GLYCOFLAVONOIDS OF Gleditschia australis

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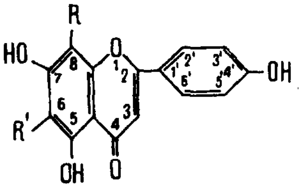
In the glumes of the pods of Gleditschia australis Hemsl. (Australian honeylocust) we have found by one- and two-dimensional paper chromatography not less than eight substances of flavonoid nature.

In order to free it from saponins, a methanolic extract of the pod glumes was reprecipitated with ethyl acetated repeatedly. Flavonoids were separated by chromatography on a column of polyamide and then by preparative paper chromatography. Five individual compounds were isolated, with R_f 0.03, 0.016, 0.027, 0.32, and 0.59 (15% acetic acid).

Substance (I), $C_{21}H_{20}O_{10}\cdot H_2O$, mp 221-223°C, $[\alpha]_D+44°$ (c 0.7; methanol), R_f 0.59, mol. wt. 447 (potentiometric titration), λ_{max}^{MeOH} 272, 334 nm (log ε 4.28; 4.30); $\lambda_{max}^{+CH_3COONa}$ 281, 386 nm; $\lambda_{max}^{+NaOCH_3}$ 280, 332, 402 nm; $\lambda_{max}^{+Zr(NO_3)_2}$ 285, 310, 356, 390 nm.

Substance (II), $C_{21}H_{20}O_{10}\cdot H_2O$, mp 260-264°C; $[\alpha]_D -13°$ (c 0.33; methanol), R_f 0.27, UV spectrum similar to that of substance (I).



On treatment with 5% HCl in 50% ethanol at 90°C for 2 h, the flavonoids (I) and (II) underwent mutual isomerization. On acid hydrolysis by Kiliani's method [1], the glycosides (I) and (II) gave the same products: apigenin and glucose.

In the NMR spectrum of apigenin (in DMSO), a signal at δ 7.8 ppm corresponds to the H-2',6' protons; a signal at δ 6.86 ppm to the H-3',5' protons; a singlet at δ 6.65 ppm to H-3, and doublets at δ 6.40 ppm and at δ 6.12 ppm to H-8 and to H-6, respectively [2]. The NMR spectrum of substance (I) lacks the signal of the H-6 proton, which shows that the glucose is attached in this position. In the NMR spectrum of flavonoid (II) conversely, the signal of the H-6 proton is present but the signal of the H-8 proton is absent, which shows the presence of a substituent in position 8.

Thus, on the basis of their physicochemical constants, the results of hydrolysis, and their UV and NMR spectra, compound (I) has been identified as saponaretin (4',5,7-trihydroxyflavone 6-C-β-D-glucopyranoside) and substance (II) as the vitexin (4',5,7-trihydroxyflavone 8-C-β-D-glucopyranoside). The study of these flavonoids is continuing.

LITERATURE CITED

1. H. Kiliani, Ber., 63, 2866 (1930).
2. W. Olechnowiec-Stepien et al., Herba polonice, 1968, No. 3, 179.

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