DIVERSOSIDE – A NEW COUMARIN FROM THE ROOTS OF Ferula diversivitata

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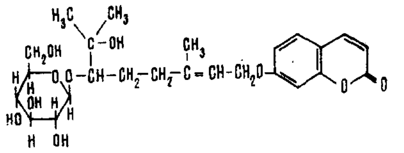
In a study of the coumarins of the roots of Ferula diversivitata (Rgl. et Schmalh), from the water-soluble part of a methanolic extract, by chromatography, we have isolated a lactone with the composition $C_{25}H_{34}O_{10}$ with mp 154-155°C (from aqueous ethanol), $[\alpha]_D^{20}+10°$ (c 1.0; ethanol), readily soluble in ethanol, sparingly soluble in water, and insoluble in organic solvents. On acid hydrolysis, the substance which we have named diversoside was split into umbelliferone and one molecule of D-glucose [1]. The maxima in the UV spectrum [244, 255, and 327 nm (log ε 4.01, 3.86, and 4.50)] showed the presence in diversoside of the chromophore of 7-hydroxycoumarin. Its IR spectrum has absorption bands at (cm^{-1}) 1735 (α-pyrone carbonyl), 1620, 1562, and 1515 (aromatic nucleus), 3250-3600 (hydroxy groups), and 840 (trisubstituted double bond). In the NMR spectrum (CF_3COOH) of diversoside, in the weak field there are the signals corresponding to a 7-monohydroxy-substituted coumarin [2]. In the strong-field region there are three-proton singlets at 0.90 and 0.95 ppm (methyls on a quaternary carbon atom) and at 1.20 ppm (3 H) (methyl group on a double bond), and also a doublet at 4.50 ppm, J = 6.0 Hz (2 H) (methylene protons in a $Ar-OC\underline{H}_2-CH$ grouping), and a triplet at 5.02 ppm, J = 6.0 Hz (1 H) (olefinic proton).

A multiplet in the 3.2-3.9 ppm region (7 H) is due to the protons of a sugar residue and of a methine proton present in the geminal position to the glucose. A poorly resolved doublet at 4.30 ppm, J = 9 Hz (1 H) is due to the β-anomeric proton of D-glucose. The enzymatic hydrolysis of diversoside gave us the aglycone with the composition $C_{19}H_{24}O_5$, mp 123-124°C (yield ≈68%), M^+ 332. It was identified by its melting point and NMR and mass spectra as marmin [3, 4].

The acetylation of diversoside with acetic anhydride in the presence of sodium acetate gave a substance $C_{29}H_{42}O_{14}$ with mp 121-122°C in the 2.1 ppm region of the NMR spectrum (in $CDCl_3$) of which the signals of four acetyl groups appeared; the positions of the signal of the proton present in the geminal position to the glucose were the same in the tetraacetate of the glycoside and in the aglycone – quartet at 3.2 ppm, $J_1 = 9$ Hz, $J_2 = 4$ Hz. This shows that the marmin is glucosidated at the secondary hydroxyl.

The presence in the IR spectrum of the glycoside of absorption at 900 cm^{-1} shows that the glucose is bound by a β-glycosidic bond, and bands at 1020, 1040, and 1085 cm^{-1} show that it has the pyranose form. The latter is in harmony with the value of the molecular rotation difference between the glycoside and the aglycone.

The facts given permit the conclusion that diversoside has the following structure:



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