GC-MS ANALYSIS OF THE ESSENTIAL OILS OF SOME PLANTS OF THE ASTERACEAE DUMORT FAMILY

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An investigation has been made of the chemical composition of essential oils (EOs) of plants of the family Asteraceae Dumort: Achillea filipendulina Lam., Artemisia persica Boiss., Artemisia leucodes Schrenk, and Artemisia lehmanniana Bunge. It has been shown that the composition of the EOs of plants of one and the same species depends on the conditions and growth sites.

The chemical composition of essential oils (EOs) and also of some other components of the plant Achillea filipendulina Lam. has been considered previously [1-3]. Dembitskii [1] has given a comparative analysis of the EOs of the raw material over the course of 10 years (1966-1976). The amounts of the main components changed: achillenol from 38 to 45%; filipendulyl acetate from 12 to 16.5%; bornyl acetate from 3.5 to 5.5%; and borneol from 4 to 6%. However, according to Khakimov and Tsukervanik [2], the main components of the OE are free borneol (~35%) and its esters (~30%). In addition to this, the OE was found to contain an unidentified monoterpene alcohol with the composition $C_{10}H_{18}O$ (~20%). These contradictory results were the reason for performing an analysis of the EOs of Achillea filipendulina and Artemisia persica Boiss.

The OEs from the flowers with peduncles of *A. filipendulina* gathered in Tashkent province, were isolated by steam distillation [4]. The yield of oil amounted to 0.4-0.5% of the air-dry weight of the raw material. The GC-MS analysis of the OE revealed 21 components.

In the low-temperature part of the chromaatogram, peaks of monoterpene hydrocarbons having a molecular mass of 136 a.m.u. were observed — α -pinene, β -pinene, cyclofenchene, and 2,5-dimethyl-3-methylenehepta-1,5-diene — and then oxidized monoterpenes were observed — 1,8-cineole, terpin hydrate, borneol, bornyl acetate, ascaridol, and nerolidol — these being the main components of the EO.

Table 1 gives information on the qualitative and quantitative composition of the EO of *Achillea filipendulina* with the inclusion of minor components, as well. The results that we have obtained differ considerably from those given in the literature.

According to the literature [5], the EO of *Artemisia persica* growing in the Turin (Italy) Botanical Garden from seed obtained from the Botanical Garden of the Academy of Sciences of the Republic of Uzbekistan (Tashkent, Uzbekistan) contains 1,8-cineole (26.6%), artemone (6.7%), davanone (15.0%), camphene (3.3%), and *p*-cymene (5.4%), these making up 57.1% of the total weight of the EO. At the same time, other authors [6] give the following composition for the EO of *A. persica*: α -pinene, 12%; camphene, 23%; camphor, 16%; borneol and bornyl acetate, 33%.

We have investigated the EO of A. persica growing in Tashkent province. Steam distillation gave a yield of the EO of $\sim 0.7\%$. A mass chromatogram showed the presence of 19 components, the bulk consisting of p-cymene, p-methylbut-2-enal, thujone, camphor, perillyl aldehyde, piperitone, bornyl acetate, isobornyl acetate, and a ketone of unknown structure.

On comparing the results of our investigations with literature information [5], substantial differences were observed in both the qualitative and quantitative ratios of the components.

Table 2 gives the qualitative and quantitative chemical composition of the EO of Artemisia persica.

Analysis of the EO of *Artemisia leucodes* Schrenk. was carried out in connection with the fact that work is being conducted in IKhRV AN RUz on the introduction of the antiatherosclerolic drug "Oligvon" isolated from the epigeal part of *A. leucodes* [7]. In the production of the drug, about 2% of the EO is isolated in parallel.

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TABLE 1

Name	Scan по.	мм	Empirical formula	Amount, %
2,5-Dimethyl-3-methylenehepta	_			
1,5-diene	39	136	C10H16	4.9
α-Pinene	47	136	$C_{10}H_{16}$	4.8
Cyclofenchene	55	136	$C_{10}H_{16}$	4.6
β -Pinene	75	136	C ₁₀ H ₁₆	3.3
<i>p</i> -Cymene	115	134	$C_{10}H_{14}$	3.5
1,4-Cineole	122	154	C ₁₀ H ₁₈ O	8.3
Terpin hydrate	137	190	$C_{10}H_{20}O_2$	11.7
1,8-Cineole	145	154	$C_{10}H_{18}O$	3.4
Octahydro-7a-methyl-1H-				
inden-I-one	166	152	$C_{10}H_{16}O$	3.1
5-Methylspiro[3.5]-	•			
nonan-1-one	172	152	$C_{10}H_{15}O$	3.5
7a-Methyl-1,2,3,3a,4,7a-				
hexahydro-5H-inden-5-one	181	150	C ₁₀ H ₁₄ O	4.5
Borneol	199	154	C ₁₀ H ₁₈ O	7.7
Perillyl aldehyde	210	150	$C_{10}H_{14}O$	4.3
Cyclohexa-1,5-dien-4-(1-	217	152	C ₁₀ H ₁₆ O	1.8
isopropyl)methanol [sic]				
Dehydro-B-ionone	225	194	C13H22O	1.4
Cyclohexanol-2-methylene-3-				
(1-isopropyl) acetate [sic]	232	190	$C_{12}H_{18}O$	1.4
Bornyl acetate	242	196	C12H20O2	9.9
Ascaridol	254	168	C ₁₀ H ₁₆ O	7.4
Nerolidol	263	222	C15H26O	7.1
Ūnidentified	297	220	$C_{15}H_{24}O$	2.6

TABLE 2

Name	Scan no.	MM	Empirical formula	Amount, %
Ocimene	18	136	C10H16	3.2
Camphene	50	136	$C_{10}H_{16}$	1.9
p-Pheliandrene	90	130		0.0
a-Terpinene	120	130		12.0
Fonchone	135	1.59		0.0
Icofenchone	187	152		10.1
Thuione	107	152	$C_{10}H_{16}O$	64
Isoborneol	216	154	CueHuo	17
Decane-5 6-dione	220	170	CuHuiO	17
Perillyl aldehyde			010111302	
	238	150	CaHuO	85
Unidentified	250		-10-1140	2.1
Piperitone	268	152	C ₁₀ H ₁₆ O	8.5
5-Methylspiro[3.5]nonan-			-10-10-	
1-one	274	152	C10H15O	3.1
Bornyl acetate	285	196	$C_{12}H_{20}O_2$	5.1
7-Hydroxy-p-menthen-2-one	296	154	$C_9H_{14}O_2$	8.4
Anisketone	428	164	$C_{10}H_{12}O_{2}$	1.3
Davanone	430	236	$C_{15}H_{24}O_2$	10.5
Isomer of davanone	481	236	$C_{15}H_{24}O_2$	2.1

According to Kurbatov the yield of the EO of A. leucodes is 0.13%, and the main component is camphor. According to our results (Fig. 1a), 92-94% of the total EO obtained consists of camphor, while cineole, Δ^3 -p-menthene, isofenchene, and others were detected as minor components (Table 3).

Thus, from the production wastes of the drug "Oligvon" it is possible to produce an EO with a high level of camphor, which can easily be isolated in the individual state.

We have investigated the epigeal part (leaves and flower heads) of *Artemisia lehmanniana* Bunge, gathered on August 4-5, 1992, in the Eastern Tamir (village of Chechekty). The essential oil of this plant is used as a perfume in the Khodzhent soap-boiling factory [9]. However, there is no information on its chemical composition. As a result of GLC—MS analysis we obtained a chromatogram (Fig. 1b) consisting of an unresolved triplet of peaks each component of which showed in the mass spectrum a molecular mass of 152 a.m.u. On top of this, their fragmentation led to mass spectra indistinguishable from one another. From their m/z values and intensities of the peaks they were very close to the spectra of thujone (1), isothujone (2), and sabinol (3).

TABLE 3

Name	Scan no.	мм	Empirical formula	Amount, %
Cineole	115	154	$\begin{array}{c} C_{10}H_{18}O\\ C_{13}H_{18}\\ C_{10}H_{16}O\\ C_{10}H_{16}O\\ C_{10}H_{16}O\\ C_{10}H_{14}O_2\\ C_{10}H_{16}O_2 \end{array}$	2.2
p-Menthene	146	138		0.9
Camphor	210	152		92.2
Isofenchene	234	152		2.5
2-(4-Ethylphenoxy)ethanol	335	166		0.9
Octa-1,7-dien-3-ol acetate	390	168		1.2



Fig. 1



To determine the nature of the main component, making up 79% of the weight of the EO, we analyzed its PMR spectrum in deuterochloroform (CDCl₃). It showed signals at (ppm) 0.05 (d.d, 1H, $J_1 = 4 \text{ Hz}$, $J_2 = 6 \text{ Hz}$) – the characteristic signal of a methine proton of a cyclopropane ring; 0.75 (d, 3H, J = 7 Hz); 0.85 (d, 3H, J = 7 Hz); 0.85 (d, 3H, J = 7 Hz); - the protons of the methyl groups of an isopropyl radical; 1.05 (d, 3H, J = 8 Hz) – the protons of a secondary methyl group; and 1.95 (d, 1H, J = 19 Hz) and 2.46 (d, 1H, J = 19 Hz) – the protons of a methylene group conjugated with a keto group in the α -position.

According to the PMR spectral results, the structure of the main component of the EO of A. lehmanniana corresponds to thujone (1). And, consequently, two peaks in the mass spectrum correspond to isothujone (2) and sabinol (3).

Table 4 gives the qualitative and quantitative composition of the EO of A. lehmanniana.

EXPERIMENTAL

The mass spectrograms of the EOs were obtained on a MS-25RF instrument under the conditions given in [10], the temperature programming regime for each EO being as follows: 1) Achillea filipendulina – from 40 to 200°C and 200 to

TABLE 4

Name	Scan no.	ММ	Empirical formula	Amount, %
Cineole α -Pinene Thujone Isothujone Sabinol Cuminaldehyde Camphene β -Elenene Tetradecane Myristic acid Palmitic acid	178 207 278 295 357 447 485 510 557 897	$154 \\ 136 \\ 152 \\ 152 \\ 148 \\ 136 \\ 204 \\ 198 \\ 228 \\ 256 \\$	$\begin{array}{c} C_{10}H_{18}O\\ C_{10}H_{16}\\ C_{10}H_{16}O\\ C_{10}H_{16}O\\ C_{10}H_{15}O\\ C_{10}H_{12}O\\ C_{10}H_{12}O\\ C_{10}H_{15}\\ C_{15}H_{24}\\ C_{14}H_{50}\\ C_{14}H_{20}O_{2}\\ C_{15}H_{32}O_{2}\end{array}$	$1.2 \\ 0.9 \\ 79.2 \\ 8.9 \\ 5.1 \\ 0.4 \\ 0.3 \\ 1.4 \\ 1.6 \\ 0.2 \\ 0.5$

250°C at the rates of 5 and 10 deg/min; 2) Artemisia persica – from 40 to 150°C and 150 to 250°C at rates of 7 and 10 deg/min; 3) Artemisia leucodes – from 40 to 200°C and 200 to 250°C at rates of 5 and 10 deg/min; 4) Artemisia lehmanniana – from 35 to 150°C and 150 to 250°C at rates of 5 and 10 deg/min. The PMR spectrum was taken on a Tesla BS-567 A spectrometer with a working frequency of 100 MHz, solvent CDCl₃, at room temperature.

The EO was isolated by steam distillation [4], and its quantitative amount was determined by a standard method [11].

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