A NEW COUMARIN PEDICELLONE FROM Haplophyllum pedicellatum

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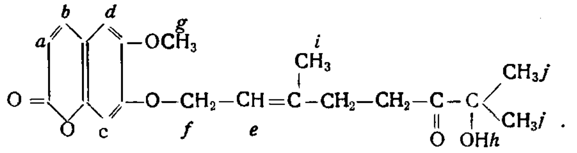
From Haplophyllum pedicellatum Juss., in addition to scopoletin, 6-methoxymarmin, and 7-geranyloxy-6-methoxycoumarin, we have isolated a new, optically inactive compound, $C_{20}H_{24}O_6$ (I), with mp 90-92°C (chloroform/petroleum ether), which we have called pedicellone. On a paper chromatogram (with formamide as the stationary phase and benzene as the mobile phase), substance (I) gave a spot with R_f 0.71 (blue fluorescence in UV light). In its chemical compositions and properties, (I), which contains a hydroxy group and a keto group, does not correspond to any known coumarin.

The UV spectrum of (I) shows absorption maxima characteristic for 6,7-disubstituted coumarins: λ_{max} 205, 230, 244, 296, 346 nm (log ε 3.63, 4.23, 3.84, 3.77, 4.10, respectively); the IR spectrum of (I) shows absorption bands at (cm^{-1}) 3450 (hydroxy group), 1718 (keto group), 1695 (C=O of a δ-lactone), 1620, 1570, and 1520 (aromatic system).

Pedicellone is readily hydrolyzed by acids. Acid hydrolysis forms scopoletin, which was identified by means of its IR spectrum and the absence of a depression of the melting point of a mixture with an authentic sample. The reduction of (I) with sodium tetrahydroborate gave a diol with mp 119-120°C the IR spectrum of which coincided with that of 6-methoxy-7-[(6,7-dihydroxy-3,7-dimethyloct-2-enyl)oxy]coumarin (6-methoxymarmin). A mixture with an authentic sample gave no depression of the melting point. This shows that, in contrast to 6-methoxymarmin, pedicellone contains a keto group capable of being reduced with sodium tetrahydroborate to an OH group. To confirm the proposed structure of (I), 6-methoxymarmin was oxidized with chromium trioxide in acetic acid. From the oxidation products a substance was isolated with mp 89-90°C the IR spectrum of which was identical with that of pedicellone. A mixture of the oxidation products and (I) melted without depression. On the basis of the above facts, the following structure has been proposed for pedicellone:



Structure (I) is confirmed by the NMR spectrum (Fig. 1), which was taken by V. A. Gindin on a Varian HA 100-MHz spectrometer in $CDCl_3$, the chemical shifts being given on the δ scale relative to the signal of HMDS. The doublets *a* and b (6.22 ppm, 1 H, and 7.60 ppm, 1 H, J 10 Hz) relate to the protons in positions 3 and 4 of the coumarin nucleus. The singlets c (6.82, 1 H) and d (6.88, 1 H) are due to the protons at C_8 and C_5, respectively. The presence of chemical shifts of the olefinic proton e (5.50, 1 H) and of the protons i of a methylvinyl group (1.76, 3 H) confirms the presence in (I) of a secondary-tertiary double bond. The doublet *f* (4.64, 2 H, J 6 Hz) is assigned to the methylene group of the $-O-CH_2-CH=$ fragment through which the connection of scopoletin with the aliphatic chain is effected. The signal j (1.36, 6 H) corresponds to the protons of the gem-dimethyl groups. The singlet signal h of the proton of the hydroxy group appears at 3.64 ppm (1H). The downfield shift of the signal as compared with the signals of the tertiary hydroxyls of known coumarins [1] shows the possibility of the formation of a hydrogen bond [2]. This

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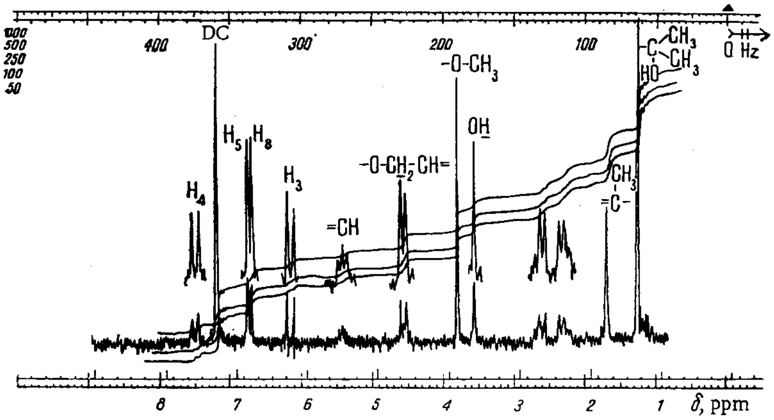

Fig. 1. NMR spectrum of pedicellone.

is evidence in favor of the vicinal location of the OH and keto groups. The absence of the signal of a proton present in the geminal position to the hydroxy group confirms its tertiary nature. The singlet g (3.90, 3 H) corresponds to a methoxy group.

On the basis of the facts presented concerning the products of chemical transformation and UV, IR, and NMR spectra, the structure of 7-[(7-hydroxy-3,7-dimethyl-6-oxooct-2-enyl)oxy]-6-methoxycoumarin is proposed for pedicellone.

The coumarin derivatives that we have isolated from Haplophyllum pedicellatum Juss. [3, 4] are biogenetically connected with one another. The change in their structure takes place through the stage of prenylation, hydroxylation, and oxidation in the sequence of changes 7-hydroxy-6-methoxycoumarin (scopoletin) → 7-geranyloxy-6-methoxycoumarin → 7-[6,7-dihydroxy-3,7-dimethyloct-2-enyl)oxy]-6-methoxycoumarin (6-methoxymarmin) → 7-[(7-hydroxy-3,7-dimethyl-6-oxooct-2-enyl)oxy]-6-methoxycoumarin (pedicellone).

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