

In a study of the chemical composition of the epigeal part of *Haplophyllum bungei* Trautv., collected in the environs of the town of Ali-Bairamly, Turkmen SSR, we have isolated five substances in the individual form: (I), mp 83-84°C; (II), mp 243-245°C; (III), mp 204-205°C; (IV), mp 188-190°C; and (V), mp 108-109°C.

A comparison of our results with those obtained previously [1] in an investigation of the same plant but collected in the environs of the town of Mary in the same phase shows that these samples differed greatly from one another with respect to their sets of coumarins.

In the present communication we give the results of a study of the last three substances (III-V).

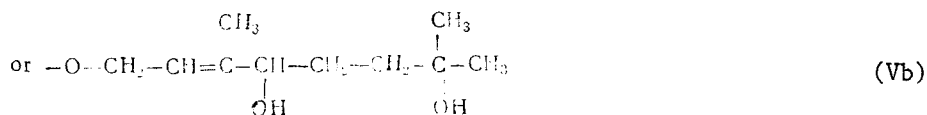
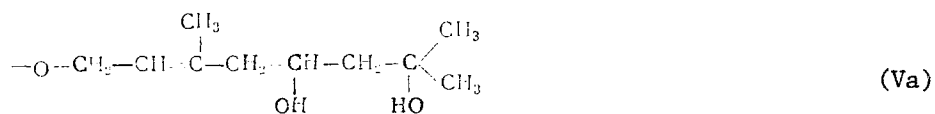
From their physicochemical constants and IR and PMR spectra, substances (III) and (IV) correspond to known coumarins - scopoletin and isoscopoletin.

Substance (V), with the composition $C_{20}H_{26}O_6$, mp 108-109°C, $[\alpha]_D^{20} +42.8^\circ$ (c 3.55; ethanol) proved to be new, not described in the literature. We have called it bungeidiol.

The IR spectrum of (V) shows absorption bands at (cm^{-1}) 3480 (OH group), 1725 (C=O of an α -pyrone), 1610, 1585, and 1520 ($-CH=CH-$ bond in an aromatic ring).

The PMR spectrum of (V) contains, in addition to the signals of the protons of 6,7-disubstituted coumarin nucleus the signals of the protons of three methyl groups, one of them at a double bond (1.72 ppm, singlet, 3 H) and two at tertiary carbon atoms bearing hydroxy groups (1.05 and 1.14 ppm, singlets, 3 H each), of a methoxy group (3.84 ppm, singlet, 3 H), of a proton geminal to a hydroxy group (3.27 ppm, quartet, $J_1 = 8$ Hz, $J_2 = 2$ Hz), and of a $Ar-O-CH_2-CH=$ grouping (4.63 ppm, doublet, $J = 7$ Hz, 5.47 ppm, and triplet, $J = 7$ Hz). The signals of the protons of two methylene groups appear at 2.20 ppm (4 H) in the form of a multiplet.

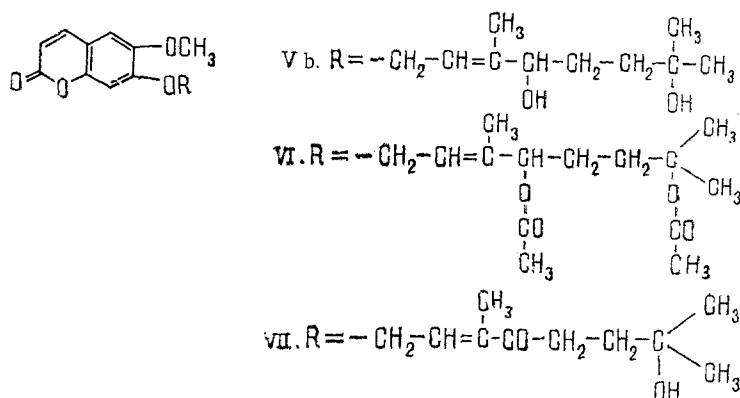
Thus, it follows from the facts presented that one of the substituents is a methoxy group which occupies position 6, since the treatment of compound (V) with 10% H_2SO_4 formed scopoletin (III), identified from its IR and PMR spectra. Consequently, the second substituent consisting of $C_{10}H_{10}O_3$ and containing two hydroxy groups is located in position 7 and has the structure



The presence of two hydroxy groups in the molecule of (V) was shown by the formation of a diacetyl derivative (VI) with the composition $C_{24}H_{30}O_3$, mp 120-121°C, the IR spectrum of which contained no absorption bands of hydroxy groups and the PMR spectrum of which contained the signals of the protons of two acetyl groups at 1.95 and 2.08 ppm (singlets, 3 H each) while, as was to be expected, the signal of the methine proton geminal to an acetoxy group underwent a very pronounced paramagnetic shift (1.91 ppm) and appeared at 5.18 ppm, which is obviously due to the presence of a double bond in the vicinal position. In the case of structure (Va), the value of this shift should not exceed 1.0-1.2 ppm. This permits the unambiguous choice of structure (Vb) for the side chain of the compound under investigation and

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the proposal for the compound as a whole of the structure of 7-(3',7'-dimethyl-4',7'-dihydroxyoct-2'-enyloxy)-6-methoxycoumarin (Vb), which was also confirmed by the results of the oxidation of (V) with chromium trioxide in acetone. This formed the liquid ketone (VII) with the composition $C_{20}H_{24}O_6$.



IR spectra were recorded on a UR-20 spectrometer (in paraffin oil), and PMR spectra on an HX-270 spectrometer (in CDCl_3 , 0 - TMS), and the purity of the compounds studied was checked on Silufol plates in the benzene-acetone (10:1 and 10:3) systems. Melting points were determined on a Kofler block.

LITERATURE CITED

1. N. F. Gashimov and N. O. Orazmukhamedova, *Khim. Prirod. Soedin.*, 653 (1978).

COUMARINS OF *Haplophyllum dauricum*.

5,7-DIHYDROXYCOUMARIN AND ITS C-GLUCOSIDE

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Continuing a study of the coumarins of *Haplophyllum dauricum* (L.) G. Don., growing in the territory of Mongolia [1, 2], we have isolated two more coumarins.

Coumarin (I) with the composition $C_9H_6O_4$, M^+ 178, mp 283-285°C (decomp.), $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}) 3330 (OH), 1666 ($\text{C}=\text{O}$ of an α -pyrone), 1600, 1560 ($\text{C}=\text{C}$ bond) was isolated from an ethyl acetate fraction of the roots [2]. It gave a positive reaction with FeCl_3 solution, and its UV spectrum ($\lambda_{\text{max}}^{\text{ethanol}}$, nm: 223 sh., 253 sh., 261, 334) is characteristic for 5,7-dihydroxycoumarins [3]. The PMR spectrum of (I) shows the signals of an H-3 proton (6.02 ppm, d, 10 Hz) and an H-4 proton (8.09 ppm, d, 10 Hz) and a broadened two-proton singlet at 6.46 ppm, d. The features of the mass and PMR spectra show the presence in (I) of two phenolic hydroxy groups. The chemical shift of the H-4 proton shows that one of these hydroxy groups is present at C-5 [4, 5]. The ortho arrangement of the hydroxy groups is excluded on the basis of the absence of bathochromic shift in UV spectrum on the addition of a solution of AlCl_3 [6].

On the basis of the facts presented, (I) must have the structure of 5,7-dihydroxycoumarin. This was confirmed by the formation of limettin (5,7-dimethoxycoumarin) [7] when it was methylated with diazomethane. 5,7-Dihydroxycoumarin has been synthesized previously [7], but we are the first to have found it as a natural substance.

The second coumarin (daurosine D), with the composition $C_{15}H_{16}O_9$, (II), mp 214-215°C, $[\alpha]_D^{22} +108.6^\circ$ (c 0.35; pyridine), $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}) 3400 (OH), 1720 ($\text{C}=\text{O}$ of an α -pyrone), and 1610 ($\text{C}=\text{C}$ bond), was isolated from a butanolic fraction of the epigeal part [2]. UV spectrum of

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