APIGENIN 5-GLUCOSIDE FROM Equisetum arvense

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The glycosidation of flavones at the 5-OH group is rarely found in nature [1, 2]. The finding in Equisetum arvense L. of luteolin 5-glucoside has been reported previously [5], but later the question of the finding of this compound was placed under doubt [1, 4].

Continuing a study of the flavonoids of the epigeal part of E. arvense L. (field horsetail) we have isolated from an ethyl acetate extract by chromatography on a polyamide sorbent a white crystalline substance with mp 255-256°C, $[\alpha]^{20}-22.7°$ (c 0.175; methanol) $\lambda_{max}^{(CH_3OH)}$ 262, 333 (log ε, 413;416); $\lambda_{max}^{(+AlCl_3)}$ 262, 335; $\lambda^{(+AlCl_3+HCl)}$ 263,335; $\lambda_{max}^{(+CH_3COONa)}$ 271, 305, 370; $\lambda_{max}^{(+CH_3ONa)}$ 270, 330, 390 nm. The band of the valence vibrations of a carbonyl group is present at 1630 cm^{-1} and that of hydroxy groups in the 3300-3400-cm^{-1} region.

From the results of quantitative acid and enzymatic hydrolytic cleavage it can be seen that the substance under investigation is a monoside containing D-glucose as the carbohydrate component and apigenin as the aglycone [5].

The compound under consideration possesses a bright-blue fluorescence in UV light, which is characteristic for flavone 5-glycosides [1]. The absence of a bathochromic shift in the presence of $AlCl_3$ for the glycoside, and also the absence of the signal of the proton of the 5-OH group in the weak field of the PMR spectrum (with dimethyl sulfoxide as solvent, B 487B radiospectrometer) in comparison with apigenin shows that the glucose is attached at position 5.

The capacity of the glycoside for being split by β-glucosidase shows the β-configuration of the glycosidic bond. On comparing the molecular rotations of the glycoside with the corresponding figures for phenyl glycosides it can be seen that the carbohydrate substituent is β-D-glucopyranose. The pyranose form is also confirmed by the results of IR spectroscopy (1100, 1070, and 1030 cm^{-1}) [16]. A doublet at δ 5.02 ppm (1H, J = 6 Hz) corresponds to the anomeric proton of the β-glucose in position 5 [7].

Thus, the compound under investigation has the structure of apigenin 5-O-β-D-glucopyranoside.

Apigenin 5-glucoside has been isolated previously from Amorpha fruticosa [8] and was later synthesized, but its physicochemical constants, with the exception of the melting point, were not given. The melting point of the apigenin 5-glucoside that we have identified (255-256°C) differs from that given in the literature (295°C) [8, 9].

This is the first time that apigenin 5-O-β-D-glucopyranoside has been found in the family Equisetaseae.

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