Chemistry of Natural Compounds, Vol. 37, No. 4, 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

L. M. Khalilov,[1] E. A. Paramonov,[1] A. Z. Khalilova,[1] V. N. Odinokov,[1] A. A. Muldashev,[2] U. A. Baltaev,[1] and U. M. Dzhemilev[1]

UDC 543.51:547.314

The components of fragrance from four wormwood species of the Artemisia *L. genus were analyzed by GC-MS. The major and minor components of volatile essential oils typical of the studied plant species were determined.*

Key words: *Artemisia* L., volatile organic compounds, capillary gas chromatography, mass spectrometric detection, monoterpenes, sesquiterpenes.

Volatile organic compounds that are emitted by plants are an important factor in interspecies interactions in ecosystems. Investigations of the composition of volatile plant emissions increase our understanding of insect behavior and the development of modern methods for regulating their population. They can also be used to reveal correlations of the essential oil composition of certain plant species and their morphological signs. Therefore, studies of extracts of essential oil from wormwood *Artemisia glabella* Kar. et Kir. are of interest. It has been shown that the major components of plants grown in Kazakhstan and Italy are identical whereas the minor components differed slightly [1]. These results indicate that the chemical compositions of the essential oils are stable even with a significant change of soil and climate.

On the other hand, plants of the species *A. glabella* Kar. et Kir. and *A. obtusiloba* Ledeb. [1]; *A. radicans*, *A. Kuprijanov*, and *A. frigida* Willd [2]; *A. balchanorum* Krasch., *A. leucodes* Shrenk., *A. rhodantha* Rupr., and *A. scoparia* Waldst. et Kit. [3], and two species of the *Pimpinella* L. genus [4, 5] each have a characteristic composition of essential oil that correlates with their morphological signs.

Not so much the composition of the extracted essential oils as the volatile compounds emitted by the plant define the plant—insect chemical communication. Therefore, we investigated the composition of the plant fragrances using capillary gas chromatography with mass spectrometric detection (GC-MS) to analyze the volatile compounds.

We previously reported the composition of the native fragrance of two plant species, potato (*Solanum tuberosum* L.) [6] and common goutweed (*Aegopodium podagraria* L.) [7]. In the present article we report the chemical composition of the fragrance of four species of wormwood: bitter (*Artemisia absinthium* L.), common (*A. vulgaris* L.), santolino-leaved (*A. santolinifolia* Thurcz. ex Krasch.), and field (*A. campestris* L.), which are widely used in official and folk medicine [8, 9].

Table 1 lists results of the GC-MS analysis. Each of the chromatographic peaks was identified by retention index and MS properties. The retention index was compared with those given in the literature [10-12]. Coincidence within uncertainty limits was the first condition of identification. The second condition was correspondence of the MS of the analyzed compound and that given in an MS database [13].

---

1) Institute of Petroleum Chemistry and Catalysis, Academy of Sciences of the Republic of Bashkortostan and Ufa Scientific Center, Russian Academy of Sciences, Ufa-450075, prospekt Oktyabrya, 141, tel/fax 7(3472) 31 27 50, e-mail: ink@anrb.ru; 2) Institute of Biology, Ufa Scientific Center, Russian Academy of Sciences, Ufa-450054, prospekt Oktyabrya, 69, tel/fax 7(3472) 35 62 47. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 287-289, July-August, 2001. Original article submitted June 20, 2001.

TABLE 1. GC-MS Identification of Components (%) and Retention Indices (I) of Studied Wormwood Species

Compound	Mass spectrum, m/z (I, %)	I	$I_{lit.}$	*Artemisia absinthium*	*Artemisia santolinifolia*	*Artemisia vulgaris*	*Artemisia campestris*
				amount, %			
Tricyclene (**1**)	79(23), 93(100), 121(21), 136(19)	925	921	1.3			0.2
α-Thujene (**2**)	77(42), 93(100), 121(10), 136(18)	927	924	1.1	5.0	0.8	2.4
α-Pinene (**3**)	67(10), 77(29), 93(100), 136(7)	934	930	3.3	0.6	53.7	41.0
Camphene (**4**)	79(42), 93(100), 121(75), 136(19)	949	944	0.3	0.2	1.8	1.2
Sabinene (**5**)	69(27), 77(48), 93(100), 136(15)	971	964	7.4	13.7	0.9	4.5
β-Pinene (**6**)	69(33), 79(27), 93(100), 136(12)	975	969	0.7	0.8	7.4	29.7
Myrcene (**7**)	41(98), 69(81), 93(100), 136(16)	989	983	33.2	0.2	8.8	2.8
α-Phellandrene (**8**)	77(31), 93(100), 119(8), 136(24)	1003	996	0.3	1.2	1.0	
α-Terpinene (**9**)	93(90), 105(20), 121(100), 136(49)	1011	1007	0.8	2.7	0.3	0.6
Cumol (**10**)	91(18), 119(100), 134(35)	1022		0.9	10.8	4.3	
Limonene (**11**)	67(80), 68(100), 93(90), 136(27)	1024	1021	1.0		1.4	6.4
β-Phellandrene (**12**)	68(37), 77(25), 93(100), 136(19)	1026	1022	0.7	1.8		
1,8-Cineol (**13**)	43(100), 71(43), 108(50), 154(35)	1028	1023	0.8	13.7	1.0	
cis-Ocimene (**14**)	79(27), 93(100), 121(17), 136(5)	1035	1027				2.8
trans-Ocimene (**15**)	79(50), 93(100), 121(120), 136(15)	1043	1050			0.7	2.9
γ-Terpinene (**16**)	77(43), 93(100), 121(129), 136(33)	1048	1049	0.9	3.4	0.9	1.7
trans-Chrysanthenol (**17**)	81(100), 109(85), 121(71), 152(30)	1081	1077			13.1	
α-Terpinolene (**18**)	79(49), 93(100), 121(90), 136(75)	1085	1079	0.2	0.7		0.3
Linalool (**19**)	71(100), 80(21), 93(79), 121(19)	1094	1088	1.5			
cis-Sabinene hydrate (**20**)	71(100), 93(50), 111(45), 154(11)	1101	1090		0.5		
α-Thujone (**21**)	81(100), 95(60), 110(81), 152(10)	1102	1094	20.8	23.1		0.4
β-Thujone (**22**)	81(98), 95(60), 110(100), 152(14)	1107	1102	13.7	7.0	0.5	

TABLE 1. (Continued)

Compound	Mass spectrum, *m/z* (I, %)	*I*	$I_{lit.}$	*Artemisia absinthium*	*Artemisia santolinifolia*	*Artemisia vulgaris*	*Artemisia campestris*
				amount, %			
Camphor (**23**)	81(83), 95(100), 108(30), 152(28)	1137	1123			0.5	
Sabinol (**24**)	92(100), 109(27), 134(25), 152(9)	1140	1134	2.5			
Lavandulol (**25**)	69(100), 93(25), 11(48)	1153	1150	0.3			
endo-Borneol (**26**)	95(100), 110(25), 121(21), 154(11)	1169	1154			0.6	
1,4-Terpineol (**27**)	71(100), 93(48), 111(71), 154(19)	1186	1178	0.4	0.4		
3-Methyl-6-(1-methylethyl)-2-cyclohexen-1-one (**28**)	82(100), 95(49), 110(98), 152(23)	1212			11.0		0.8
Sabinyl acetate (**29**)	43(27), 91(100), 92(49)	1281	1277	6.6			
α-Copaene (**30**)	77(15), 105(98), 119(100), 204(18)	1385	1372	0.2	1.4	0.6	0.7
β-Bourbonene (**31**)	81(100), 123(75), 161(31), 204(10)	1399	1385	0.2			
β-Elemene (**32**)	53(51), 81(100), 93(91), 161(35)	1411	1394			0.6	
trans-Caryophyllene (**33**)	69(80), 93(100), 133(75), 204(15)	1434	1422	0.6	0.6	0.4	1.0
β-Selinene (**34**)	79(90), 93(85), 105(100), 204(60)	1489	1475		0.9		

Clearly monoterpenes dominate the volatile compounds of *A. absinthium*: myrcene (**7**), α-thujone (**21**), β-thujone (**22**), sabinene (**5**), sabinyl acetate (**29**), and sabinol (**24**). They also contain sesquiterpenes: α-copaene (**30**), β-bourbonene (**31**), and *trans*-caryophyllene (**33**). The main component of the fragrance of *A. santolinifolia* is the monoterpene ketone **21**. Other compounds in the order of their content are **13** > **28** > **10** > **22** (Table 1). The major component of the fragrance of *A. vulgaris* and *A. campestris* was identified as α-pinene (**3**). A common minor component of these two species was β-pinene (**6**).

The sharper wormwood odor of *A. absinthium* and *A. santolinifolia* compared with the other two studied species *A. vulgaris* and *A. campestris* is apparently due to the presence of terpenoids **13** and **21**.

The majority of the identified compounds that define the fragrance of the studied wormwood species is found in their essential oils [9].

Thus, using the four species of *Artemisia* as examples, it has been shown that the composition of their volatile compounds, both qualitatively and quantitatively, is specific. Therefore, it can be used for chemotaxonomic classification of the plants.

EXPERIMENTAL

The compositions were determined by GC-MS using the HP MS-Engine system with an HP-5989B mass spectrometer, HP-5890 chromatograph, and an HP-7694 automated device for performing the vapor analysis. A capillary column [0.2 mm × 25 m, phenyl (5%), methylsilicone (95%)] was used. The chromatography column was temperature programmed at 35°C for

15 min followed by an increase of temperature to 200°C at 5°C/min. The injector temperature was 220°C. The carrier gas was He flowing at 0.9 mL/min.

The analyzed samples were ground aerial parts (3 g each) collected during flowering and dried in air. A weighed sample was placed in an automated vapor sampler where a vial with the sample was thermostatted at 100°C for 20 min. Then, the vapor (1 mL) was transferred through the heated (150°C) capillary into the GC injector.

Plants were collected in the Southern Ural territory of the Republic of Bashkortostan in the summer of 2000.

REFERENCES

1. G. A. Atazhanova, A. D. Dembitskii, N. I. Zhizhin, and S. M. Adekenov, *Khim. Prir. Soedin.*, 193 (1999).
2. G. A. Atazhanova, A. D. Dembitskii, T. D. Yakovleva, M. Yu. Ishmuratova, V. G. Mikhailov, and S. M. Adekenov, *Khim. Prir. Soedin.*, 478 (1999).
3. K. H. C. Basher, T. Ozek, B. Demirchakmak, Kh. R. Nuriddinov, et al., *Khim. Prir. Soedin.*, 383 (1997).
4. N. P. Mekhtieva, *Khim. Prir. Soedin.*, 904 (1993).
5. N. P. Mekhtieva, *Khim. Prir. Soedin.*, 760 (1997).
6. L. M. Khalilov, A. Z. Khalilova, V. N. Odinokov, U. A. Baltaev, E. A. Paramonov, and U. M. Dzhemilev, *Khim. Prir. Soedin.*, 472 (1999).
7. E. A. Paramonov, A. Z. Khalilova, V. N. Odinokov, and L. M. Khalilov, *Khim. Prir. Soedin.*, 466 (2000).
8. I. N. Putyrskii and V. N. Prokhorov, *Universal Encyclopedia of Medicinal Plants* [in Russian], Minsk-Moscow (2000).
9. P. D. Sokolov, ed., *Plant Resources of the USSR* [in Russian], Nauka, Leningrad (1993), Vol. 7.
10. I. G. Zenkevich, *Rastit. Resur.*, No. 1-2, 48 (1996).
11. I. G. Zenkevich, *Rastit. Resur.*, No. 1, 16 (1997).
12. I. G. Zenkevich, *Rastit. Resur.*, No. 1, 30 (1999).
13. *Mass-Spectral Database*, J. Wiley and Sons, New York (1992), Version c.03.00, 138K.