errors in botanic determination of plants.

Based on the results of chromatogram-mass spectrometric analysis, it can be concluded that *A. argyrophylla* strongly differs from *A. frigida* by the biosynthesis of

Table 2. Composition of essential oils from *A. frigida* (samples nos. 1–15) and *A. argyrophylla* (sample no. 16) as indicated by chromatography-mass spectrometry data

Name of the component	J	Sample number according to Table 1															
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
santolina triene	908	0.2	0.3	0.3	0.1	0.3	0.5	0.2	0.2	0.2	1.4	0.3	+	0.4	0.3	0.3	2.4
tricyclene	920	0.1	0.2	0.2	0.1	0.2	0.2	0.2	0.3	0.3	0.1	0.1	+	0.1	0.1	0.2	+
$\alpha$ -thujene	926	8.7	1.2	1.1	2.6	1.4	1.3	1.8	1.8	1.6	1.0	2.2	0.2	2.2	1.7	1.6	1.5
$\alpha$ -pinene	932	4.4	5.1	4.1	5.8	6.7	3.9	4.6	4.6	4.8	2.9	5.5	3.6	5.8	4.6	5.0	0.9
camphene	946	0.7	0.5	0.5	0.5	1.1	1.0	0.6	0.6	0.1	1.1	0.4	0.4	0.3	0.3	0.6	1.2
verbenene	952	2.1	0.5	0.5	0.9	0.6	0.5	0.5	0.5	0.7	0.4	0.7	0.4	0.8	1.0	1.0	0.3
sabinene	972	0.2	0.2	0.1	0.1	0.1	0.2	0.2	0.2	0.1	0.1	0.1	+	0.1	0.1	0.1	0.8
$\beta$ -pinene	975	0.3	3.4	1.5	0.8	1.1	1.3	1.3	0.5	2.1	1.3	0.6	0.2	0.7	0.8	0.6	0.8
oct-1-en-3-ol	978	0.2	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.1	0.1	0.1	+	0.1	0.1	0.1	1.2
$\beta$ -myrcene	991	0.2	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.1	1.2
yomogi alcohol	1000	0.2	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1	+	0.1	+	+	0.1	0.1	0.1
$\alpha$ -phellandrene	1004	1.2	1.7	1.8	1.2	1.7	2.1	2.4	2.4	0.5	0.5	1.2	0.9	1.6	1.6	1.1	0.5
3Z-hexenyl acetate	1008	2.1	0.8	1.2	2.3	0.7	0.9	1.0	1.0	1.7	1.0	1.0	0.5	1.2	1.1	1.3	0.5
$\alpha$ -terpinene	1016	0.7	0.4	0.2	0.2	0.1	+	+	+	0.1	0.1	0.8	0.1	0.6	0.5	0.3	0.1
<i>para</i> -cymol	1024	0.2	0.5	0.4	0.1	0.3	0.2	0.2	0.2	0.2	0.1	0.3	0.1	0.1	0.1	+	0.1
limonene	1028	19.5	18.5	23.4	14.9	14.4	21.9	19.3	19.3	9.5	9.0	10.8	16.4	8.9	16.3	33.8	9.3
$\beta$ -phellandrene	1031	0.4	0.4	0.4	0.4	2.4	2.9	2.9	2.9	2.9	13.8	0.1	+	+	+	+	11.1
1,8-cineole	1037	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	+	+	+	+	0.1
santolina alcohol	1038	+	0.2	0.1	0.1	0.3	0.2	0.5	0.5	0.3	0.1	0.2	0.1	0.1	0.1	0.1	0.1
<i>cis</i> - $\beta$ -ocimene	1048	2.1	2.6	3.0	1.8	3.2	2.9	3.4	3.4	0.8	1.0	2.1	1.5	2.7	2.8	2.0	1.0
<i>trans</i> - $\beta$ -ocimene	1058	0.4	3.5	3.3	0.5	1.1	2.2	2.0	2.0	0.2	0.3	0.5	0.4	0.7	0.4	0.4	12.9
$\gamma$ -terpinene	1062	0.4	0.6	0.6	0.4	0.7	0.7	0.8	0.8	0.2	+	0.6	0.4	0.6	0.5	0.4	0.3
artemisia ketone	1066	0.4	0.6	1.2	0.3	0.3	1.0	1.0	1.0	0.1	0.2	0.1	0.2	0.1	0.2	0.3	3.1
<i>trans</i> -sabinene hydrate	1083	0.4	1.2	1.2	0.2	1.2	0.3	0.6	0.6	0.1	0.2	0.1	0.2	0.1	0.2	0.3	0.1
artemisia alcohol	1088	0.2	0.2	0.2	0.2	1.2	0.3	0.5	0.5	0.2	+	0.9	0.1	0.3	0.7	0.1	0.1
terpinolene	1097	0.2	0.2	0.4	0.2	0.6	0.3	0.3	0.3	0.1	0.2	0.1	0.2	0.1	0.2	0.3	0.1
<i>cis</i> -sabinene hydrate	1100	0.3	0.3	0.4	0.7	0.7	0.7	0.7	0.7	0.2	0.2	0.6	0.4	0.6	0.5	0.4	0.3
linalool	1103	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1
phyllipholon	1105	0.3	0.4	0.4	0.7	0.7	0.7	0.7	0.7	0.2	+	+	+	+	+	+	0.1
isopentenyl-3-methylbutanoate	1108	0.4	0.4	0.4	2.3	2.4	2.9	2.9	2.9	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
$\alpha$ -thujone	1109	0.4	0.4	0.4	+	+	+	+	+	+	+	1.3	0.1	+	+	1.0	12.8
pentyl valerate	1109	0.4	0.4	0.4	+	+	+	+	+	+	+	+	+	+	+	+	+

Table 2. (Contd.)

Name of the component	Sample number according to Table 1																
	J	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
isochrysanthenone	1109			0.1	+	0.1	0.1	0.1	+	0.1	+	0.1	0.1				0.1
l-octene-3- acetate	1113	0.4	0.2	0.2		0.2	0.2	0.1	0.1	0.2	0.1	+				+	0.1
<i>trans</i> -chrysanthenol	1116																
b-thujone	1118	1.8			1.5	0.1	1.0	1.5			6.6	0.3	0.1			0.3	3.0
<i>cis</i> - <i>para</i> -menth-2-ene-1-ol	1121	0.4	0.5	0.7	0.3	0.4	0.5	0.5	0.4	0.1	0.2	0.2	0.1	0.1	0.2	0.2	0.1
chrysanthenone	1124	0.3	0.3	0.4	1.1	1.1	0.8	0.5	0.6	0.1	0.4	0.6	1.0	0.7	0.2	0.3	3.1
<i>trans</i> -pinocarveol	1139	0.2	0.3								+	0.1					0.5
<i>trans</i> - <i>para</i> -menth-2-ene-1-ol	1140	0.2				0.2	0.3		0.3	0.1	0.5	0.2	0.1	0.1	0.1	0.2	3.2
camphor	1145	6.7	24.1	22.6	21.9	14.9	15.7	18.1	18.2	6.7	16.4	33.4	24.6	40.0	37.4	26.3	3.2
isoborneol	1148							0.1	0.1			+	+	+	+	+	0.1
pinocarvone	1161		0.2		0.5		0.3		0.3	0.3	0.3	+					0.4
<i>cis</i> -chrysanthenol	1162	8.7	0.3	0.2	0.5	0.3		0.2	0.6		0.3	1.2	0.8	0.6	0.4	1.0	0.4
borneol	1165	4.1	6.1	9.4	4.8	4.4	4.2	6.6	4.8	12.3	3.8	5.2	6.4	5.4	7.7	3.9	0.3
lavandulol	1167										+						0.3
isopinocampnon	1173											0.1		0.1		0.1	0.3
santolina alcohol acetate	1173				0.2	1.8		0.7			4.8						2.1
artemisia alcohol acetate	1174										+						3.9
terpine-4-ol	1177	1.9	4.3	6.5	2.8	4.3	4.6	4.0	5.0	1.5	2.0	2.2	1.6	2.3	4.7	2.8	0.8
$\alpha$ -terpineol	1190	0.7	1.5	2.1	1.4	1.8	1.0	1.6	1.8	0.3	0.5	0.7	1.5	0.4	1.8	2.2	0.7
<i>cis</i> -piperitol	1195	0.2	0.2					0.2	0.1		+	0.1	+				
myrtenol	1196			0.3	0.3			0.2	1.2	0.1	0.3	0.1	+	1.8	0.3	0.1	2.3
methyl chavicol	1198											0.1		0.2			
<i>trans</i> -piperitol	1207	0.3			0.1			0.3	0.2	0.1	0.1	0.1	+	+	+	0.1	
substance 1 <sup>†</sup>	1210		0.5	0.8				0.3	0.2	0.1	+	0.2	0.2	+	+	0.1	
fragranol	1214																
<i>trans</i> -carveol	1219		0.1	0.1	0.2			0.2	0.2	0.1	0.1	+	0.1	+	+	1.3	
bornyl formiate	1229	0.1			0.1					0.1	+		+	+			
3 <i>Z</i> -hexenyl-2-methyl butanoate	1234		0.1	+	0.2				0.2	0.3	0.2		0.1	+	0.2		
<i>trans</i> -chrysanthenyl acetate	1236									0.1		0.7		+	0.2		
3 <i>Z</i> -hexinyl-3-methyl butanoate	1237		0.1						0.1	0.2			0.1	+			
<i>n</i> -hexyl-2-methyl butanoate	1238				0.2				0.1	0.1	0.3		+	+			
carvone	1243		0.4	0.4	0.2		0.2	0.2	0.3	0.1	0.2	0.1	0.2	+		0.2	

Table 2. (Contd.)

Name of the component	J	Sample number according to Table 1															
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
		Content of component in % of whole oil*															
piperitone	1254	0.2	0.2	0.2	0.2	1.3	0.1	1.1	0.1	0.1	2.0						
geraniol	1255	0.6	0.5	0.5	0.5	1.1	0.6	0.4	0.1	0.2	0.2	0.6	0.2	0.2	0.3	0.2	0.2
<i>cis</i> -chrysanthenyl acetate	1262	2.8	6.5	5.7	6.9	10.5	6.8	3.8	7.5	22.0	3.9	9.9	4.9	6.9	1.4	0.2	0.2
isopiperitone	1274	0.3	0.4	0.2	0.9	0.4	0.2	0.1	0.1	0.1	0.3	9.9	4.9	6.9	1.4	0.2	0.2
bornyl acetate	1287	0.1	0.2	0.3	0.1	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.1
lavandulyl acetate	1292	0.1	0.2	0.3	0.1	0.2	0.2	0.2	0.2	0.1	0.2	0.5	0.3	0.2	0.2	0.8	0.8
thymol	1293																
<i>trans</i> -sabinyl acetate	1296																
substance 2 <sup>+</sup>	1297																
carvacrol	1298			0.2													
dimethyl ether of thymoquinone	1299																
terpine-4-ol acetate	1301				0.3						+						0.3
myrtenyl acetate	1326				0.2	0.2			1.5	0.2	0.1	1.6	0.1		0.1		1.5
bicycloelemene	1335	0.2	0.1	0.1	0.2			0.2	0.1	0.1	+	0.1	0.1				
<i>trans</i> -carvyl acetate	1339	0.1	0.1	0.1	0.2				0.1	0.1	+	0.1	0.1				
silyperphol-6-ene	1343										0.4						
fragranyl acetate	1346																
$\alpha$ -terpenyl acetate	1350	0.6	0.3	0.4	2.4	1.2	0.5	0.6	0.3		0.1	0.2	0.1	0.7	0.8	0.5	0.1
eugenol	1358				0.2		0.2	0.1	0.1	0.1	0.1	2.2	0.1		0.1	0.1	0.1
7-terpenyl acetate	1364				0.1		0.2	0.2	0.2	0.1	0.2	0.3	+		+		
cyclosativen	1368									0.3							0.1
$\alpha$ -copaene	1376	0.3	0.3	0.2	0.5	0.8	0.3	0.3	0.5	1.1	0.3	0.3	0.2	0.1	0.2	0.4	0.4
$\beta$ -burbonene	1385	0.2	0.2	+	0.1	0.3	0.2	0.2	0.1	0.2	+	0.2	0.1	+	+	0.1	0.1
$\beta$ -elemene	1393	1.0	2.1	0.4	0.4	2.4	1.6	2.0	0.4	1.2	0.2	0.4	0.1	0.1	0.3	0.3	0.3
substance 3 <sup>§</sup>	1397			0.2			0.4	0.9									0.1
Z-Zhasmone	1399																
methyleugenol	1406		0.3		0.1			0.2	0.1	0.1	0.1	0.1			0.2	0.1	0.1
bornyl isobutanoate	1416																
<i>cis</i> - <i>threo</i> -Davanofuran	1417							0.1	+		0.3						0.1
caryophyllene	1420	0.6	0.3	0.2	0.4	0.6	0.3	0.3	0.3	0.6	0.2	2.3	0.3	0.1	0.3	0.5	0.5
$\beta$ -copaene	1430	0.1	0.1	0.1		0.2	0.1	0.1	+	0.1	+	+	+				
humulene	1454	0.1	0.1		0.1	0.2	0.1	0.1	0.1	0.2	+	0.2	+				0.1s



Table 2. (Contd.)

Name of the component	J	Sample number according to Table 1																
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	
$\beta$ -farnesene	1458	0.1			0.2				0.1	0.3	0.1	0.2		+				0.1
allo-aromadendrene	1464	0.1			0.1				0.3	0.3				+				0.1
dehydrosequiceneole	1470																	0.2
4,5-di- <i>epi</i> -aristolochene	1471				0.6	0.6	0.1											
selina-4,11-diene	1477	0.4	0.2	0.1	0.3	0.2	0.2	0.2	0.6	0.1	0.1	0.2	0.3				0.1	0.1
germacrene D	1483	4.7	5.2	1.9	6.2	12.6	2.6	10.0	14.6	3.6	6.0	6.0	10.6	7.7	3.9	0.1	4.9	0.1
$\beta$ -selinene	1488	0.9	0.3	0.1	0.9	1.2	0.3	0.3	0.7	0.4	0.4	0.5	0.2	+	0.2	0.2	0.2	0.2
bicyclogermacrene	1497	1.3	0.7	0.3	1.8	1.3	0.3	0.5	2.9	1.2	0.5	0.5	3.7	2.3	0.7	0.5	1.3	0.1
1-phenyl-2,4-hexadiin	1498							0.3										
$\alpha$ -murolene	1502								0.3				0.1					
<i>trans</i> -sabinyl-2-methyl butanoate	1504				0.1				0.3	0.2			0.1	+	0.1		0.2	0.2
germacrene A	1506		0.1		0.4	1.4	0.2		2.6	0.6			0.1	+	0.1		0.2	0.1
$\beta$ -bisabolene	1510		0.2	+	0.4	0.5	0.1	0.2	0.8	0.2	1.6	1.6	1.0	1.4	0.1	0.2	0.8	0.1
$\gamma$ -cadinene	1515							+	0.1	0.2			0.1			+		0.1
$\epsilon$ -cadinene	1525		0.1		0.2	0.3	0.1	0.1	0.6	0.1	0.2	0.2	0.2	0.1	0.1	+	0.1	0.1
<i>E</i> - $\alpha$ -bisabolene	1544									+	0.2	0.2	0.1					
<i>E</i> -nerolidol	1565	0.8			0.1					+	0.3	0.3	0.1	0.1	+	+	0.3	0.3
spatulenol	1578	0.3			0.1					+	0.1	0.1	0.2			0.1	0.2	0.2
caryophyllene oxide	1584	0.4			0.1					+	0.1	0.1	0.1	+	0.1	0.1	0.3	0.3
davanone	1588												0.1					0.5
ledol	1606	0.3											+					
substance 4 <sup>¶</sup>	1632	1.1			0.2								+					
substance 5 <sup>††</sup>	1643				0.3													
$\beta$ -eudesmol	1651	0.8																
$\alpha$ -bisabolol oxide B	1656									0.3								0.3
substance 6 <sup>§§</sup>	1661				0.5													
$\alpha$ -bisabolol oxide A	1685																	0.3
<i>E</i> -sesquivalandulyl acetate	1739												0.1					0.3

\* Components are listed whose content in at least one sample is no lower than 0.1%; sign “+” denotes that the component is present, but its content is less than 0.1%. † m/z: 137(25%), ‡ 121(25), 109(100), 91(25), 81(40), 69(40), 57(25), 41(30). †† m/z: 150(70%), 107(100), 91(30), 43(70); ††† m/z: 150(100%), 135(70), 107(60), 95(30), 91(80), 79(40), 77(30). †††† m/z: 222(1%), 204(10), 189(5), 164(70), 121(100), 105(50), 93(40), 79(50), 43(80). ††††† m/z: 234(5%), 205(10), 161(15), 133(30), 122(100), 69(70). @ m/z: 236(10%), 221(5), 125(35), 94(100), 79(30), 43(30).

some secondary metabolites, the main components of the essential oil. Therefore, the classification of the silver-leaved wormwood *A. argyrophylla* as an individual species but not as a representative of the *A. frigida* subsection has not only morphological but also serious chemical grounds.

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