PRIMFLASIDE: A NEW FLAVONOL GLYCOSIDE FROM PRIMULA TURKESTANICA

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From a methanolic extract of the leaves of Primula turkestanica by chromatography on a polyamide sorbent we have isolated a flavonoid glycoside (0.17%) with the composition $C_{31}H_{36}O_{21} \cdot H_2O$, mp 193–195° C (Kofler block), $[\alpha]_D$ −100° (c 0.2, dimethylformamide), mol wt 765 (ebullioscopically); the acetate has mp 123–126° C, R_f 0.50 [butan-1-ol–acetic acid–water (4 : 1 : 5)], 0.54 [ethyl acetate–formic acid–water (10 : 2 : 3)], 0.55 (15% solution of acetic acid).

The substituents in the glycoside, which we have named "primflaside," are present in positions 3, 5, 7, 3', and 4'. In the NMR spectrum of the silylated glycoside [1] a signal at δ 7.55 ppm corresponds to the H-2' and H-6' protons, a doublet with δ 6.88 ppm to H-5', a signal with δ 6.38 ppm to H-8, a singlet at 6.11 ppm to H-6, a doublet at δ 5.65 ppm to H-1 of glucose, and a multiplet with δ 3.43 ppm to the signals of the protons of the carbohydrate part of the glycoside.

The substituents in positions 5, 7, 3', and 4' are free hydroxyl groups: $\lambda_{max}^{C_2H_5OH}$ 259, 363; $\lambda_{max}^{CH_3COONa}$ 262, 373; $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 267, 387; $\lambda_{max}^{AlCl_3}$ 272, 405; $\lambda_{max}^{C_2H_5ONa}$ 262, 405 mμ.

The acid hydrolysis of primflaside with 5% H_2SO_4 gave 42.7% of an aglycone $C_{15}H_{10}O_7$ with mp 305–310° C, R_f 0.62 [benzene–ethyl acetate–acetic acid–formamide (24.5 : 73.5 : 2)], mol wt 302 (mass spectrometry); acetate with mp 195–197° C. The constants of the aglycone correspond to those of quercetin, which was confirmed by the results of a direct comparison with an authentic sample.

The hydrolysate after the separation of the aglycone was shown by paper chromatography to contain D-glucose and L-arabinose (1 : 2).

The oxidation of primflaside with hydrogen peroxide [2] and subsequent treatment with ammonia solution gave a triose with R_f 0.09 [butanol–acetone–water (2 : 7 : 1)] and 0.36 [butanol–pyridine–water (6 : 4 : 3)] at an R_f value for rhamnose of 1. Acid hydrolysis of the triose gave D-glucose and L-arabinose.

The results obtained show that the carbohydrate substituent is attached in position 3.

REFERENCES

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