Industrial Crops and Products 83 (2016) 462–469

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Short communication

Chemical composition of volatile organic compounds of *Artemisia vulgaris* L. (Asteraceae) from the Qinghai–Tibet Plateau

Svetlana Vasylievna Zhigzhitzhapova[a,b], Larisa Dorzhievna Radnaeva[a,b], Qingbo Gao[c], Shilong Chen[c], Faqi Zhang[c,*]

[a] *Baikal Institute of Nature Management, Siberian Branch, Russian Academy of Sciences, Ulan-Ude 670047, Russia*
[b] *Buryat State University, Ulan-Ude 670000, Russia*
[c] *Key laboratory of Adaption and Evolution of Plateau Biota, Northwest Institute of Plateau Biology, Chinese Academy of Sciences, Xining 810001, P.R. China*

ARTICLE INFO

Article history:
Received 18 September 2015
Received in revised form
30 December 2015
Accepted 30 December 2015
Available online 15 January 2016

Keywords:
Artemisia vulgaris
Hydrodistillation
Headspace extraction
Principal component analysis
Chemotypes

ABSTRACT

Plants growing in different climate retain the general direction of the biosynthesis of the volatile organic compound (VOC). The aim of this study was to investigate the VOC composition in *Artemisia vulgaris* L. growing on the Qinghai–Tibet Plateau. The VOCs were isolated by hydrodistillation or by headspace extraction, and their composition was analyzed by gas chromatography–mass spectrometry (GC–MS). There were 96 VOCs identified in the samples, accounting for 91–97% of the total. Monoterpenes (80.33%) were the main components of VOCs released by headspace extraction. The major components of essential oil obtained by hydrodistillation were monoterpenes (44.49%) and sesquiterpenes (29.98%). The monoterpenes 1,8-cineole, camphor, and α- and β- thujones were the main VOCs detected after both hydrodistillation and headspace extraction. Sesquiterpenes (*cis*-davanone, germacrene D) also accounted for a significant proportion of compounds in the essential oil. A principal component analysis (PCA) based on the types of components of essential oils of *A. vulgaris* collected from different countries showed that the moisture conditions at the collection site was the main factor explaining variations in VOC composition, and were located between "European" and "Siberian" chemotype, which indicated that the essential oil profile does not fully reflect zonal climatic features.

1. Introduction

Plants produce and store a wide variety of substances, many of which are volatile compounds. In most cases, the term volatile organic compound (VOC) refers to plant secondary metabolites—organic chemicals with a high vapor pressure at room temperature. The VOCs are responsible for most plant scents or odors. Essential oils are mixtures of natural volatile compounds isolated by hydrodistillation. Another method to isolate and analyze volatile compounds is headspace extraction, which sends VOCs into the vapor headspace.

The genus *Artemisia* is the largest and most widely distributed genera within the family Asteraceae. Many members of the genus *Artemisia* are aromatic plants. *Artemisia* species are well known for their volatile oil that is used in the food and pharmaceutical industries and in folk medicine to treat gastrointestinal diseases (Turi et al., 2014). The chemical composition of essential oils from various *Artemisia* spp. in the flora of Qinghai and Buryatia have been analyzed in previous studies (Shang et al., 2012; Soktoeva et al., 2013; Zhigzhitzhapova et al., 2014a,b,c). Many *Artemisia* species are distributed in Europe, Asia, and North America, but *Artemisia vulgaris* L. is the species that has been recognized as having medicinal properties. As well as having a therapeutic effect, the essential oil of *A. vulgaris* has insecticidal properties (Wang et al., 2006; Govindaraj and Ranjitha Kumari, 2013), and some components of the essential oil exhibit allelopathic effects (Barney et al., 2005).

The aim of this work is, firstly, to analyze the VOCs extracted from *A. vulgaris* using two different methods (hydrodistillation and headspace extraction), and secondly, to test the impact of climate of the regions where the plant grows on the composition of VOCs. To our knowledge, this is the first report on the composition of VOCs extracted from *A. vulgaris* by headspace extraction.

* Corresponding author: Fax: +86 971 6143282.
E-mail address: fqzhang@nwipb.cas.cn (F. Zhang).

http://dx.doi.org/10.1016/j.indcrop.2015.12.083
0926-6690/

Table 1
Collection information for *Artemisia vulgaris* samples used in this study.

Collection date	Voucher No.	Location	Latitude Longitude	Elevation (m)	Yield[a]	Color of essential oil
18-08-2014	hang2014102	Tongde, Qinghai, P.R. China,	N35°16′25″ E100°21′47″	2885	0.23%	Light green

[a] v/w vs. dried material.

2. Material and methods

2.1. Plant material

Plant materials were collected from Tongde Province, Qinghai–Tibet Plateau. Details of the collection site are shown in Table 1. The plant materials were collected during the flowering period in August, 2014, and were air-dried before being ground into a fine powder. Voucher specimens have been deposited in the herbarium of the Northwest Institute of Plateau Biology (HNWP), Chinese Academy of Sciences, Xining, P.R. China, and the Baikal Institute of Nature Management, Siberian Branch of the Russian Academy of Sciences, Russia.

2.2. Isolation of the essential oil by hydrodistillation

A 30–40 g portion of the powdered plant material was extracted by hydrodistillation for 3 h in a Clevenger-type collector apparatus. The resulting essential oil was isolated using the method described in the Pharmacopoeia of USSR (State pharmacopoeia of the USSR, 1990). The essential oil produced in this study was extracted from the entire aerial parts of the plant.

2.3. Headspace extraction

For each sample, up to 3 g dried material was crushed and added to a 20-ml headspace vial, and then immediately sealed with an aluminum cap with a silicone rubber septa. The vials were then transferred to a headspace tray and analyzed with an Agilent 7890A/5975C gas chromatograph (Agilent, Santa Clara, CA, USA) coupled with an Agilent 7697A automatic headspace sampler. The vial was heated to 120 °C and maintained at that temperature for 20 min with agitation. The temperature of the sampling needle and transmission lines was 150 °C.

2.4. Analysis of the essential oil

The essential oil was analyzed by GC–MS with an Agilent Technologies 7890A/5975C gas chromatograph coupled to an Agilent 7683B quadrupole mass selective detector. The GC system was equipped with an Agilent DB-5MS UI capillary column (30 m × 0.25 mm × 0.25 μm), and the MS system was operated in electron impact mode at 70 eV with the electron multiplier set at 2200 V. Helium (99.999% purity) was used as the carrier gas at a flow rate of 1 ml/min. The oven temperature was programmed to increase from 40 °C to 150 °C at a rate of 4 °C/min, then from 150 °C to 280 °C at a rate of 20 °C/min, and then kept constant at 280 °C for 6 min. The split ratio was adjusted to 1:1. The injector and detector temperatures were set to 280 °C and 250 °C, respectively. The MS data were acquired in scanning mode at a speed of 2.5 s per scan. The chemical constituents in the essential oil were identified by comparison of the GC–MS data with those held by the National Institute of Standards and Technology, and by comparisons of their MS and calculated linear retention indices (RI) with values reported in the literature (Tkachev, 2008). The RIs were determined relative to the retention times of *n*-alkanes (C8–C25) that were injected after the essential oil under the same chromatographic conditions. The RIs for all components were determined according to the standard method for *n*-alkanes.

2.5. Statistical analyses

The chemical composition data were subjected to multivariate statistical analysis using principal component analysis (PCA). All statistical analyses were conducted using Sirius ver. 6.0 software (Kvalheim and Karstang, 1987). Compounds found in all or the majority of the samples were subjected to statistical analysis and their relative values (i.e., percentage of the sum) were logarithmically transformed. This process allowed us to derive an equation that could be used to define quantitative differences among individual compounds.

3. Results and discussion

Volatile compounds were isolated from *A. vulgaris* samples by hydrodistillation and headspace extraction, and their composition was determined by gas chromatography–mass spectrometry (GC–MS). The VOCs detected after hydrodistillation and headspace extraction are shown in Table 2. In total, 96 components were identified in the samples, accounting for 91–97% of the total in each sample. Monoterpenes were the dominant component (80.33%) detected after headspace extraction. The major components of the essential oil were monoterpenes (44.49%) and sesquiterpenes (29.98%). Using both extraction methods, the main monoterpenes were 1,8 cineole, camphor, and α- and β- thujone. Sabinane (3.79%) was the fourth most abundant VOC detected after headspace extraction. Sesquiterpenes (*cis*-davanone, germacrene D) made up a significant proportion of the essential oil (Table 2).

Several studies have analyzed the constituents of essential oils of *A. vulgaris* from different regions. The VOC composition of oils was similar between *A. vulgaris* plants collected from the Qinghai–Tibet Plateau and those collected from other countries. Yomogi alcohol, artemisia ketone, carvone, carvacrol, trycyclene, β-farnesene, and spathulenol were detected in *A. vulgaris* samples collected in other countries but not in those collected from the Qinghai–Tibet Plateau. Bornylacetate, *iso*-thujol, *neo*-thujyl acetate, davana ether, and δ-elemene were detected in *A. vulgaris* samples collected from the Qinghai–Tibet Plateau but not in those collected from other locations. The VOC composition depends on many factors and may differ from sample to sample, but all of the components can be classified into kinship groups according to their carbon skeleton (Table 1). Bicyclic monoterpenes (α- and β-thujone, camphor, borneol, and α- and β-pinenes) were the main components of *A. vulgaris* essential oil in samples from most countries. Analyses of essential oils extracted from *A. vulgaris* showed that thujones were the main VOC in wild plants from Turkey (Erel et al., 2012), Croatia (Jerkovic et al., 2003), and India (Misra and Singh, 1986); camphor and borneol were the main VOCs in plants from the Krasnoyarsk territory (Russia) (Aljakin et al., 2011), France (Jerkovic et al., 2003), China (Wang et al., 2006), and Buryatia (Russia) (Zhigzhitzhapova et., 2014c); and β-pinene was the major VOC in *A. vulgaris* plants from Bashkorkostan (Russia) (Khalilov et al., 2001). The essential oils from *A. vulgaris* plants cultivated in India contained high contents of camphor and α-thujone (Govindaraj and Ranjitha Kumari,

Table 2
Chemical composition of essential oils from aerial parts of *Artemisia vulgaris* L. from different countries or regions.

Experimental	RI[a] Literature (Tkachev, 2008)	Compound	Peak area (%) in different country/region: China in the current study (hydrodistillation)	China in the current study (headspace extraction)	India (Misra and Singh, 1986)	Bashkortostan[b] (Khalilov et al., 2001).	Croatia[c] (Jerkovic et al., 2003)	France[d] (Jerkovic et al., 2003)	Serbia[e] (Blagojevic et al.,2006)	Turkey (Erel et al.,2010)	Krasnoyarsk[f] (Alyakin et al., 2011)	Buryatia[g] (Zhigzhitzhapova et al., 2014a)	Mongolia (Shatar et al.,2006)	Iran[h] (Bamoniri et al.,2010)
		∑ *Aromatics*:	0.29	0.02										
964	958	Benzaldehyde	0.01				0.6							
1023	1021	Pseudocemene	0.02											
1031	1042	P henylacetaldehyde	0.06				0.3–0.5	0.2–1.4						
1360	1359	Eugenol	0.13	0.02	0.92		0.2–0.8	0.5–1.3						
1404	1406	Methyl eugenol	0.07					1.0–6.8			0.53			
		∑ *Aliphatic*:	0.85	1.00										
790	794	Oct-1-ene		0.49										
800	801	Hexanal		0.40										
854	851	(*E*)-2-Hexenal	0.10											
1715	1712	Pentadecanal	0.34									0.0–3.7		
1841	1846	Hexahydrofarnesyl acetone	0.16					0.3				0.5–2.2	0.50	
		∑ *Monoterpenes*:	44.49	80.33										
		∑ *Acyclic monoterpenes*:	0.48	1.18										
990	991	β-Myrcene	0.37	0.97	tr	8.8		1.3	1.3		0.42		0.95	2.12
1048	1048	*trans*-β-Ocimene	0.11	0.18		0.7		1.5			0.30		1.71	
1241	1241	Cumin aldehyde		0.03							0.30	0.1		
		cis-Ocimene									0.31		0.23	
		Linalool			1.14		0.4–2.8	0.9–1.0		1.01	0.49	0.4–1.2	1.09	
		Geraniol			1.53		0.1–0.3	0.3–0.4						
		Neryl 2-methylbutanoate									0.36	4.0		
		∑ *Irregular monoterpenes*:	1.48	5.71										
850	849	(*Z*)-Salvene		0.31										14.87
906	908	Santolina triene	0.09	0.51					4.0					
1086	1084	Artemisia alcohol	1.39	2.03									0.23	
1177	1174	Artemisia alcohol acetate		2.86										
		Yomogi alcohol										0.3–0.7	0.39	
		Artemisia ketone						0.7–14.9				1.8–4.2	3.49	
		Monocyclic monoterpenes:	9.68	30.02										
989	990	2,3-Dehydro 1,8-cineole	0.05									0.1		
1006	1004	α-Phellandrene	0.02	0.14		1.0	0.4–12.9				0.17	0.1		
1015	1017	α-Terpinene	0.23			0.3					0.53			
1026	1024	*para*-Cymene	0.61	1.54	3.30		0.6–2.9	2.9	tr		0.72	0.1–1.1	0.55	
1030	1028	Limonene	0.13		0.53	1.4							0.55	
1031	1031	1,8-Cineole	6.27	26.34	0.25	1.0	2.0–15.2	15.1	28.9	8.47	8.77	0.2–20.5	5.45	18.64
1093	1088	Terpinolene	0.10	0.36							0.41	0.1		
1130	1121	*cis*-p-Menth-2-en-1-ol	0.07									0.3–0.4		
1180	1177	Terpinen-4-ol	0.98	0.64	tr		1.1–1.9	2.0–4.0	2.2	0.24	1.53	1.4–7.2	0.93	0.82
1192	1191	α-Terpineol	1.08	0.92	2.21		0.1–1.0	0.9				0.5–4.5	0.57	
1221	1219	*trans*-Carveol	0.08	0.03			0.1–0.2	0.7				0.1		
1276	1273	Isopiperitenone		0.02										
1353	1351	α-Terpineol acetate	0.06	0.03										
		γ-Terpinene				0.9	0.4–1.0	1.0	0.3		0.97	0.7	0.36	0.43
		trans-Piperitol										0.1–0.2	0.36	
		Thymol					0.2–1.8	0.2–0.9				0.1–0.4	0.21	
		cis-Carveol					0.1–0.3	0.2–0.4				0.1		
		Carvone								0.46	0.14	0.1–0.6		
		Carvacrol					0.1–0.2	0.3–0.4				0.3–0.8		
		Ionone					0.2–0.7	0.6–0.9			0.28			
		Ionol									0.17	0.4		
		∑ *Bicyclic monoterpenes*:	32.85	43.42										
		∑ *Isocamphane monoterpenes*:	0.15	1.70										

953	947	Camphene	0.15	1.70	0.45	1.8			0.1		4.06	0.3–6.8	0.21	
		∑ *Carane monoterpenes*:		1.09										
1000	1000	2-Carene		1.09										
		∑ *Camphene monoterpenes*:	3.36	7.34										
1141	1144	Camphor	2.92	7.31	3.01	0.5	0.5–8.7	2.3–12.9	1.4	0.40	29.50	0.3–36.6	2.33	
1165	1166	Borneol	0.44	0.03	tr		2.4–4.2	5.6–27.0		0.25	14.71	2.1–5.5	0.56	
		iso-Borneol				0.6						0.1–1.6		
		Bornylacetate			tr		0.2–0.3	2.2–4.9	tr		2.99	0.5–1.8		
		∑ *Pinane monoterpenes*:	2.87	4.13										
939	932	α-Pinene	0.34	2.00	0.27	53.7	1.3–15.1	0.3–1.6	5.9		0.63	0.2–0.8	0.96	0.33
957	952	Verbenene	0.01	0.16							0.08			0.89
980	975	β-Pinene	0.61	1.61	2.21	7.4		1.0	tr		0.41	0.1–0.4	0.89	
1124	1126	Chrysanthenone	1.67									0.8	0.35	
1212	1210	Verbenone		0.15							0.32			
1237	1237	*trans*-Chrysanthenyl acetate	0.17	0.11			16.3–24.6	0.5–1.8						
1263	1263	*cis*-Chrysanthenyl acetate	0.07	0.10								0.3		
		Pinocarveol						0.8		0.46				0.82
		Pinocarvone								0.42	0.53		0.22	1.96
		trans-Chrysanthenol				13.1						0.2–12.4		
		Myrtenol					0.1	0.5–1.1				0.3		
		∑ *Thujane monoterpenes*:	20.25	22.46										
929	926	α-Thujene	0.02	0.53	tr	0.8			1.0		0.07	0.1		
1108	1106	α-Thujone	2.52	4.48	56.3		0.1–8.5	0.4	1.2	56.13			1.51	
1119	1117	β-Thujone	16.93	17.05	7.49	0.5	5.3–20.8	1.0–1.2	13.5	12.02			0.17	
1137	1135	*iso*-Thujol	0.62	0.37										
1282	1280	*neo*-Thujyl acetate	0.16	0.03										
		Thujenal							2.2		0.41	0.1–0.2		
		∑ *Sabinane monoterpenes*:	6.22	6.70										
974	973	Sabinene	0.56	3.79	tr	0.9	1.3–4.1	2.6	13.7		1.65	0.2	2.09	
1068	1066	*trans*-Sabinene hydrate	1.19	1.16			0.2–0.3	0.6–1.1				0.2–1.8	0.12	1.46
1099	1098	*cis*-Sabinene hydrate		0.38				0.1–0.2				0.3–1.6	0.13	
1142	1140	*cis*-Sabinol	1.33	0.75										
1290	1295	Sabinyl acetate	2.69	0.62			2.4–3.0							
1497	1504	*trans*-Sabinyl -2-methylbutanoate	0.45											
		∑ *Tricyclic monoterpenes*:												
		Trycyclene									0.14	0.1–0.2		
		∑ *Sesquiterpenes*:	29.98	4.14										
		∑ *Acyclic sesquiterpenes*:	12.05	1.32										
		∑ *Furan ring in chain*:	11.27	1.24										
1232	1230	*nor*-Davanone		0.07										
1490	1495	Davana ether	0.25											
1516	1515	Davana ether (isomer 1)	0.40	0.03										
1524	1534	Davana ether (isomer 2)	0.46	0.03										

Table 2 (*Continued*)

RI[a]		Compound	Peak area (%) in different country/region											
Experimental	Literature (Tkachev, 2008)		China in the current study (hydrodistillation)	China in the current study (headspace extraction)	India (Misra and Singh, 1986)	Bashkortostan[b] (Khalilov et al., 2001).	Croatia[c] (Jerkovic et al., 2003)	France[d] (Jerkovic et al., 2003)	Serbia[e] (Blagojevic et al.,2006)	Turkey (Erel et al.,2010)	Krasnoyarsk[f] (Alyakin et al., 2011)	Buryatia[g] (Zhigzhitzhapova et al., 2014a)	Mongolia (Shatar et al.,2006)	Iran[h] (Bamoniri et al.,2010)
1532	1538	Artedouglasia oxide A	0.25	0.03										
1562	1566	*trans*-Davanone	0.22	0.02			0.3	0.1–3.8					0.30	
1581	1590	*cis*-Davanone	9.69	1.08										
		∑ *Farnesans sesquiterpenes*:	0.78	0.08										
1504	1510	(*E*,*E*)-α-Farnesene	0.53	0.06							0.52	0.5–1.5		
1567	1565	Nerolidol	0.25	0.02			0.5					0.4–1.5	0.51	
		β-Farnesene					0.2–2.2					0.2–1.8	1.26	1.01
		(*E*,*Z*)-α-Farnesene									0.62	0.7		
		∑ *Monocyclic sesquiterpenes*:	7.29	1.75										
		∑ *Bisabolane sesquiterpene*:	0.51	1.07										
1467	1471	Dehydrosesquicineole	0.08									0.5		
1497	1506	(*Z*)-α-Bisabolene	0.02											
1506	1511	β-Bisabolene	0.07	0.04			0.1–0.3							
1520	1524	β-Sesquiphellandrene		0.03										
1546	1545	(*E*)-α-Bisabolene	0.02	0.11										
1687	1688	α-Bisabolol		0.96				5.4				0.9	27.71	
1790	1803	α-Bisabolol acetate	0.34											
		ar-Curcumene					0.2	0.3–0.7						
		γ-Bisabolene											0.17	
		α-Bisabolol oxide B											4.67	
		∑ *Germacrane Sesquiterpenes*:	5.98	0.56										
		∑ *Series of germacrane*:	4.58	0.38										
1484	1484	Germacrene D	4.58	0.38							4.28	0.5–21.0	11.99	
		Germacrene B					0.3–1.0	0.7–1.4						
		∑ *Series of humulane*:	1.40	0.18										
1457	1456	α-Humulene	0.67	0.16			0.6–3.4	1.0–3.3	0.5		0.83	0.3–0.7	0.52	5.47
1618	1612	Humulene-6,7-epoxide	0.73	0.02					1.2	1.27		0.4–2.7		
		∑ *Elemane sesquiterpenes*:	0.80	0.12										
1390	1392	β-Elemene	0.29	0.09		0.6	0.2–2.0	1.1	1.4		0.20	0.1–2.1		2.51
1338	1338	δ-Elemene	0.41	0.03										
		∑ *bicyclic sesquiterpenes*:	9.62	0.74										
		∑ *Bicyclic compounds with cyclopropane ring:*	0.72	0.04										
1495	1500	Bicyclogermacrene	0.72	0.04							0.59	1.5		1.69
		∑ *Cadaline sesquiterpenes*:	1.47	0.10										
1498	1502	α-Muurolene		0.01			0.1–0.2				0.39			
1511	1517	γ-Cadinene	0.40	0.03	1.17		4.6–7.0	3.5–6.8						
1520	1527	δ-Cadinene	0.26	0.05			0.3–0.9	0.9–1.7	1.3		2.51	1.5		0.78
1643	1643	T-Cadinol	0.81	0.01										
		T-Muurolol						0.3				0.5		
		∑ *Eudesmane sesquiterpenes:*	4.69	0.24										
1475	1477	Selina-4,11-diene	0.12								0.53	0.2–0.9		
1486	1488	β-Selinene	1.19				1.0–2.1	4.2	4.7			0.8–4.8	1.16	
1659	1651	β-Eudesmol	3.38	0.24								0.5–2.7		
		∑ *Caryophyllane sesquiterpenes*:	0.73	0.24										

1417	1422	Caryophyllene	0.73	0.20	1.51	0.4	0.7–6.4	3.0–8.2	2.3	0.94	2.41	0.4–7.8	5.56	24.76
1583	1586	Caryophyllene oxide		0.04			0.6–3.2	2.3–8.7	6.5	10.19	2.24	2.7–14.1	1.79	0.95
		$\sum$ *Guaiane sesquiterpenes*	1.33	0.05										
1629	1632	Guaia-6,10(14)-dien-4-beta-ol	1.33	0.05								0.3–1.9		
		$\sum$ *Isodaucane sesquiterpenes*:		0.02										
1590	1598	Salvial-4(14)-en-1-one		0.02							0.35	0.3–1.7		
		$\sum$ *Isoprenologs*:	0.68	0.05										
		trans-7-*epi*-Sesquisabinene hydrate	0.05											
1433	1436	*trans*-α-Bergamotene	0.63	0.05										
		$\sum$ *tricyclic sesquiterpenes*:	1.02	0.33										
		$\sum$ *Copane sesquiterpenes*:	0.41	0.22										
1374	1378	α-Copaene	0.41	0.22		0.6	0.3–0.7	0.2–1.9	0.6		1.17	0.2–0.8	0.45	2.46
		$\sum$ *Longipinanes*:	0.10	0.09										
1350	1352	α-Longipinene	0.10	0.09				0.9–1.5				0.5–1.4		
		$\sum$ *Aromadendranes*:	0.17											
1406	1412	α-Gurjunene	0.05				0.6–0.8	1.4–2.1	tr		0.10			
1460	1464	*allo*-Aromadendrene	0.12				0.6	0.1-1.7			0.29			
		Spathulenol					1.3–3.6	3.1–4.3		1.39		2.4–10.3	2.40	1.75
		Palustrol					0.2–0.5	0.9–1.0						
		$\sum$ *Cubebane-type sesquiterpenoids*:	0.34											
1517	1516	Cubebol	0.34											
		$\sum$ *Bourbonane sesquiterpenoids*:		0.01										
1382	1387	β-Bourbonene		0.01			0.2–1.3	0.2–0.9	tr		0.50	0.3–0.5	0.58	
		$\sum$ *Aristolanes*:		0.01										
1648	1654	Vulgarone B		0.01										
		Total	75.36	85.38										

[a] RI, Retention indices: only for our data; literature—for (5%-phenyl)-methylpolysiloxane phase.

[b] Cumene (0.43%).

[c] 1-Octen-3-ol (0.6%), pulegone (0.4–0.6), thujol (0.1–2.4%), α-elemene (0.2%), calarene (0.3–1.2%), 2.2.4-trimethylcyclohexenecarboaldehyde (2.5–16.6%), nerol (0.2%), β-damascenone (0.1%), α-cadinol (0.9–1.2%).

[d] Geranylacetate (0.2%), perilla aldehyde (1.2%), filililfolide A (2.2–3.0%), *cis*-chrysanthenol (1.0–5.6%), thujol (2.9–6.2%), β-guaiene (0.3%), benzyl alcohol (0.3–0.7%), filifolene (2.2–3.0%), vulgarol B (1.0%), aromadendrene epoxide (0.7–0.9%).

[e] *trans*-sabinene hydrate acetate (2.5%), γ-humulene (1.1%), aromadendrene (0.9%), γ-gurjunene (2.8%);

[f] *n*-Butyl-2-mehylbutanoate (0.09%), geranylacetone (0.34%), β-phellandrene (0.25%), bornylformiate (0.53%), myrtenal (0.51%), *trans*-cadina-1,4-diene (0.33%), α-calacarene (0.56%), β-colocarene (0.78%), isocaryophyllene epoxide (0.17%), chamazulene (0.28%), β-oplanone (0.97%), β-copaene (0.28%), dehydrosabinaketone (0.11%), sabinaketone (0.17%), phellandral (0.67%).

[g] Octen-3-ol (0.2–0.3%), nonanal (0.1–0.5%), *cis*-carveol (0.3%), piperitone (0.2–15.1), *cis*-carveol acetate (0.1%), *cis*-chrysanthenol (0.2–1.8%), thujenol (0.1%), *cis*-*threo*-davanofuran (1.2%), isogermacrene (0.1–0.2%), germacra-4(15), 5.10(14)-trien-1-ol (2.2–3.1%), elemol (0.2–4.1%), bicycloelemene (0.1%), zonarene (1.5%), α-selinene (0.8%), γ-eudesmol (0.4–2.2%), selin-6-en-4-ol (1.7–15.6%), caryophylla-4(12), 8(13)-diene-5alpha-ol (1.0–2.0%), guaia-6,10(14)-dien-4-beta-ol (0.3–2.0%), alismol (2.5–4.1%), mint oxide (0.3–0.7%), copaborneol (0.6–0.9%), *triquinane*: silphiperfol-5-ene (0.1%), 7-*epi*-silphiperfol-5-ene (0.1%), silphiperfol-6-ene (0.7%), petasitene (0.3%), silphiperfol-6-en-5-one (0.2%), modheptene (0.4–0.7%), presilphiperfolan-9alpha-ol (0.1–39.7).

[h] Artemisia triene (0.79%), 1-octene-3-ol (2.06%), isogeraniol (0.95%), β-cububene (11.82%).

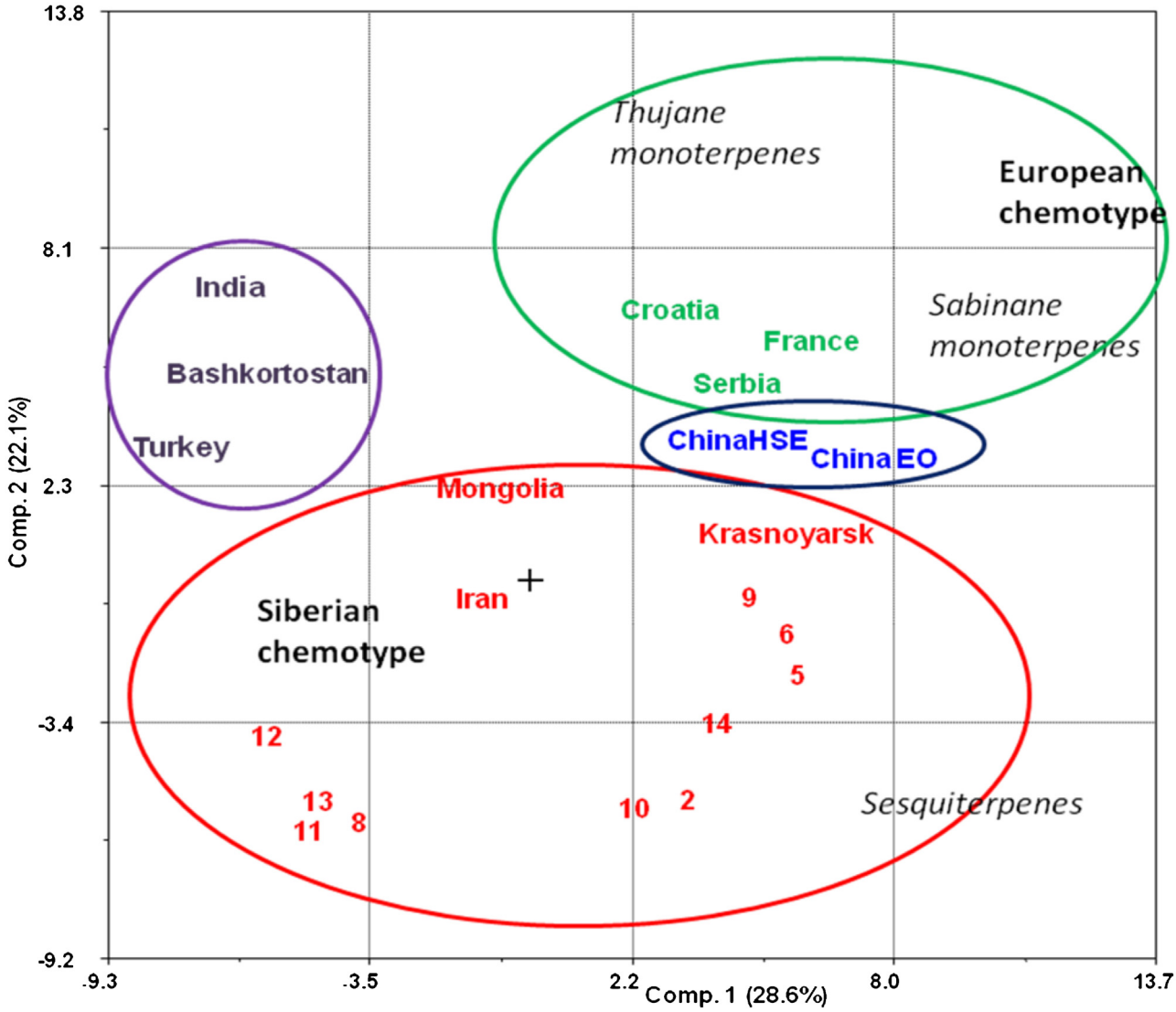

Fig. 1. Principal component analysis biplot of *Artemisia vulgaris* samples collected from different countries. Numerals indicate *A. vulgaris* samples from Buryatia (Russia) according to Zhigzhitzhapova et al., 2014c. China EO—essential oil obtained by hydrodistillation of *Artemisia vulgaris* samples from the Qinghai–Tibet Plateau (China); China HSE—volatile organic compounds isolated by headspace extraction from *A. vulgaris* samples from the Qinghai–Tibet Plateau (China).

2013). The monocyclic monoterpenoid 1,8-cineole was the main component of essential oil from aerial parts of *A. vulgaris* plants collected in Serbia. Caryophyllane and humulane sesquiterpenes were found in the essential oils of *A. vulgaris* plants from all countries, but the sesquiterpene antibiotic triquinanes was identified only in aerial parts of plants from Buryatia (Russia) and in roots of plants from Serbia (Blagojevic et al., 2006). Sesquiterpene compounds dominated in the essential oil of *A. vulgaris* plants from Mongolia (Shatar et al., 2006) and Iran (Bamoniri et al., 2010).

The exact VOCs composition of essential oils from wild *A. vulgaris* plants differed depending on the collection site, but the types of components were the same. Overall, the biosynthesis of certain structural types of compounds depended on the moisture conditions of the *Artemisia* habitats. Thujones were the major VOCs in samples from the Qinghai–Tibet Plateau, Turkey, and Croatia. The main VOC in samples from Siberia and France was camphor, while sesquiterpenes were the dominant VOCs in the Mongolian and Iranian samples (Table 2).

The PCA based on the structural groups (classification of terpenes by Semenov, 2000) of VOCs in essential oils of *A. vulgaris* from different countries showed that the moisture conditions at the collection site were the main factor contributing to variation in VOCs composition. Three clusters could be distinguished on the biplot (Fig. 1). Samples from European countries with a humid climate (Croatia, Serbia, France) comprised the first cluster, and were characterized by high contents of β-thujone and sabinane monoterpenes in their essential oils. Samples from three semihumid territories—Anatolia (Turkey), Nilgiri (India), and South Ural (Bashkortostan)—formed the second cluster. The third cluster represented samples from semiarid and arid areas—Krasnoyarsk, Buryatia, Mongolia, and Iran. Sesquiterpenes were the predominant component of essential oils extracted from these samples. The samples collected from the Qinghai–Tibet Plateau clustered together in the PCA biplot, confirming that the same main groups of compounds were detected after headspace extraction and hydrodistillation. They located between the “European” and “Siberian” chemotypes (Fig. 1). The climate of the Qinghai–Tibet Plateau is semiarid and arid, but the collected plants were growing in an intrazonal ecotope (fallow land). Therefore, the essential oil profile does not fully reflect zonal climatic features.

4. Conclusions

The main groups of components of essential oils of *A. vulgaris* were similar, regardless of the growth site, the year of collection, and the method of VOC extraction. Plants growing in different climate retain the general direction of the biosynthesis of VOC. The variety of the identified compounds is determined by a multiplicity of oxidation pathways. Plants grown in drier conditions tended to produce higher quantities essential oil and sesquiterpenes with greater structural diversity.

The structural groups of VOCs detected were very similar between samples extracted by hydrodistillation and those extracted by headspace extraction, as evidenced by their close grouping in the PCA biplot. Compared with hydrodistillation, headspace extraction has several advantages; for example, it is faster, and requires less plant material. The predominance of monoterpenes in the sample subjected to headspace extraction suggested that these compounds are important for adaptation to environmental conditions (Dudareva et al., 2006), and may closely reflect the native composition of plant volatiles. Therefore, headspace extraction will be a useful method for studies in which the exact ratio of the components is not so important; for example, in studies on toxicants or substances produced under particular environmental conditions. When essential oils are to be used for medical purposes, it is important to determine their exact composition. Therefore, hydrodistillation would be the best extraction method for that purpose.

Acknowledgments

This research was supported by the International Scientific and Technological Cooperation projects of Qinghai Province (grant 2014-HZ-812), the National Natural Science Foundation of China (grant 31270270, 31400322, 31200281 and 31110103911), the CAS "Light of West China" Program, Youth Innovation Promotion Association CAS, the Ministry of Education and Science of the Russian Federation (State task no. 19.1168.2014/K), Programs of Basic Scientific Research of the State Academies of Sciences (project V.46.5.2) and Russian Foundation for Basic Research (grant 15-44-042330). We thank Elena Dylenova, (Pharmacy Department, Buryat State University) for language editing.

References

Aljakin, A.A., Efremov, A.A., Angaskieva, A.S., Grebennikova, V.V., 2011. Chemical composition of essential oils of *Artemisia absinthium* L. and *Artemisia vulgaris* L., growing in the Krasnoyarsk krae [on Russian]. Himija Rastitel′nogo Syr′ja 3, 123–127.

Bamoniri, A., Mirjalili, B.B.F., Mazooch, A.A., Batooli, H., 2010. Chemical composition of *Artemisia vulgaris* L. from Kashan area isolated by nano scale injection. J. Org. Chem. 4 (2), 533–536.

Barney, J.N., Hay, A.G., Weston, L., 2005. Isolation and characterization of allelopathic volatiles from Mugwort (*Artemisia vulgaris*). J. Chem. Ecol. 31 (2), 247–265.

Blagojevic, P., Radulovic, N., Palic, R., Stojanovic, G., 2006. Chemical composition of the essential oils of Serbian wild-growing *Artemisia absinthium* and *Artemisia vulgaris*. J. Agric. Food Chem. 54, 4780–4789.

Dudareva, N., Negre, F., Nagegowda, D.A., Orlova, I., 2006. Plant volatiles: recent advances and future perspectives. Crit. Rev. Plant Sci. 25, 417–440.

Erel, S.B., Reznicek, G., Senol, S.G., Karabay, N.U., Konyalioplu, S., Zeybek, A.U., 2012. Antimicrobial and antioxidant properties of *Artemisia* L. species from western Anatolia. Turk. J. Biol. 36, 75–84.

Govindaraj, S., Ranjitha Kumari, B.D., 2013. Composition and larvicidal activity of *Artemisia vulgaris* L. stem essential oil against *Aedes aegypti*. Jordan J. Biol. Sci. 6 (1), 11–16.

Jerkovic, I., Mastelic, J., Milos, M., Jutcau, F., Masotti, V., Viano, J., 2003. Chemical variability of *Artemisia vulgaris* L. essential oils originated from the Mediterranean area of France and Croatia. Flavour Frag. J. 18, 436–440.

Khalilov, L., Paramonov, E.A., Khalilova, A.Z., Odinokov, V.N., Muldashev, A.A., Baltaev, U.A., Dzehemilev, U.M., 2001. Identification and biological activity of volatile organic compounds emitted by plants and insects. IV—composition of vapor isolated from certain species of *Artemisia* plants. J. Nat. Prod. 37, 339–342.

Kvalheim, O.M., Karstang, T.V., 1987. A general purpose program for multivariate data analysis. Chemom. Intell. Lab. Syst. 2, 235–237.

Misra, L.N., Singh, S.P., 1986. α-Thujone, the major component of the essential oil from Artemisia vulgaris growing wild in Nilgiri hills. J. Nat. Prod. 49, 941.

Semenov, A.A., 2000. Essays on Chemistry of Natural Compounds [on Russian]. Nauka, Novosibirsk.

Shang, Z.H., Hou, Y., Long, R.J., 2012. Chemical composition of essential oil of *Artemisia nanschanica* Krasch. from Tibetan plateau. Ind. Crops Prod. 40, 35–38.

Shatar, S., Bodoev, N.V., Zhigzhitzhapova, S.V., Altancjecjeg, S., Namzalov, B.B., 2006. Essential Oils Plants of the Pool of the River Selenga [on Russian]. Izdatel′stvo Burjatskogo Gosuniversiteta, Ulan-Udje.

Soktoeva, T.E., Ryzhova, G.L., Dychko, K.A., Khasanov, V.V., Zhizhitzhapova, S.V., Radnaeva, L.D., 2013. Artemisinin content in *Artemisia Annua* L. extracts obtained by different methods. Russ. J. Bioorg. Chem. 39, 761–764.

State pharmacopoeia of the USSR, 1990. General methods of analysis. Medicinal herbs [on Russian]. Medicine, vol. 2., 11th ed.

Tkachev, A.V., 2008. Investigation of Plant Volatiles [on Russian]. Izdatel′sko-poligraficheskoe predprijatie «Ofset», Novosibirsk.

Turi, C.E., Shipley, P.R., Murch, S.J., 2014. North American *Artemisia* species from the subgenus Tridentatae (Sagebrush): a phytochemical, botanical and pharmacological review. Phytochemistry 98, 9–26.

Wang, J., Zhua, F., Zhoua, X.M., Niua, C.Y., Leia, C.L., 2006. Repellent and fumigant activity of essential oil from *Artemisia vulgaris* to *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae). J. Stored Prod. Res. 42, 339–347.

Zhigzhitzhapova, S.V., Radnaeva, L.D., Chen, S.L., Fu, P.C., Zhang, F.Q., 2014a. Composition of essential oil of *Artemisia hedinii* Ostenf Et Pauls. on the Qinghai–Tibetan Plateau. Ind. Crops Prod. 62, 293–298.

Zhigzhitzhapova, S.V., Randalova, T.E., Radnaeva, L.D., 2014b. The composition of the essential oils of *Artemisia frigida* Willd., growing in the watershed of lake Baikal [on Russian]. Himija Rastitel′nogo Syr′ja 3, 151–158.

Zhigzhitzhapova, S.V., Randalova, T.E., Radnaeva, L.D., Taraskin, V.V., Chimittsyrenova, L.I., 2014c. Essential oils of *Artemisia vulgaris* L., growing on the territory of the Republic of Buryatia: composition and comparison with literature data [on Russian]. Basic Res. 8 (Part 1), 68–73.