FLAVONOL GLYCOSIDES OF Astragalus propinquus

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The raw material for the investigation was the epigeal part of Astragalus propinquus, collected in the flowering phase in the Selengian Aimak of the Mongolian People's Republic.

By using column chromatography on polyamide sorbent, we isolated four individual compounds of flavonoid nature – substances 1-4, consisting of yellow powders soluble in methanol, ethanol, and aqueous ethanol, and insoluble in ether and chloroform.

Substance 1 has mp 169-171°C, $[\alpha]_D^{20} - 68.2°$ (c 0.33; methanol). R_f 0.40 (15% acetic acid, system 1) and 0.75 [butan-1-ol–acetic acid–water (4:1:2), system 2].

Substance 2 has mp 176-178°C, $[\alpha]_D^{20} + 135°$ (c 0.5; methanol). R_f 0.53 (1) and 0.54 (2).

Substance 3 has mp 190-192°C, $[\alpha]_D^{20} + 140°$ (c 0.25; methanol). R_f 0.51 (1) and 0.44 (2).

Substance 4 has R_f 0.64 (1) and 0.40 (2).

In the cyanidin reaction, the compounds obtained give a crimson-red pigment which does not pass into the octanol layer, showing their glycosidic nature [1]. On acid hydrolysis with 0.05% hydrochloric acid, the aglycone of substance 1 was detected in 3 min, that of substance 2 in 4 min, that of substance 3 in 3 min, and that of substance 4 in 5 min.

The aglycones were separated by extraction with ether and the positions of the three hydroxy groups were determined by UV spectroscopy [2]. On the basis of the results obtained, and also the results of demethylation with hydriodic acid in liquid phenol and acetic anhydride [3], the results of alkaline degradation, and of comparative chromatography in several solvent systems, the aglycone of substances 1 and 2 was identified as 3,4',5,7-tetrahydroxy-3'-methoxyflavone or isorhamnetin, the aglycone of substance 3 as 3,3',4',5,7-pentahydroxyflavone or quercetin, and the aglycone of substance 4 as 3,4',5-trihydroxy-7-methoxyflavone or rhamnocitrin.

In the hydrolyzate of substance 1 as the carbohydrate component we found D-glucose, from substances 2 and 3 we obtained a mixture of D-glucose and L-rhamnose, and from substance 4 L-arabinose. The ease of acid hydrolysis of substances 1-4 and their dark brown fluorescence on chromatograms in filtered UV light permitted the assumption that the carbohydrate substituents were located at C_3 [4], which was confirmed by UV spectroscopy [2].

On the basis of the chromatographic behavior of the glycosides in various systems [5], stepwise acid hydrolysis, and peroxide cleavage, it was established that substances 1 and 4 are monosides and substances 2 and 3 are biosides.

The configuration of the glycosidic bond and the position of the linkage in the biose were determined by enzymatic hydrolysis with rhamnodiastase and a preparation of the fungus Aspergillus oryzae, and also by spectral investigations in the UV region. All the glycosides were found to have β-glycosidic bonds, and the oxide rings of the sugars of substances 1-3 were found to have the pyranose form. The latter was confirmed by the results of a polarimetric analysis.

On the basis of the investigations performed, it has been established that substance 1 is isorhamnetin 3-β-D-glucopyranoside, compound 2 is isorhamnetin 3-[6-β-L-rhamnopyranosyl-β-D-glucoside], substance

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3 is quercetin 3-[6-β-L-rhamnopyranosyl-β-D-glucoside], and substance 4 has been characterized provisionally as rhamnocitrin 3-β-L-arabinoside and has been called propingoside. This is the first time that all these substances have been isolated from this species of Astragalus.

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