STRUCTURE OF THE COUMARIN REOSELIN

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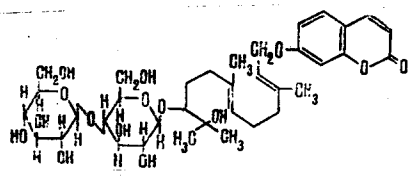
On studying the coumarin composition of the roots of Ferula pseudooreoselinum (Rgl. et Schmalh.) growing in the region of the village of Zarkent, Tashkent oblast, by chromatography we isolated a lactone with the composition $C_{36}H_{52}O_{15}$, mp 155-156°C, $[\alpha]_D^{20}$ −22° (c 1.0; ethanol). On the basis of its physicochemical properties and the products of acidic and enzymatic hydrolysis, it was identified as the glycosylated terpenoid coumarin reoselin [1]. The structure of the terpenoid part of the molecule of reoselin and the position of the sugar residues were not established and the spectral characteristics of the compound were not given in the previous paper, and we therefore proceeded to study them.

According to the literature [1], reoselin is an ether of umbelliferone and a sesquiterpene dihydroxy ketone $C_{15}H_{28}O_3$ glycosylated with glucose and fructose. The maxima in the UV spectrum [244, 255, and 327 nm (log ε 3.62, 3.55, and 4.17, respectively)] show the presence in reoselin of the chromophore of a 7-hydroxycoumarin. The signals in the NMR spectrum (doublets at 7.68 and 6.18 ppm, J = 10 Hz, quartet at 6.85 ppm, J_1 = 9 Hz, J_2 = 2.5 Hz, doublets at 7.37 ppm, J = 9 Hz, and 6.88 ppm, J = 2.5 Hz) show that reoselin is a 7-monohydroxy-substituted coumarin. In the strong-field region there are three-proton singlets at 1.27 and 1.31 ppm (methyls on a quaternary carbon atom), and 1.61 and 1.50 ppm (methyls on a double bond), and also a doublet at 4.57 ppm, J = 6 Hz (2 H) – methylene protons in an $Ar-OCH_2-CH-C$ grouping. A multiplet in the 3.60-5.03-ppm region (14 H) is due to the protons of a sugar residue. The enzymatic and acid hydrolysis of reoselin gave us the aglycone, with the composition $C_{24}H_{32}O_5$, mp 60-61°C (yield ~ 55%), which formed an acetonide, $C_{27}H_{36}O_5$, mp 53-54°C. It was identified by IR, NMR, UV, and mass spectra as karatavicinol, isolated previously from Ferula karatavica [2]. In addition to the aglycone (yield ~ 50%), D-glucose was obtained. In the NMR spectrum of the aglycone, the signals of the protons of the sugar residue were absent, but a quartet appeared at 3.49 ppm, J_1 = 9 Hz, J_2 = 2.5 Hz, corresponding to a hemihydroxyl methine proton. This unambiguously shows that reoselin is a bioside at a secondary hydroxyl.

The NMR spectrum of the glycoside shows doublets at 5.03 and 4.95 ppm, J = 8 Hz (1 H each) due to the β-anomeric protons of two D-glucose residues. The presence of the β configuration is also confirmed by the multiplicity of the signal of the H-2 and H'-2 protons of the sugar residues in the spectrum of the octacetate, which consists of a broadened triplet in the 4.85 ppm region with J = 8 Hz (2 H) [3] and by the calculated value of M_D according to Klyne. Thus, the D-glucose residues are connected to one another and to the aglycone by β-glycosidic bonds. Absorption bands at 1085, 1040, and 1100 cm^{-1} in the IR spectrum of the glycoside show that the D-glucose residues are present in the pyranose form [4]. By the exhaustive methylation of reoselin with subsequent hydrolysis we obtained 2,3,6-tri-O-methylglucose and 2,3,4,6-tetra-O-methylglucose, which were identified by TLC and by paper chromatography [5]. Consequently, the sugar residues are connected to one another in the 1 → 4 position and reoselin is a biocide of karatavicinol with the following structure:



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The NMR spectra were taken on a JNM-4H-100/100 MHz instrument in pyridine-d on the standard HMDS scale, the UV spectra on a Hitachi spectrometer, and the IR spectra on a UR-10 instrument (KBr).

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