

Composition of Essential Oil of *Artemisia gmelinii* Web. ex Stechm. of Priolkhonian Flora (Lake Baikal)

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Abstract—*Artemisia gmelinii* Web. ex Stechm. is a pan-Asian mesoxerophyte shrub. *A. gmelinii* has found application in folk medicine. The composition of the essential oil has been studied for plants growing in different parts of the area. This article demonstrates the composition of essential oils of plants of the Priolkhonian flora (Lake Baikal), in particular in Aya Bay. Raw materials were collected during expeditionary work in 2019. The essential oil was obtained by hydrodistillation from air-dried raw materials in the year they were collected. Oil analysis was performed by chromatography–mass spectrometry. Data on the composition of the essential oil for visualization were processed using principal component analysis. γ -amorphene, isohumbertiol B, caryophylline oxide, caryophylla-4 (12), 8(13)-diene-5 α -ol, ylangenol, caryophyllene, and cabrevia oxide B are dominant components of the essential oil of plants from Aya Bay. Based on our own data and published data, we show that the component composition of essential oils is the result of the action of abiotic and biotic environmental factors and ensures that the plants are best suited to their growing conditions. On the other hand, regardless of where the plant grows, the directions of biosynthesis of the constituent essential oils are preserved, which makes it possible to distinguish various chemotypes of essential oils. The composition of the essential oils can be divided into two chemotypes: Indian, characterized by a high content of irregular monoterpenoids in the composition, and Siberian, characterized by a high content of monoterpenoids menthane type. Among the plants of the Siberian chemotype, there is a tendency to the formation of two lines—the western, with a prevalence of camphor terpenoids (camphor, borneol, etc.), and the eastern (alpine) sector of the range, with the accumulation of sesquiterpenic compounds in essential oils.

Keywords: subsection Abrotanum, *Artemisia gmelinii* Web. ex Stechm., essential oils, component composition, hydrodistillation, chromatography–mass spectrometry

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INTRODUCTION

Artemisia gmelinii Web. ex Stechm. a mesoxerophytic dwarf shrub. This wormwood grows in Russia (western and eastern Siberia and the Far East), China, Mongolia, Afghanistan, North India, Japan, Kazakhstan, Korea, Kyrgyzstan, Nepal, North Pakistan, Tajikistan, Uzbekistan, and Western Europe (Krasnoborov et al., 1997).

A. gmelinii has found application in folk medicine for the treatment of rhinitis, cough and fever, and liver diseases; as an antihelminthic agent; and externally, for abscesses and acne (Ligaa et al., 2009; Zhambaldorchzhe, 2011). Experimental studies have shown that aqueous and alcoholic extracts from the aerial part of the plant and essential oil accelerate blood clotting and have choleric, protistocidal, antibacterial, anthelmintic and fungicidal activities (Khanina et al., 2000).

The composition of the essential oil of *A. gmelinii* has been studied for plants growing in different parts of the range: Western and Eastern Siberia (Altai Republic, Krasnoyarsk krai, and Tomsk oblast (Khanina et al., 2000)), the Republic of Buryatia and Irkutsk oblast (Zhigzhitzhapova et al., 2010), in Primorsky krai in the Far East (Ozek et al., 2014), Mongolia (Zhigzhitzhapova et al., 2010), Kazakhstan (Suleimenov et al., 2010), and Himalaya (India (Haider et al., 2012; Pandey et al., 2014) and Nepal (Shrestha et al., 2013)), as well as introduced forms (Siberian Botanical Garden, Tomsk (Khanina et al., 2000)).

This work presents data on the composition of the essential oil of *A. gmelinii*, growing in the Olkhon region, and the correlation between the chemical composition and the ecological–geographical habitat is shown using the example of data analysis on the composition of essential oils.

MATERIALS AND METHODS

Raw materials for the production of the essential oil were collected during expeditions in 2019 in the Olkhon region (mainland, Aya Bay, to coordinates: 52°47'21" N, 106°36'02" E, 462.0 m a.s.l.) in the flowering phase. It is a high rocky ridge with outcrops of carbonate rocks opening to Lake Baikal. The slope of the ridge has a southwestern exposure, a gently elongated sandy–fine earth trough. Phytocenosis—chamerodos—wheatgrass—gmelin—wormwood steppe. Description made by Professor Namzalov (no. 42 dated August 14, 2019). Herbarium specimens are kept in the herbarium of the Buryat State University.

The essential oil was obtained by hydrodistillation from air-dry raw materials in the year of harvest (raw material weight 51 g; distillation duration 3 h from the moment of boiling). Oil analysis was performed by chromatography—mass spectrometry on an Agilent Packard HP 6890 N gas chromatograph with a quadrupole mass spectrometer (HP MSD 5973) as a detector and an Agilent 7890B gas chromatograph with a 7000C triple quadrupole mass spectrometer. We used a 30-m HP-5 MSD quartz column with an inner diameter of 0.25 mm. The percentage composition of the essential oil was calculated from the areas of gas chromatographic peaks without using correction coefficients. The qualitative analysis is based on a comparison of retention times and indices, as well as total mass spectra, a library of chromatography—mass spectrometric data for volatile substances of plant origin (Tkachev, 2008), and the NIST14 electronic library.

For the purpose of visualization, the data on the component composition of the essential oil were processed by the method of principal components (PCA analysis, software package Sirius version 6.0, Pattern Recognition Systems, a/s, Norway).

RESULTS

Fifty-seven components have been identified in the essential oil of *A. gmelenii* collected in Aya Bay. Most of them are terpenoids—monoterpenoids, sesquiterpenoids, and diterpenoids; representatives of isochromones and aromatic and aliphatic compounds are also found. The dominant components are sesquiterpenoids γ -amorphene (13.6%), isohumberthiol B (5.5%), caryophyllene oxide (4.9%), caryophylla-4 (12), 8(13)-diene-5 α -ol (4.3%), ylangenol (3.9%), caryophyllene (3.8%), and diterpenoid cabrevia oxide B (3.1%) (Table 1). A comparison with our previously published data on the composition of essential oil of Gmelin's wormwood from the Olkhon region (Primorsky ridge) and from the island of Olkhon showed that they differ both in qualitative and quantitative content of their main components. Thus, γ -amorphene, isohumberthiol B, caryophylla-4 (12), 8(13)-diene-5 α -ol, ylangenol, and cabrevia oxide B were identified only in the sample from the Aya Bay. Caryo-

phyllene and its oxide were previously found in the oils of *A. gmelenii* in the Olkhon region, but in smaller quantities. It should be noted that the main sesquiterpenoids previously found in the Olkhon region, γ -elemen, spathulenol, and presilphiperfolan-9 α -ol, were not found in the plant oil from the Aya Bay. At the same time, the main components of essential oils from the Primorsky Ridge and Olkhon Island are monoterpenoids 1,8-cineole, camphor, borneol, terpineol-4, identified in the essential oils of plants from the Aya Bay in smaller quantities. Essential oils from *A. gmelenii* of the Aya bay have more in common with those from Olkhon Island (Table 1).

DISCUSSION

Since the components of essential oils are active participants in the processes that ensure the adaptation of plants to various abiotic factors of plant growth, and also participate in the plant—plant and plant—animal interactions (Bagnoli et al., 2012; Loreto et al., 2014; Gols, 2014; Muhlemann et al., 2014), the composition of the oil is variable. At the same time, summarizing data on the composition of essential oils of *A. gmelenii* in Central Asia (Zhigzhitzhapova et al., 2010) and the results presented in this article, it should be noted that the composition of essential oils contains a common group of components (constant components), such as *p*-cymene (0.1–3.3%), 1,8-cineole (1.4–40.3%), terpinolene (0.1–0.6%), terpinen-4-ol (0.7–7.7%), camphor (2.7–31.0%), borneol and its acetate (2.1–17.6%), caryophyllene and its oxide (0.4–4.9%), and germacrene D (0.6–6.3%). Taking into account the isomeric components (α -, γ -terpenenes, α -, β -pinenes), 18 compounds are constant for essential oils of *A. gmelenii* from different regions of Asia: *p*-cymene, 1,8-cineole, α - and γ -terpenenes, terpinolene, terpinen-4-ol, α -terpineol, camphene, camphor, borneol and its acetate, pinocarvone, α - and β -pinenes, germacrene D, caryophyllene and its oxide, and spathulenol. Constant components in separate samples of essential oil can act as both major and minor components of the oil. Thus, 1,8-cineole was not detected in one of the samples from Russia (Altai Republic) (Khanina et al., 2000), and varies from 0.04% (Western Himalaya, India (Pandey et al., 2014)) to 40.3% (Russia, Republic of Buryatia (Zhigzhitzhapova et al., 2010)). Camphor was not found in two essential oils of plants: from Western Himalaya (Chamoli district) (Pandey et al., 2014) and in one of the samples from Russia (Altai Republic), while in samples from Krasnoyarsk krai its content reaches 39.9% (Khanina et al., 2000). *P*-cymene is not found in samples from Nepal and Russia (Altai Republic); in other essential oils its content is 0.3–4.2%.

At the same time, the components that are contained in certain essential oils in significant quantities are not found in essential oils from other countries. For example, in essential oils from plants growing in

Table 1. Component composition of essential oils of *Artemisia gmelinii* Web. ex Stechm. growing in the Olkhon region (Lake Baikal)*

Type/Component	Content of components, % of whole oil			
	<i>J</i>	2019	Zhigzhitzhapova et al., 2010 (collection 2008)	
	<i>Acyclic monoterpenoids</i>			
Linalool	1100	0.2	0.4	
Hotrienol	1107	1.2		
	<i>Monocyclic monoterpenoids</i>			
	<i>menthane type</i>			
<i>p</i> -cymene	1024	0.1	1.1	3.3
1,8-cineole	1031	1.4	20.3	36.5
Terpinolene	1088	0.1	0.3	0.6
<i>cis-p</i> -menten-2-ol-1	1121	0.1	0.5	0.6
Terpinen-4-ol	1177	0.7	5.6	7.7
α -terpineol	1191	0.3	1.8	1.7
<i>cis</i> -piperitol			0.3	
Piperitone			0.4	
α -terpinene			0.7	1.5
γ -terpinene			1.4	2.6
α -terpinyl acetate				0.5
<i>p</i> -mentene-1				0.3
	<i>Isocamphane type</i>			
Camphene			0.6	
	<i>Camphor type</i>			
Camphor	1141	2.7	11.3	21.4
Isoborneol	1156	0.1	0.8	0.7
Borneol	1166	2.1	6.5	9.6
Bornyl acetate	1287	0.3	0.8	1.8
	<i>Pinane type</i>			
<i>cis</i> -chrysanthenol	1162	0.2		
Pinocarvone			0.4	1.0
α -pinene			0.1	0.4
β -pinene			0.2	0.7
	<i>Thujane type</i>			
<i>trans</i> -sabinene hydrate				0.4
<i>cis</i> -sabinene hydrate				0.7
	<i>Tricyclic monoterpenoids</i>			
Tricyclene				0.2
	<i>Acyclic sesquiterpenoids</i>			
	<i>Farnesane type</i>			
β -farnesene	1458	0.9	0.2	
Nerolidol	1565	1.6	0.6	
Furanosequiterpenoids				
Davana ether (isomer 1)			0.3	
Davana ether (isomer 2)			0.5	
Davanon			0.6	
<i>cis-threo</i> -davana ether			5.8	
	<i>Monocyclic sesquiterpenoids</i>			
	<i>Bisabolane type</i>			
<i>ar</i> -curcumene			2.9	
α -zingiberene	1499	2.9	1.8	
β -bisabolene	1511	2.6	0.6	
α -bisabolol	1688	0.3		
	<i>Germacrane type</i>			
Germacra-4 (15), 5.10 (14) -triene-1-ol	1690	0.6		
Germacrene D			1.7	1.1
	<i>Humulan type</i>			
Humulene	1456	0.1	0.3	
Humulene epoxide -6.7	1606	1.5	0.8	
	<i>Element type</i>			
γ -elemene			7.4	

Table 1. (Contd.)

Type/Component	Content of components, % of whole oil		
	<i>J</i>	2019	Zhigzhitzhapova et al., 2010 (collection 2008)
	<i>Other types of monocyclic sesquiterpenoids</i>		
Isohumbertiol B	1536	5.5	
	<i>Bicyclic sesquiterpenoids</i>		
	<i>With cyclopropane ring</i>		
Bicycloelemene	1339	0.2	
	<i>Cadaline type</i>		
	<i>Cadinane series</i>		
d-cadinene	1527	1.6	
Cadina-4,10(15)-diene-9 β -ol			0.5
<i>trans</i> -cadina-1,4-diene			0.3
	<i>Amorphene series</i>		
γ -amorphene	1496	13.6	
	<i>Eremophyllane type</i>		
	<i>Eudesmane series</i>		
Eudesma-4 (15), 7-diene-1 β -ol	1688	0.3	
	<i>Selinane series</i>		
β -selinene			1.0
	<i>Guaiane type</i>		
α -guaiane			0.3
	<i>Kessane type</i>		
Kessane	1530	0.9	
	<i>Caryophyllane type</i>		
Caryophyllene	1422	3.8	0.7
Caryophyllene oxide	1586	4.9	2.9
Caryophylla-4 (12), 8(13)-diene-5 α -ol	1637	4.3	
10,10-Dimethyl-2,6-dimethylenebi-cyclo(7.2.0)undecan-5 β -ol	1644		
	<i>Tricyclic sesquiterpenoids</i>		
	<i>Aromadendrane type</i>		
Viridiflorol	1591	0.6	
Spathulenol			3.5
	<i>Cubebane type</i>		
β -cubebene	1392	0.6	
Cubebol	1516	1.1	
	<i>Copane type</i>		
α -copaene	1378	1.7	0.4
β -copaene	1432	0.3	
Ylangenol	1666	3.9	
Ylangenal	1675	0.3	
Mustakone	1687	0.5	
Copaborneol		0.2	0.9
	<i>Triquinans</i>		
Presilphiperfol-7-ene	1333	0.1	
Silphin-1-ene	1344	0.1	
Silphiperfol-5-ene			0.4
Presilphiperfolane-9 α -ol			4.8
	<i>Diterpenoids</i>		
Scareol oxide	1883	1.7	
Saussurea lactone	1806	0.5	
	<i>Isochromones</i>		
Cabrevia oxide B	1462	3.1	
Cabrevia oxide C	1469	0.4	
Cabrevia oxide D	1479	2.3	
	<i>Aromatic compounds</i>		
Benzaldehyde	958	0.3	
Methyl salicylate	1192	0.2	
Isobutyl benzoate	1321	0.1	
Eugenol	1359	0.2	

Table 1. (Contd.)

Type/Component	Content of components, % of whole oil			
	<i>J</i>	2019	Zhigzhitzhapova et al., 2010 (collection 2008)	
Butyl benzoate	1374	0.1		
Isoamyl benzoate	1438	2.2		
2-phenylethyl benzoate	1856	0.4		
Dihydromethyleugenol			0.8	
	<i>Aliphatic compounds</i>			
Octen-1-ol-3	979	0.3	0.3	0.6
Nonen-1-ol-3	1080	0.1		
Decadienal-2.4	1317	0.1		
Jasmone	1399	0.7		
Hexahydrofarnesylacetone	1846	0.7		

* Retention indices *J* indicated only for the component composition of the essential oil from the sample of the 2019 collection year. An empty cell indicates that the component was not found.

the state Uttarakhand, India, the dominant component is artemisiaketone (40.7–53.34%) (Haider et al., 2012; Pandey et al., 2014). Artemisiaketone is also found in essential oils from plants of the flora of the Far East in an amount of 0.7% (Ozek et al., 2014). Plants growing in Nepal are distinguished by the fact that they are herbaceous perennials and the main components are flamenol (15.17%), 2-methyl-1-methylene-3- (1-methylethenyl)-cyclopentane (3.93%), and 3-ethyl-3-methoxy-2-cyclopentenone (3.51%) (Shrestha et al., 2013).

Two loci can be distinguished on the biplot obtained on the basis of analysis of the data on the composition of the basic and constant compounds of essential oils of *A. gmelinii* from different countries (Fig. 1). The first locus is represented by samples from India (Haider et al., 2012; Pandey et al., 2014) and Nepal (Shrestha et al., 2013); that is, areas belonging to the Himalayan mountain system. Samples from India combine a high content of artemisiaketone, while it is absent in oil from Nepal, which is high in flamenol and *ar*-curcumene. The second locus consists of samples from Russia (Siberia and the Far East), Kazakhstan, and Mongolia. They are characterized by a high content of borneol; camphor; 1,8-cineole; and spathulenol. Four samples on the biplot were between both loci. A sample from the Altai Republic (Ust-Koksinsky district) (Khanina et al., 2000) is similar to the sample from India (Uttarakhand state, Chamoli district (Pandey et al., 2014)) due to the high content of chrysanthenyl acetate. What both populations of *A. gmelinii* have in common is that they grow in more severe places than other populations in the same regions. For example, the area where sagebrush from the Chamoli district of India grows is characterized by the authors as a cold desert (Pandey et al., 2014). The plant population from the Altai Republic (Khanina et al., 2000) is close to the Katun valley, with glacial feeding and the influence of cold winds of the Altai ridges, which creates more extreme continental conditions than in the whole of Western Siberia.

It is noteworthy that, on the biplot, the points (Tomsk (SBS 1 and 2)) corresponding to the samples of essential oils from cultivated plants are located near the point denoting the sample from Nepal (Fig. 1). Although both samples contain the main components of compounds inherent in plants of the Siberian locus—borneol; camphor; 1,8-cineole; and spathulenol—the sample from Nepal contains significant amounts of flamenol and *ar*-curcumene, and that from Altai contains irregular monoterpenoids (acetate of artemisiia alcohol and yomogi alcohol). Plants from Nepal and cultivated in Tomsk, unlike other populations, are herbaceous perennials.

The point corresponding to the sample from the essential oil of *A. gmelinii* from Aya Bay is located on the biplot outside the Siberian locus, since it does not contain terpenoids, or contains a small amount, which is what defines the Siberian locus, i.e., borneol, camphor, 1,8-cineole, and spathulenol. The reason, most likely, is the influence of various factors on the composition of the oil, including weather, edaphic, etc. At the same time, of all the samples of the Siberian locus, the samples from the Olkhon region (Primorsky Ridge 2008 and Olkhon 2008) are closest to the sample of Aya Bay 2019 on the biplot (Fig. 1).

The variety of individual compounds in the composition of essential oils is associated with the processes of the secondary transformation of terpene hydrocarbons; therefore, the constituents of the essential oil can be brought into several groups according to structural types. When analyzing the data on the group composition of essential oils of *A. gmelinii*, a biplot (GK1–GK2) was obtained. In this case, the samples form two loci (Fig. 2). Samples from India, as well, when analyzed by the content of the constant main constituents of essential oils, form a single group; we will call it the Indian chemotype. They are characterized by the accumulation of irregular monoterpenoids in essential oil.

The essential oils of plants growing in the territory of Asian Russia, Kazakhstan, Mongolia, and Nepal

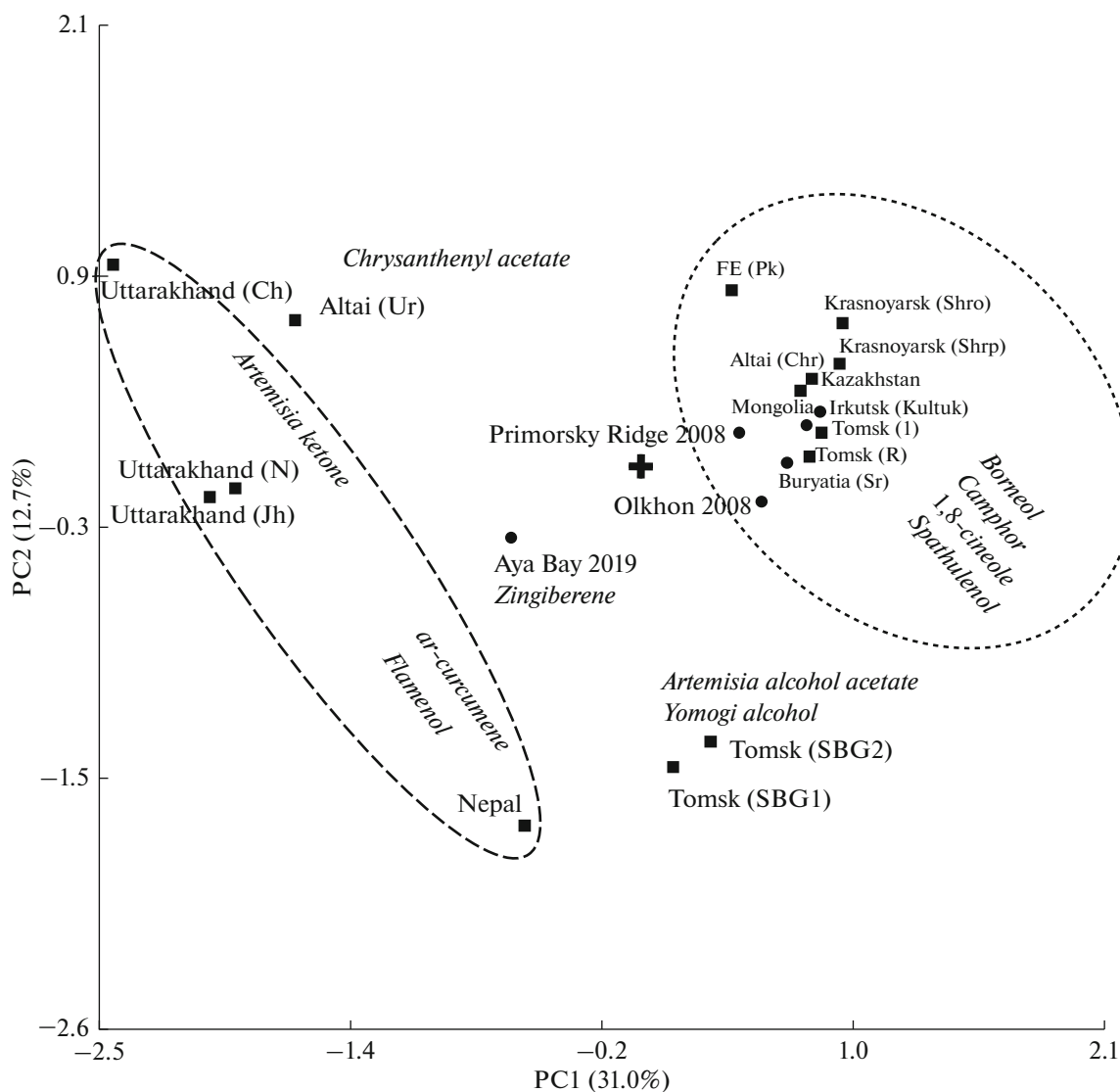


Fig. 1. Principal component method. Biplot (GK1-GK2) of data on the composition of basic and constant compounds in essential oils of *Artemisia gmelinii*. Samples of essential oils are indicated by squares (literature data) and circles (our own data) for *Artemisia gmelinii* from different countries: Russia: Bukhta Aya 2019—Irkutsk oblast, Aya Bay (this article); Olkhon 2008—Irkutsk oblast, Olkhon Island; Primorskiy Ridge 2008—Irkutsk oblast, Primorskiy ridge; Buryatia (Sr)—Republic of Buryatia, Selenginsky raion; Irkutsk (Kultuk)—Irkutsk oblast, settlement of Kultuk (Zhigzhitzhapova et al., 2010); Altai (Ur)—Republic of Altai, Ust-Kokinsky raion; Altai (Chr)—Republic of Altai, Charyshsky raion; Tomsk (1)—Tomsk oblast, environs of Tomsk; Krasnoyarsk (ShRo)—Krasnoyarsk krai, Sharypovsky raion, outskirts; Krasnoyarsk (ShRp)—Krasnoyarsk krai, Sharypovsky raion, meadow; Tomsk (R)—Tomsk oblast, environs of Tomsk, according to Rutovsky's method, Tomsk (SBS1)—Siberian Botanical Garden, Tomsk, flowering phase; Tomsk (SBS2)—Siberian Botanical Garden, Tomsk, fruiting phase (Khanina et al., 2000); FE (Pk)—Far East, Primorsky krai, Partizansky raion (Ozek et al., 2014); Mongolia: Mongolia—Bulgan aimak (Zhigzhitzhapova et al., 2010); Kazakhstan: Kazakhstan—Karaganda region (Suleimenov et al., 2010); Uttarakhand, India: Uttarakhand (N)—Niti valley, Uttarakhand (D)—Jelami valley (Haider et al., 2012), and Uttarakhand (Ch), Chamoli district (Pandey et al., 2014); and Nepal: Nepal—Mustang region (Shrestha et al., 2012).

form a locus that can be called the Asian chemotype. The characteristic constituents of the essential oils of these samples are a high content of menthane monoterpenoids. In this case, samples from the experimental site of the Siberian Botanical Garden at Tomsk State University (Tomsk SBS 1, 2), as well as the mountainous Altai (Altai (Ur)) and Priolkhonye

(Bukhta Aya 2019), take their rightful place in geographic origin at the locus of the Asian chemotype. The position of the Nepal point on the biplot can be explained by the dry climate of the Mustang region of Nepal, being in the rain shadow of the Dhaulagiri mountain massif. Apparently, this circumstance brings the growing conditions of *A. gmelinii* in Nepal

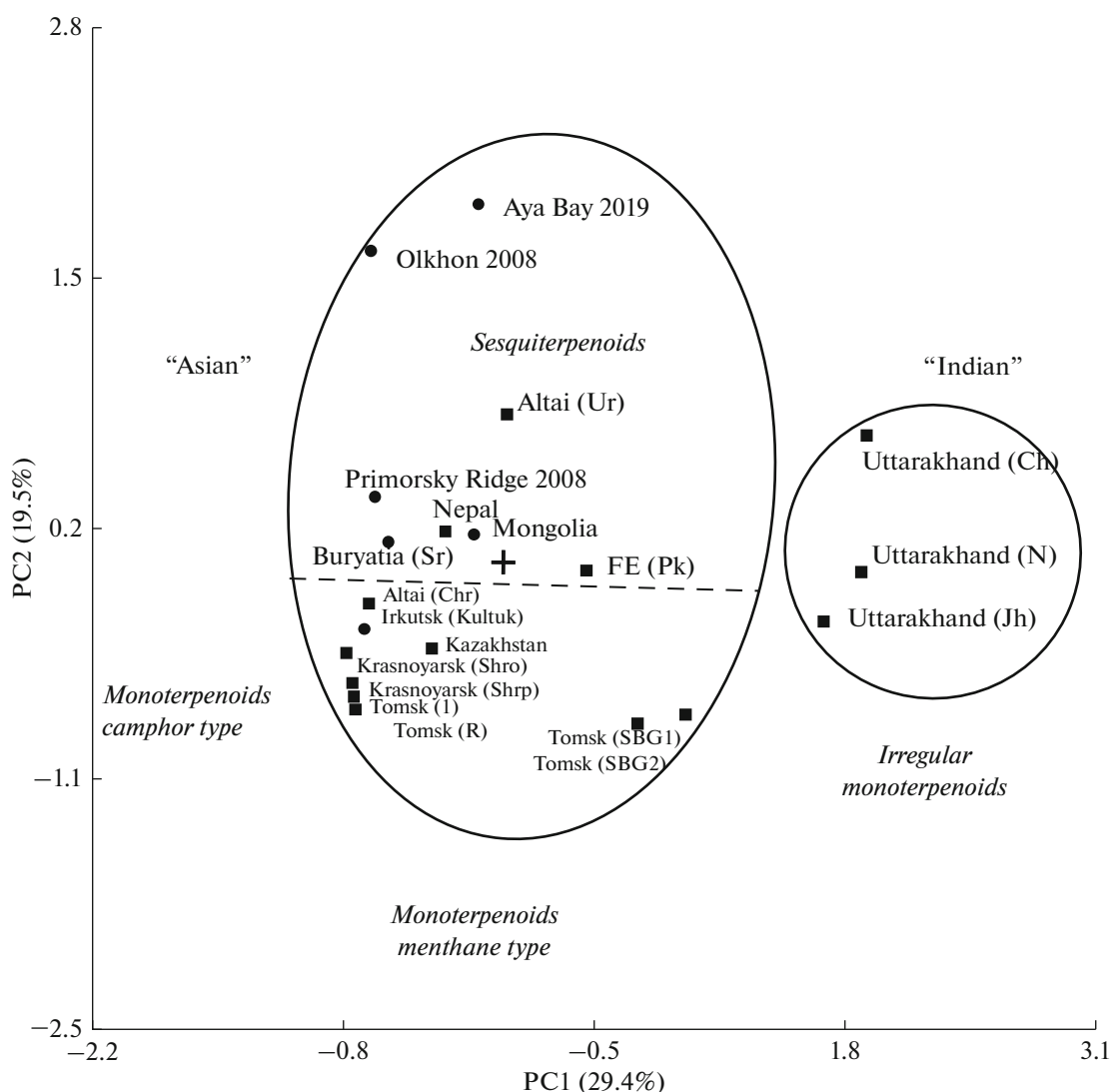


Fig. 2. Principal component method. Biplots of data-group composition of essential oils of *Artemisia gmelinii* (GK1–GK2). See Fig. 1 for designations.

closer to the semiarid and arid conditions of Siberia, Kazakhstan, and Mongolia. The biplot in the lower part of the locus contains mainly samples from the western, more moisture-rich territories. The greatest contribution to their distribution is made by camphor-type monoterpenoids, whereas samples from more arid eastern territories, including the Olkhon region, are located in the upper part of the locus. Their distribution is influenced by the content of sesquiterpenoids of various structural types in essential oils.

CONCLUSIONS

Thus, the component composition of essential oils is the result of the action of abiotic and biotic environmental factors on the plant during its development and ensures the best adaptation of plants to the conditions

of a particular growing area. At the same time, the directions of biosynthesis of constituent essential oils are under genetic control, which is expressed at the chemical level in the existence of various chemotypes of essential oils. Within the vast area of *Artemisia gmelinii*, under the influence of the ecological and geographical conditions of the places, two chemotypes of essential oils are formed: Indian, with the predominance of irregular monoterpenoids in the essential oil, in particular artemisiaketone, and Siberian, with the dominance among the components of menthane-type monoterpenoids, including 1.8 cineole. In plants, there is a tendency to the formation of two lines—the western one, with a predominance of monoterpenoids of the camphan type (camphor, borneol, etc.), and the eastern (high-mountain) sector of the range, where accumulation of sesquiterpene compounds occurs.

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COMPLIANCE WITH ETHICAL STANDARDS

Conflict of interests. The authors declare that they have no conflicts of interest.

Statement on the welfare of humans or animals. This article does not contain any studies involving animals performed by any of the authors.

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