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THE COMPOSITION OF THE ESSENTIAL OILS OF Thymus marschallianus

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The essential oil of Thymus marschallianus was obtained by steam distillation of freshly-gathered flowering plants growing at various heights of the Trans-Ili Ala-Tau range (Kazakhstan). The number of components detected was 49, of which 35 were identified. No appreciable differences in the composition of the essential oil with a change in the height of growth of the plant were observed. The essential oil of Th. marschallianus and of a number of species growing in various countries have been compared.

Some species of thyme are widely used in folk medical practice as sudorific and diuretic agents and sedatives in diseases of the respiratory tracts, and also in the form of lotions and ointments in acute rheumatism and various skin diseases [1]. In scientific medicine, extracts of common thyme and wild thyme are used for the preparatin of pertussin. They are cultivated for this purpose in the Ukraine in Krasnodar krai, and in Bashkir.

In Kazakhstan, Thymus marschallianus Willd. grows on the steppe slopes of the hilly area and the foothills before the forest zone of the mountains, on the gravels of old river beds that are now steppe formations, and on heathergrass—sheep's fescue steppes [2]. In order to study the possibility of the practical use of this species and to determine its position in the genus, we have investigated two samples of the essential oil from populations growing in the foothills of the Trans-Ili Ala-Tau.

Preliminary GLC analysis revealed no differences in the qualitative component compositions of the essential oils of the two populations. The quantitative ratios of the components in the samples of oils differed little and they were therefore investigated together. On a chromatogram of the hydrocarbon fraction of the essential oil, not less than 24 substances were counted (Fig. 1). Terpene hydrocarbons were represented mainly by p-cymene, γ-terpinene, and α-pinene.

A comparison of the IR spectra and retention times of the sesquiterpene hydrocarbons with authentic samples permitted the identification of α-gurjunene, β-elemene, β-caryophyllene, himachalene, β-humulene, γ-cadinene, ar-curcumene, and β-cadinene.

The substance responsible for peak 23 could not be identified in this way. The constants of this hydrocarbon were n_D^{20} 1,4912; d_{20}^{20} 0,8745; $[\alpha]_D^{20}$ —76°. Its molecular weight was 204. According to its IR and mass spectra it contained an isopropylidene group (band at 1380 cm^{-1}; M − 43), a trisubstituted $>C=CH-$ double bond (810, 1670, 3058 cm^{-1}), and a $>C=CH_2$ methylene double bond (890, 1635, 3080 cm^{-1}). On hydrogenation over Adams platinum oxide in glacial acetic acid, three moles of hydrogen were added with the formation of a hydrocarbon having n_D^{20} 1.4553, with the IR spectrum of bisabolane. Consequently, one of the main components of Th. marschallianus is β-bisabolene, although the constants obtained for it differed somewhat from those given in the literature: d_4^{20} 0,8716, n 1,4912; $[\alpha]_D^{20}$ − 54° [6].

The oxygen containing compounds of the essential oil of Th. marschallianus (Fig. 2) were well separated on programmed columns with an ester phase.

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TABLE 1. Chemical Compositions of the Essential Oils of a Number of Thymus species

Component	Species and collection site								
	Th. trautvetter Klok. et Shost [8], **Azerbaidzhan**	Th. fominii [9], **Azerbaidzhan**	Th. eriphorus Ronn [10] **Azerbaidzhan**	Th. capitatus [11], **Greece**	Th. quinquecostatus Celak [12], **Japan**	Th. vulgare L. [13], **Egypt**	Th. vulgare L. [14], **Chile**	Th. Zygis L. [15], **Spain**	Th. marsch., **Kazakhstan**
α-Pinene	0,9	6,5	0,8	1,5	0,8	2,5	2,0	3,5	3,3
Camphene	0,2	0,7	0,1	0,1	0,8	2,7	0,1	6,0	0,9
β-Pinene	0,1		0,1		0,7	4,2	0,4	0,8	0,7
Sabinene	0 2		1,1						0 8
Δ^3-Carene						5,1			2,0
β-Myrcene	1,2		0,1			4,3			0 5
α-Terpinene									2,5
Limonene	2,1	6,8	2,0	0,3	0,8	3,4	1,5	0,8	0 6
1,8-Cineole						10,0	41,0		2,2
γ-Terpinene		8,2				11,0–18,0		8,9	19,3
p-Cymeme	0,6	10 9	0,8	0,1	4,9			30,3	22.4
Oct-1-en-1-ol					4 5				—
β-Caryophyllene	2,9	2,7	1,6		0 7				2,2
Caryophyllene oxide	2,5		2.1						—
β-Bisabolene					2,2				5.7
ar-Curcumeme									0 6
Linalool + Linalyl acetate	9,7		15,7	0.3		18,0–21.0		3,7	1,1
Camphor								3,5	0 2
Methyl ether of thymol		8,1			3,7 + 3,8				1 3
Terpinenol-4	9,4	8,1		3,3	8,8	Tr.	0,9	9,0	3,0
Borneol + bornyl acetate									1 5
α-Terpineol									0,6
Geraniol + geranyl acetate	16.9		11,5	0,4		Tr.			0 1
Bisabolol			3,1			0,8			0.5
Nerolidol									
Thymol	2,4	15.8	22,0	9,8	56,1	10,0–20,0	—	3,1	20.0
Carvacrol	—	15,8	—	67,0	8,3	8,0–14,5	43.0	22,2	1,5

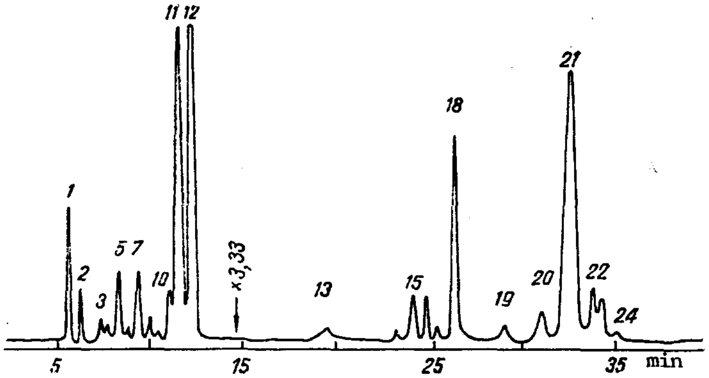

Fig. 1. Chromatogram of the hydrocarbon fraction of the essential oil of Th. marschallianus: 1) α-pinene; 2) camphene; 3) β-pinene; 4) sabinene; 5) Δ^3-carene; 6) β-myrcene; 7) α-terpinene; 8) limonene; 9) β-phellandrene; 10) 1,8-cineole; 11) γ-terpinene; 12) p-cymene; 15) α-gurjunene; 17) β-elemene; 18) β-caryophyllene; 19) himachalene; 20) β-humulene; 21) β-bisabolene; 22) ar-curcumeme; 23) β-cadinene.

Among all the substances that we isolated, one, eluted by petroleum ether on alumina after the sequiterpene hydrocarbons and isolated in this way in the pure state, had never been found previously. According to its IR spectrum, it was an aromatic compound (bands at

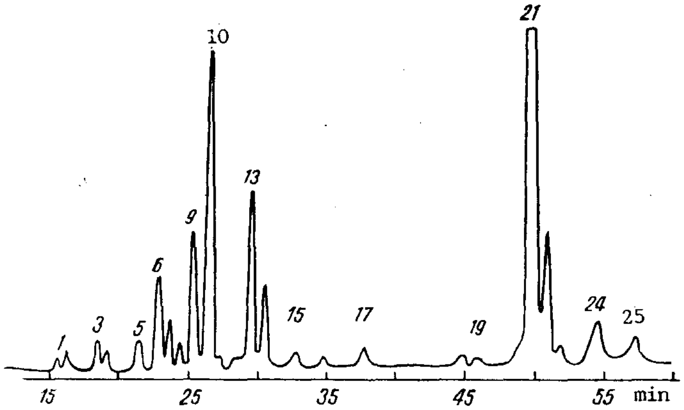

Fig. 2. Chromatogram of the oxygen-containing compounds of the essential oil of Th. marschallianus: 3) α-thujone; 4) β-thujone; 5) artemisia alcohol; 6) linalool; 8) camphor; 9) methyl ether of thymol; 10) terpinen-4-ol; 13) borneol; 14) α-terpineol; 15) nerol; 16) geraniol; 20) nerolidol; 21) thymol; 22) carvacrol; 25) farnesol.

1512, 1580, and 3058 cm^{-1}) the ring of which contained substituents in the para position (strong band at 818 cm^{-1} and a weak band at 890 cm^{-1} [3, p. 183]). The PMR spectra of the substance showed the presence in it of the signals of the protons of four methyl groups. One of them (2.14 ppm) was certainly attached to a benzene ring [7], and a another gave a three-proton singlet in a weaker field (3.37 ppm) and, consequently, was connected with an oxygen atom. The third substituent was an isopropyl group, giving a six-proton doublet with its center at 1.1 ppm and a one-proton multiplet with its center at 3.18 ppm and the same spin-spin coupling constant of $\sim$7 Hz.

There were five signals in the very weak field, of which four belonged to two protons adjacent to one another in a benzene ring (AB system, doublets with centers at 6.65 and 6.25 ppm, J $\sim$ 8 Hz), one of them interacting with a third proton present in the meta position. The signal of this last proton (6.2 ppm) and also the doublet of the proton interacting with it were appreciably broadened [7]. Thus, the PMR spectrm indicated that this substance was the methyl ether of thymol or carvacrol present in the oil. The independent synthesis of these ethers that we performed answered this question in favor of the first compound.

Other substances that were isolated and were identified from their constants and IR spectra were artemisia alcohol and its acetate, α-thujone, l-linalool, and its acetate, l-camphor, d-terpinen-4-ol, l-borneol, d-α-terpineol, nerol, geraniol, bornyl isobutyrate, thymol, and carvacrol.

Thus, in the essential oil of Th. marschallianus no less than 49 components have been detected of which 35 (including the main ones) have been identified.

Table 1 compares the results of our investigation and the chemical compositions of the essential oils of some of the most fully studied species of thyme. It can be seen from this that those compounds common for the genus and also substances characteristic for each species are synthesized in the plants of the individual thyme species. The constant compounds are thymol, carvacrol, α-pinene, limonene, p-cymene, and γ-terpinene, the plants of some species synthesizing mainly thymol [12, 16, 17] and those of other species mainly carvacrol [10, 11, 18]. Only the essential oil of Th. caespititus from Spain [21] differs by the practical absence of phenols and by the presence of 68% of α-terpineol and 11% of borneol. So far as concerns the essential oil of Th. marschallianus, it is close in composition to the essential oils of Th. serpyllum and Th. vulgare L. [22] and can be used for the same purpose as them.

EXPERIMENTAL

One sample of essential oil was obtained in the upper reaches of the Turgen'-Tau at a height of 2000 m above sea level, and the other 120 km to the west in the environs of the village of Pervoe Maya, Alma-eta province, at a height of 1000 m. The plants were present in the end-of-flowering phase. The essential oil was obtained by distilling the freshly cut plants with steam at a pressure of 3-5 atm.

The first sample, obtained with a yield of 0.28%, had n_D^{20} 1.4857; d_{20}^{20} 0.8898; $[\alpha]_D^{20}$ $-6.9°$ acid No. 1.15; ester No. 13.8. The other sample had n_D^{20} 1.4873; d_{20}^{20} 0.8967; $[\alpha]_D^{20}$ $-4.9°$; acid No. 1.6; ester No. 18; yield 0.31%. The essential oil had a yellow-green color and possessed a pleasent thymol-linalool odor.

The essential oil was first separated chemically and by vacuum fractionation into acidic, phenolic, and low-boiling and high-boiling fractions. The last-mentioned fraction was separated by chromatography on alumina into hydrocarbon and oxygen-containing subfractions. In this way, 385 g of essential oil was separated into fractions of terpene hydrocarbons boiling at 54-74°C/20 mm (57%), sesquiterpene hydrocarbons (7%), oxygen-containing terpenes (11%), phenols (22%), and acids (0.03%).

The substances were isolated from the appropriate fractions with the aid of preparative GLC and were identified by comparing their constants and IR spectra with our own and literature figures [3-5]. The components of the essential oil present in small amounts were identified with the aid of GLC by comparing the retention times and those of authentic specimens.

SUMMARY

The essential oils of two populations of Thymus marschallanius Willd. growing at different heights in the Trans-Ili Ala-Tau have been investigated. A total 49 components were detected, of which 35 were identified. No appreciable differences in the compositions of the essential oils with a change in height were detected.

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