FLAVONOIDS OF Asperula oppositifolia

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From an ethanolic extract of the herb Asperula oppositifolia Rgl. et Schalh., family Rubiaceae, by chromatography on polyamide sorbent we have isolated three individual substances of phenolic nature.

Substance (1), $C_{27}H_{30}O_{16}$, mp 185-186°C (water), $[\alpha]_D^{20}$ −33° (c 0.1; dimethylformamide). The acid hydrolysis of (1) (3% H_2SO_4, 100°C, 40 min) gave D-glucose and L-rhamnose, identified by paper chromatography, and an aglycone which was identified as quercetin by its UV and IR spectra, the products of alkaline hydrolysis, elementary analysis, and a mixed melting point. Acid hydrolysis under mild conditions [1% H_2SO_4, ethanol–water (1:1), 100°C, 30 min] led to the formation of quercetin and rutinose. The characteristics described and the fact that on stepwise hydrolysis under the usual conditions the bioside did not give an intermediate monoglycoside identified it as rutin.

Substance (2), $C_{26}H_{28}O_{16}$, mp 187-191°C (from 50% ethanol), $[\alpha]_D^{20}$ −38.9° [c 0.07; methanol–dimethylformamide (1:1)], UV spectrum: λ_{max} (in ethanol) 365, 290, 260 nm. Acid hydrolysis (2% H_2SO_4, 100°C, 6 h) gave D-glucose, D-xylose, and quercetin. A comparison of the UV spectra of the aglycone and the glycoside and also the stability of the latter to alkaline hydrolysis [1] showed that the sugar is attached to the aglycone at C_3. The hydrolysis of substance (2) in cyclohexanol [2] formed, as an intermediate, quercetin 3-xyloside. Consequently, the terminal sugar in (2) is the glucose. When the glycoside was subjected to periodate oxidation [3], both sugars were decomposed, which shows the absence of a 1-3 linkage between them. The sizes of the oxide rings and the configurations of the glycosidic bonds were determined by a comparison of molecular rotations and by IR spectroscopy [4, 5]. It was found that the D-xylose is attached to the aglycone and the D-glucose to the D-xylose by β glycosidic bonds, and that both sugars have a pyranose oxide ring. This was confirmed satisfactorily by the rate of acid hydrolysis [6]. Thus, the most probable structure for substance (2) can be given as quercetin 3-[O-β-D-glucopyranosyl-(2→1 or 4→1)-O-β-D-xyloside].

Substance (3), $C_{26}H_{28}O_{16}$, mp 198-202°C (from 50% ethanol), $[\alpha]_D^{20}$ −48° [c 0.05; methanol–dimethylformamide (1:1)], UV spectrum: λ_{max} (in ethanol) 365, 305, 260 nm. Acid hydrolysis (2% H_2SO_4, 100°C, 6 h) gave D-glucose, L-arabinose, and quercetin. The hydrolysis of substance (3) in cyclohexanol gave avicularin as an intermediate product. It follows from this that, as in substance (2), the terminal sugar is D-glucose. The position of the sugar residue, the type of bond between the sugars, the sizes of the oxide rings, and the configuration of the glycosidic bonds were determined in a similar manner to the case of substance (2). On the basis of the investigation performed, we have ascribed to substance (3) the probable structure of quercetin 3-[O-β-D-glucopyranosyl-(2→1 or 4→1)-O-β-L-arabopyranoside].

Substances (2) and (3) are new natural compounds.

In addition to the flavonoids, by two-dimensional paper chromatography in the 2% acetic acid and BAW (4:1:2) systems we isolated in the individual state two phenolic acids which were identified by their IR spectra, the products of alkaline hydrolysis (0.1 N KOH, 30 min, in a nitrogen atmosphere), and by paper chromatography with authentic samples as chlorogenic and caffeic acids.

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