COUMARINS OF *Haplophyllum bungei*

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We have studied the coumarin composition of the epigeal part of *Haplophyllum bungei* Trautv., family Rutaceae, collected in Turkmenia in the environs of the town of Mary.

The comminuted raw material was treated with chloroform and the concentrated extract was separated chromatographically on a column of KSK silica gel using as the eluting solvents petroleum ether and mixtures of it with chloroform.

This gave three individual compounds. Substance (I), $C_{15}H_{16}O_3$, with mp 84-85°C, on oxidation with chromium trioxide, gave ostholic acid with mp 254-255°C.

On the basis of its chemical reactions and IR and NMR spectra, it has been established the compound (I) is osthole [1].

From its composition ($C_{15}H_{16}O_4$), melting point (81-82°C), and IR and PMR spectra, substance (II) corresponds to the known coumarin 7-(3',3'-dimethylallyloxy)-6-methoxycoumarin [2].

Substance (III) with the composition $C_{10}H_8O_4$, mp 226-227°C, corresponds to 5-hydroxy-7-methoxycoumarin. A proof of the structure was the preparation of the known natural compound limetin (5,7-dimethoxycoumarin), $C_{11}H_{10}O_4$, mp 144-146°C [3, 4], on methylating substance (III).

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COUMARINS OF *Haplophyllum schelkovnikovii*

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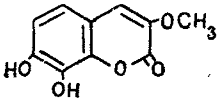
We give the results of a study of the coumarin composition of *Haplophyllum schelkovnikovii* Grossh. collected at two growth sites (the villages of Badamly and Ganza, Nakhichevan ASSR) in the fruit-bearing phase. The resin obtained from the samples of plants investigated by successive extraction with chloroform and methanol was chromatographed on a column of alumina (activity grade IV). Elution was performed with petroleum ether, mixtures of petroleum ether and chloroform (10:5, 5:1, 2:1), and chloroform. In total, six individual compounds (I-VI) possessing the properties of coumarins were obtained (Table 1).

It can be seen from Table 1 that the samples investigated differ in their sets of coumarins, which is obviously due to the climatic conditions of growth.

Of the compounds isolated, (I) corresponds to a known coumarin [1], and (II)-(VI) do not correspond in their physicochemical constants to known coumarins.

The structure of (II) was determined from its PMR spectrum which contains in the weak field signals with chemical shifts of 7.45 ppm (singlet, 1 H) and 7.41 and 6.69 ppm (doublets, J = 8.5 Hz, 1 H each) due to the protons in positions 4, 5, and 6 of the coumarin ring. In the region of aliphatic protons there is a three-proton singlet at 3.83 ppm, which shows the presence of one methoxy group in a molecule of (II). On the basis of the facts given, and also of a comparison of the PMR spectra of (I) and (II), we suggest the following most probable structure for the compound under investigation:



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The study of the structures of compounds (III-VI) is continuing. In addition to coumarin derivatives, we have isolated and identified β-sitosterol from the plant under study.

The IR spectra were taken on a UR-20 spectrometer (in paraffin oil), the PMR spectra on a Brüker HX-90 spectrometer (in deuteromethanol, 0 — TMS). The melting points were determined on a Kofler block.

TABLE 1

Compound	Site of collecting the plant		mp, °C	R_f (fluorescence in UV light) in the $CHCl_3$ system, Al_2O_3 activity grade III.	IR spectra, ν, cm^{-1}		
	Badamly	Ganza			CO of an α-pyrone	–CH=CH bond	OH group
I	+	—	151—152	0,31 (blue)	1720	1515 1580 1625	3430
II	+	—	221—222	0,10 (blue)	1700	1530 1620	3500
III	+	+	153—154	0,71 (blue)	1755	1520 1605 1640	
IV	—	+	143—145	0,44 (blue)	1750	1510 1615 1650	
V	+	+	149—150	0,16 (yellow)	1700 1715	1500 1610 1625	3290 3480
VI	+	—	111—112	0,30 (yellow)	1690	1510 1585 1630	3310

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A SESQUITERPENE ALCOHOL FROM *Ferula karatavica*

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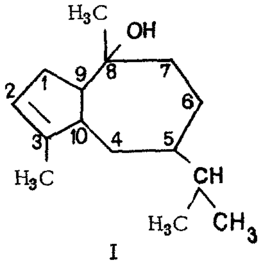
As the result of the chromatographic separation of the total extractive substances of the roots of *Ferula karatavica* on neutral alumina (activity grade IV), we have isolated a compound not described in the literature with the composition $C_{15}H_{26}O$, M^+ with m/e 222, mp 136-137°C (petroleum ether), which we have called karatavin. Its IR spectrum contains absorption bands at 3320 cm^{-1} (hydroxy group) and 1375 and 1170 cm^{-1} (isopropyl group).

The NMR spectrum of karatavin (Varian JNM-4H 100 MHz, CCl_4, 0 — TMS, δ scale) contains the signals of protons at 0.88 and 0.79 ppm ($HC(CH_3)_2$, 3 H each, doublet, J = 7 Hz), 1.21 ppm ($HO-C-CH_3$, 3 H, singlet), 1.62 ppm ($C{=}C-CH_3$, 3 H, singlet), and 5.57 ppm (=CH, 1 H, doublet, J = 4 Hz).

According to its composition and IR spectrum, the karatavin molecule contains an alcoholic group which does not undergo oxidation or acetylation. The PMR spectrum of this compound lacks the signal of a proton geminal to a hydroxy group. Consequently, the alcoholic group is tertiary.

A further comparative study of the spectral characteristics of karatavin with those of guaiol [1-3] shows that these compounds apparently have identical carbon skeletons but differ from one another in the positions of the double bond and of the tertiary alcohol group. On the basis of these facts we propose for karatavin the structure of 8-hydroxyguai-2-ene (I) or of 3-hydroxyguai-7-ene (II). Formula (I) is the more probable.



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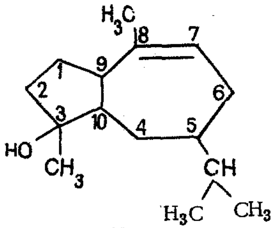

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