

## ESSENTIAL OIL COMPOSITION OF THREE SPECIES OF *Achillea* FROM KAZAKHSTAN

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*The chemical composition of essential oils of Achillea millefolium L., A. nobilis L. from Kazakhstan flora and A. grandiflora Bieb introduced in culture at the Karaganda Botanic garden were determined by GC/MS. The main component in the essential oil of A. millefolium L. and A. nobilis L. was found to be camphor, while it was  $\beta$ -pinene for A. grandiflora.*

**Key words:** *Achillea millefolium*, *A. nobilis*, *A. grandiflora*, Asteraceae, essential oil composition, GC/MS, camphor,  $\beta$ -pinene.

The *Achillea* genus (Asteraceae) plants grow widespread throughout Kazakhstan [1]. *A. millefolium* is used in folk and official medicine [2, 3]. It grows in mountain, forest, and steppe parts of Kazakhstan. The chemical composition of *A. millefolium* essential oil depends on the site of collection. According to different researchers, ascaridole (47.2%), caryophyllene oxide (20%),  $\beta$ -caryophyllene (1.5-45.5%), chamazulene (13.0%),  $\beta$ -thujone (8.3-21.7%), germacrene-D (36.3%), camphor (20.6%), and guaiazulene (9.5%) were found as the main components in the essential oil of this plant [4-11]. In our previous study, in the oil of *A. millefolium* 99 components were identified representing 81% of the oil. Artemisia ketone (10.4%), piperitone (7.5%), chrysanthenone (7.1%) and 1,8-cineole (6.6%) were reported as the main components [12].

*A. nobilis* is less studied compared to *A. millefolium*. It grows in areas bordering woods and moist meadows of North, Central, and East Kazakhstan. The composition of its essential oil of Italian origin were reported to contain germacrene-D (46%) as the main component [13]. Piperitone (10.3%),  $\beta$ -eudesmol (9.8%), and viridiflorol (9.1%) were reported as the main constituents in the oil of *A. nobilis* by our group [14].

*A. grandiflora* is not a native plant of Kazakhstan. It was introduced in culture at the Karaganda Botanic garden. Here we report the chemical composition of the essential oils obtained from *Achillea millefolium*, *A. nobilis*, and *A. grandiflora*.

Water-distilled essential oils from aerial parts of three *Achillea* species were analyzed by GC/MS. The identified compounds and their percentages are given in Table 1.

One hundred twenty-three components were identified in the oil of *A. millefolium* L. representing 93.1% of the oil. Camphor (16%), 1,8-cineole (8.7%), borneol (6.2%),  $\beta$ -eudesmol (6.1%),  $\alpha$ -terpineol (5.9%), and  $\alpha$ -bisabolol (5.5%) were found as the major compounds.

In the oil of *A. nobilis*, eighty-seven components representing 90.2% of the oil were identified. Camphor (17%), 1,8-cineole (15.6%), terpinen-4-ol (10%), borneol (7.2%), and  $\beta$ -eudesmol (7.1%) were characterized as the main components. GC/MS analysis resulted in the characterization of one hundred fourteen constituents representing 86.7% of the *A. grandiflora* oil. The main constituents of its oil were  $\beta$ -pinene (8.9%), selin-11-en-4 $\alpha$ -ol (8.5%), and  $\gamma$ -eudesmol (6.3%).

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TABLE 1. The Composition of the Essential Oils of *Achillea* Species, %

RRI	Compound	A	B	C	RRI	Compound	A	B	C
1014	Tricyclene	Tr.	0.4	Tr.	1743	$\alpha$ -Cadinene	0.2	-	-
1032	$\alpha$ -Pinene	0.6	0.6	0.8	1744	$\alpha$ -Selinene	-	-	0.2
1035	$\alpha$ -Thujene	0.1	-	0.3	1747	<i>trans</i> -Carvyl acetate	0.2	-	-
1076	Camphene	1.0	0.3	0.3	1755	Bicyclogermacrene	0.3	-	-
1093	Hexanal	-	-	Tr.	1758	<i>cis</i> -Piperitol	0.1	0.3	0.1
1118	$\beta$ -Pinene	2.1	0.2	<b>8.9</b>	1764	<i>cis</i> -Chrysanthenol	1.1	-	0.3
1132	Sabinene	1.3	1.1	0.6	1765	Geranyl acetate	0.1	0.1	-
1174	Myrcene	0.8	-	0.1	1773	$\delta$ -Cadinene	0.5	0.4	0.3
1176	$\alpha$ -Phellandrene	-	0.1	-	1776	$\gamma$ -Cadinene	0.1	-	0.2
1188	$\alpha$ -Terpinene	0.5	0.9	0.4	1782	<i>cis</i> -Carvyl acetate	0.2	-	-
1195	Dehydro-1,8-cineole	0.1	0.1	Tr.	1783	$\beta$ -Sesquiphellandrene	-	-	0.1
1203	Limonene	0.3	0.3	0.3	1786	ar-Curcumene	0.2	-	0.1
1213	1,8-Cineole	8.7	15.6	5.9	1797	<i>p</i> -Methyl acetophenone	-	0.2	-
1225	(Z)-3-Hexenal	-	-	0.1	1798	Methyl salicylate	-	-	Tr.
1244	Amyl furan (2-Pentyl furan)	-	-	0.1	1802	Cumin aldehyde	0.2	0.5	-
1246	(Z)- $\beta$ -Ocimene	0.1	-	-	1804	Myrtenol	0.2	-	1.2
1255	$\gamma$ -Terpinene	0.9	1.8	0.9	1805	$\alpha$ -Campholene alcohol	0.3	-	0.1
1266	(E)- $\beta$ -Ocimene	0.1	-	-	1808	Nerol	0.1	-	-
1280	<i>p</i> -Cymene	1.1	4.1	2.3	1811	<i>trans-p</i> -Mentha-1(7),8-dien-2-ol	-	0.1	-
1286	2-Methyl butyl 2-methyl butyrate	Tr.	-	-	1811	<i>p</i> -Mentha-1,3-dien-7-al	Tr.	-	Tr.
1290	Terpinolene	0.2	0.4	0.2	1814	<i>p</i> -Mentha-1,5-dien-7-ol	0.1	0.3	0.1
1299	2-Methylbutyl isovalerate	Tr.	Tr.	Tr.	1820	Isogeraniol	0.2	-	-
1348	6-Methyl-5-hepten-2-one	Tr.	-	0.1	1827	(E,E)-2,4-Decadienal	-	-	Tr.
1360	Hexanol	-	-	Tr.	1838	(E)- $\beta$ -Damascenone	-	0.1	0.1
1391	(Z)-3-Hexenol	Tr.	-	-	1845	<i>trans</i> -Carveol	0.1	0.1	0.1
1400	Nonanal	Tr.	-	0.1	1853	<i>cis</i> -Calamenene	-	0.1	0.1
1430	$\alpha$ -Thujone	0.4	0.8	Tr.	1857	Geraniol	0.1	0.1	0.1
1441	(E)-2-Octenal	-	-	Tr.	1864	<i>p</i> -Cymen-8-ol	Tr.	0.4	0.1
1451	$\beta$ -Thujone	0.1	0.4	0.1	1868	(E)-Geranyl acetone	Tr.	Tr.	0.2
1452	$\alpha,p$ -Dimethylstyrene	-	Tr.	Tr.	1882	<i>cis</i> -Carveol	0.4	-	0.2
1452	1-Octen-3-ol	0.2	0.2	0.2	1898	1,11-Oxidocalamenene	Tr.	0.2	-
1466	$\alpha$ -Cubebene	-	-	Tr.	1902	Benzyl isovalerate	Tr.	-	-
1474	<i>trans</i> -Sabinene hydrate	1.1	0.4	0.5	1924	Geranyl isovalerate	-	-	Tr.
1480	Nerol oxide	-	0.1	-	1941	$\alpha$ -Calacorene	0.1	0.3	0.1
1487	Isoneroloxide	0.1	-	-	1945	1,5-Epoxy-salvial(4)14-ene	0.1	0.2	0.1
1497	$\alpha$ -Copaene	0.1	0.2	0.3	1948	<i>trans</i> -Jasmone	0.1	-	-
1507	(E,E)-2,4-Heptadienal	0.1	-	-	1957	Gubebol	Tr.	-	-
1522	Chrysanthenone	0.1	-	-	1958	(E)- $\beta$ -Ionone	0.1	-	Tr.
1532	Camphor	16.0	17.0	4.0	1969	<i>cis</i> -Jasmone	0.4	0.1	0.2
1541	Benzaldehyde	0.1	-	0.1	1984	$\gamma$ -Calacorene	0.1	0.1	-
1547	Dihydroachillene	0.1	-	-	1988	2-Phenylethyl-2-methylbutyrate	0.1	Tr.	-
1553	Linalool	0.3	0.4	0.5	2001	Isocaryophyllene oxide	0.1	-	Tr.
1556	<i>cis</i> -Sabinene hydrate	0.5	0.3	0.3	2008	Caryophyllene oxide	2.3	0.7	3.7
1562	Isopinocampone	-	-	0.1	2029	Perilla alcohol	-	0.3	Tr.
1568	1-Methyl-4-acetylcyclohex-1-ene*	0.1	0.3	-	2037	Salvial-4(14)-en-1-one	0.1	0.1	0.3
1571	<i>trans-p</i> -Menth-2-en-1-ol	0.2	0.7	0.2	2050	(E)-Nerolidol	2.4	-	0.9
1582	<i>cis</i> -Chrysanthenyl acetate	0.6	-	0.6	2056	13-Tetradecanolide	0.2	-	-
1586	Pinocarvone	0.2	0.1	1.2	2057	Ledol	0.1	-	-
1588	Bornyl formate	-	Tr.	Tr.	2071	Humulene epoxide-II	0.4	0.6	0.7
1594	<i>trans</i> - $\beta$ -Bergamotene	0.1	-	-	2073	<i>p</i> -Mentha-1,4-dien-7-ol	-	-	-

TABLE 1. (continued)

RRI	Compound	A	B	C	RRI	Compound	A	B	C
1597	Bornyl acetate	0.9	0.7	1.9	2074	Caryophylla-2(12),6(13)-dien-5-one	0.2	1.1	-
1600	$\beta$ -Elemene	-	0.1	0.2	2088	1- <i>epi</i> -Cubenol	0.4	-	-
1602	6-Methyl-3,5-Heptadien-2-one	-	-	0.1	2092	$\beta$ -Oplophenone	-	0.2	0.3
1610	Calarene (= $\beta$ -gurjunene)	-	-	Tr.	2096	Elemol	0.1	0.3	0.3
1611	Terpinen-4-ol	3.1	10.0	3.0	2113	Cumin alcohol	-	0.2	-
1612	$\beta$ -Caryophyllene	2.1	-	1.5	2131	Hexahydrofarnesyl acetone	0.2	0.9	0.6
1626	2-Methyl-6-methylene-3,7-octadien-2-ol	0.1	-	-	2144	Spathulenol	0.7	-	0.9
1631	Hexyl tiglate	-	0.1	-	2156	$\alpha$ -Bisabolol oxide B	0.2	-	-
1638	<i>cis-p</i> -Menth-2-en-1-ol	0.2	0.5	0.2	2170	Unknown-I	-	-	2.6
1642	Thuj-3-en-10-al	Tr.	0.2	0.1	2179	3,4-Dimethyl-5-pentylidene-2(5H)-furanone	Tr.	-	-
1648	Myrtenal	0.2	0.1	0.9	2181	Isothymol	-	-	0.2
1651	Sabinaketone	-	0.4	0.1		(=2-Isopropyl-4-methyl phenol)			
1655	Isobornyl propionate	-	0.1	-	2185	$\gamma$ -Eudesmol	-	1.2	6.3
1658	Sabinyl acetate	-	-	1.1	2186	Eugenol	1.3	0.4	-
1661	<i>trans</i> -Pinocarvyl acetate	0.2	-	1.7	2192	Nonanoic acid	-	0.1	-
1662	Pulegone	-	0.2	-	2198	Thymol	0.1	-	0.4
1664	<i>trans</i> -Pinocarveol	-	0.2	-	2209	T-Muurolol	0.1	-	0.6
1668	( <i>Z</i> )- $\beta$ -Farnesene	0.1	-	-	2214	ar-Turmerol	0.1	-	-
1681	( <i>Z</i> )-3-Hexenyl tiglate	-	0.1	-	2232	$\alpha$ -Bisabolol	5.5	0.1	-
1682	$\delta$ -Terpineol	0.3	0.4	-	2239	Carvacrol	0.1	0.1	0.1
1686	Lavandulol	0.2	-	0.9	2250	$\alpha$ -Eudesmol	0.2	7.1	0.5
1687	$\alpha$ -Humulene	0.3	-	1.2	2257	$\beta$ -Eudesmol	6.1	0.2	1.4
1688	Selina-4,11-diene	-	-	1.3	2264	Intermedeol	-	0.2	0.1
	(=4,11-Eudesmadiene)				2273	Selin-11-en-4a-ol	2.3	0.4	8.5
1689	<i>trans</i> -Pipertiol	-	0.3	-	2298	Decanoic acid	0.2	-	-
	(= <i>trans-p</i> -Menth-1-en-3-ol)				2316	Caryophylla-2(12),6(13)-dien-5 $\beta$ -ol	0.4	-	-
1694	Neral	0.1	-	-		(=Caryophylladienol I)			
1693	$\beta$ -Acoradiene	-	-	0.3	2324	Caryophylla-2(12),6(13)-dien-5 $\alpha$ -ol	0.6	0.2	0.7
1700	<i>p</i> -Mentha-1,8-dien-4-ol	-	0.1	-		(=Caryophylladienol II)			
	(=Limonen-4-ol)				2365	( <i>Z</i> )-Methyl jasmonate	0.4	-	-
1703	Salicylaldehyde	Tr.	-	-	2369	(2E,6E)-Farnesol	-	-	2.1
1704	$\gamma$ -Curcumene	0.1	-	-	2389	Caryophylla-2(12),6-dien-5 $\alpha$ -ol	-	-	0.4
1704	$\gamma$ -Muurolene	-	0.1	0.1		(=Caryophylladienol I)			
1706	$\alpha$ -Terpineol	5.9	3.7	2.0	2392	Caryophylla-2(12),6-dien-5 $\beta$ -ol	0.4	0.2	0.7
1719	Borneol	6.2	7.2	2.1		(=Caryophylladienol II)			
1726	$\alpha$ -Zingiberene	0.3	-	-	2500	Pentacosane	Tr.	-	0.1
1726	Germacrene D	2.4	0.3	0.5	2503	Dodecanoic acid	-	-	Tr.
1740	$\alpha$ -Muurolene	-	0.4	-	2606	$\beta$ -Costol	0.3	-	-
1741	$\beta$ -Bisabolene	-	-	0.5	2622	Phytol	0.1	-	0.1
1742	Geranial	-	-	0.1	2670	Tetradecanoic acid (=Myristic acid)	0.1	-	0.2
					2931	Hexadecanoic acid	0.7	-	0.7
						<b>Total</b>	<b>93.1</b>	<b>90.2</b>	<b>86.7</b>

**A:** *A. millefolium*; **B:** *A. nobilis*; **C:** *A. grandiflora*. RRI: Relative retention indices calculated against *n*-alkanes. %: Calculated from TIC data. Tr.: Trace (< 0.1%). \*Correct isomer not identified.

Unknown-I (RI: 2170): EIMS, 70 eV, *m/z* (I, %): 204(60.0), 189(23.5), 161(73.2), 149(37.4), 135(10.6), 121(19/9), 108(27.8), 93(30.8), 81(38.1), 59(100), 43(26.5).

## EXPERIMENTAL

**Plant Material.** *A. grandiflora* Bieb: Karaganda Botanic garden, *A. millefolium* L.: Karaganda region, near Spassk place. Voucher No. 1987.08.24.01 (collection of the botanic garden of the Institute of Phytochemistry), *A. nobilis* L.: Karaganda region, Karkaraly village. Voucher No. 1998.05.24.01.06 (collection of the botanic garden of the Institute of Phytochemistry).

**Oil Isolation.** Air-dried aerial parts of the plant material were subjected to hydrodistillation for 3 h using a Clevenger type apparatus. Yields of essential oils are 0.33% for *A. millefolium*, 0.21% for *A. nobilis*, and 0.18% for *A. grandiflora*.

**GC/MS Analysis.** The essential oils were analyzed by GC/MS using a Hewlett Packard GCD G1800A system. An HP-Innowax FSC column (60 m × 0.25 mm  $\varnothing$ , with 0.25 mm film thickness) was used with helium as carrier gas (0.7 mL/min). GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min, then kept constant at 220°C for 10 min and then programmed to 240°C at a rate of 1°C/min. Alkanes were used as reference points in the calculation of relative retention indices (RRI). Split ratio was adjusted at 50:1. The injector temperature was at 250°C. MS were taken at 70 eV. Mass range was from 35 to 425 *m/z*. Library search was carried out using the Wiley GC/MS Library and the TBAM Library of Essential Oil Constituents. Relative percentage amounts were calculated from TIC by a computer.

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