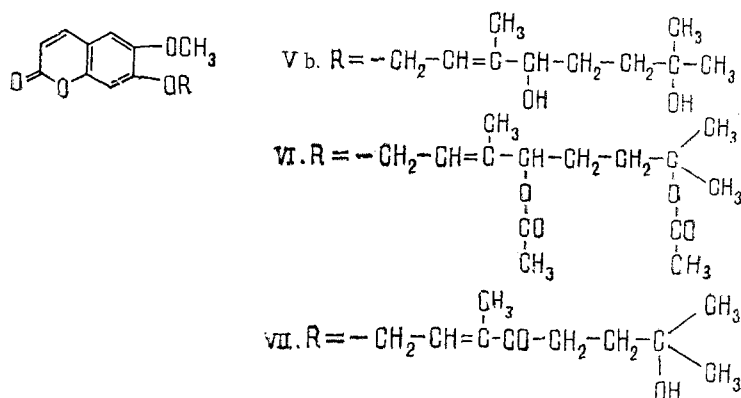


the proposal for the compound as a whole of the structure of 7-(3',7'-dimethyl-4',7'-dihydroxyoct-2'-enyloxy)-6-methoxycoumarin (Vb), which was also confirmed by the results of the oxidation of (V) with chromium trioxide in acetone. This formed the liquid ketone (VII) with the composition  $C_{20}H_{24}O_6$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



IR spectra were recorded on a UR-20 spectrometer (in paraffin oil), and PMR spectra on an HX-270 spectrometer (in  $\text{CDCl}_3$ , 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.

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#### COUMARINS OF *Haplophyllum dauricum*.

##### 5,7-DIHYDROXYCOUMARIN AND ITS C-GLUCOSIDE

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UDC 547.15/17:582.89

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.),  $\nu_{\text{max}}^{\text{KBr}}$  ( $\text{cm}^{-1}$ ) 3330 (OH), 1666 ( $\text{C}=\text{O}$  of an  $\alpha$ -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  $\text{FeCl}_3$  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  $\text{AlCl}_3$  [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.

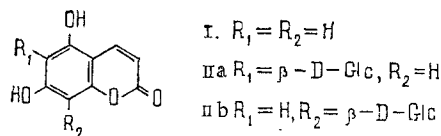
The second coumarin (daurosides D), with the composition  $C_{15}H_{16}O_9$  (II), mp 214–215°C,  $[\alpha]_D^{22} +108.6^\circ$  (c 0.35; pyridine),  $\nu_{\text{max}}^{\text{KBr}}$  ( $\text{cm}^{-1}$ ) 3400 (OH), 1720 ( $\text{C}=\text{O}$  of an  $\alpha$ -pyrone), and 1610 ( $\text{C}=\text{C}$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

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from *Khimiya Prirodnikh Soedinenii*, No. 5, pp. 650–651, September–October, 1982. Original article submitted April 27, 1982.

(II):  $\lambda_{\max}$  (ethanol, nm): 225, 253 sh., 262, 333 ( $\log \epsilon$  4.28, 3.99, 3.99, 4.22) is almost identical with that of (I). The PMR spectrum of dauroside D ( $\text{Py-d}_5$ ) shows the signals of an H-3 proton (6.04 ppm, d, 10 Hz), an H-4 proton (7.90 ppm, d, 10 Hz), and one aromatic proton (6.46 ppm, s). The presence in the spectrum of a signal of an anomeric proton (5.66 ppm, d, 9 Hz) and a group of signals in the 3.82–4.58 ppm region (6 H) shows that (II) is a monoglycoside. The acetylation of (II) with acetic anhydride in the presence of pyridine led to a hexaacetate with mp 202–204°C (III). The PMR spectrum ( $\text{CDCl}_3$ ) of this hexaacetate showed the signals of the methyl protons of four aliphatic (1.60, 1.83, 1.85, 1.87 ppm) and two aromatic (2.21 and 2.30 ppm) acetyl groups. Consequently, dauroside D contains two phenolic hydroxy groups.

The acid hydrolysis of (II) with 5%  $\text{H}_2\text{SO}_4$  for 6 h proved unsuccessful. This fact, and also the value of the SSCC of the anomeric proton [8] suggested that (II) is a coumarin C-glycoside. In actual fact, the mass spectrum of (II) is characteristic for C-glycosides [9]. The spectrum lacks the peak of the molecular ion but it has strong peaks of ions  $m/z$  322 ( $M - \text{H}_2\text{O}$ ), 304 ( $M - 2\text{H}_2\text{O}$ ), 286 ( $M - 3\text{H}_2\text{O}$ ), 231, 230, 206, 203, 191, 178, and others. The hydrolysis of (II) with Kiliani's mixture led to D-glucose, with a minor amount of D-arabinose. From a mixture of substances of coumarin nature, 5,7-dihydroxycoumarin was isolated by preparative TLC and identified. Thus, dauroside D is a C-glucoside of (I).

According to the PMR spectrum, the C-3 and C-4 positions of the coumarin nucleus are not substituted. Consequently, the glucose residue is present at either C-6 or C-8, and dauroside D has the structure (IIa) or (IIb).



The SSCC value of the anomeric proton ( $J_{1',2'} = 9 \text{ Hz}$ ) shows the  $\beta$ -glucopyranose form of the sugar moiety [8]. C-Glycosylation is frequently found among flavonoids and xanthenes [10], but no coumarin C-glycosides have been found previously: dauroside D is the first coumarin C-glycoside.

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