HYPOLAETIN 7-GLUCOSIDE FROM *Caryopteris mongolica*

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The epigeal part of Caryopteris mongolica Bunge (family Verbenaceae) collected in the flowering phase was extracted with petroleum ether and then with 70% aqueous methanol. The methanol was distilled off and the residue was extracted with ethyl acetate. After the elimination of the solvent, the resinous residue was chromatographed on polyamide. The column was washed with water and then 40% aqueous methanol eluted a yellow crystalline substance which was recrystallized from acetone–water (7:3). Yield 0.1%, composition $C_{21}H_{20}O_{12} \cdot H_2O$, mp 264-265°C, $[\alpha]_D^{20} -632°$ (c 0.19; formamide), R_f 0.43 (Leningrad "M" ["slow"] paper, 60% AcOH). UV spectrum: MeOH 258 (shoulder), 277, 301, 344 nm (log ε 4.27, 4.29, 4.19, 4.29); NaOAc 258, 277, 337; NaOAc + H_3BO_3 267, 380; NaOMe 266, 345, 394; $ZrOCl_2$ 267, 310, 436; $ZrOCl_2$ + citric acid 268, 370 mm. In the mass spectrum there was a peak with M^+302, corresponding to the aglycone $C_{15}H_{10}O_7$.

Enzymatic hydrolysis (enzyme of the grape snail) gave glucose and the aglycone hypolaetin (3',4',5,-7,8-pentahydroxyflavone), $C_{15}H_{10}O_7$, mp 287-291°C, R_f 0.39 (under the same conditions). The UV spectrum shows the addition of the sugar to the 7-OH group of the aglycone (NaOAc 290 nm). Attempts at acid hydrolysis led to the formation of a mixture of aglycones with R_f 0.39 and 0.32, since on heating in an acid medium hypolaetin is readily converted into the more stable 6-hydroxy isomer (3',4',5,6,7-pentahydroxyflavone) [1].

The NMR spectrum of the glycoside after trimethylsilylation [2] (100 MHz, CCl_4, TMS) contained signals at (δ, ppm): 7.42 (double doublet, J = 2.5, J_1 = 8 Hz, H-6'), 7.33 (doublet, J = 2.5 Hz, H-2'), 6.84 (doublet, J = 8 Hz, H-5'), 6.30 (singlet, H-3), 6.26 (singlet, H-6), 4.95 (doublet, J = 7 Hz, H-1 of β-D-glucose in position 7), 3.1-3.7 (multiplet, the six protons of glucose). The NMR spectrum of the glycoside taken in dimethyl sulfoxide had a singlet at 12.35 ppm, which is characteristic for a 5-OH group, and singlets of the H-3 and H-6 protons at δ 6.66 and 6.62, respectively.

Acetylation of the glycoside led to the octaacetate $C_{37}H_{36}O_{20} \cdot H_2O$ with mp 229-233°C, in the NMR spectrum of which there were the signals of four aliphatic and four aromatic acetyl groups. The signals of the H-3 and H-6 protons appeared in the acetate at δ 6.53 and 6.76, and the correctness of their assignment in this compound and in the glycoside was confirmed by an analysis of literature data [2-7]. The evidence given indicates that the compound studied is 3',4',5,7,8-pentahydroxyflavone 7-O-β-D-glucoside, which has been isolated previously from Juniperus macropoda [7, 8].

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