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FLAVONOIDS OF Astragalus adsurgens

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We have studied the flavonoids of the epigeal part of Astragalus adsurgens Pall., family Fabaceae, growing in the Tuva ASSSR. The dried and comminuted herbage was extracted with 80% ethanol, and the extract was evaporated to an aqueous residue, which was treated successively with chloroform and ethyl acetate. The ethyl acetate fraction and the aqueous residue after evaporation were separated on columns of polyamide sorbent at a ratio of the mixture of substances being separated to sorbent of 1:30 [1]. The columns were washed with water and with aqueous ethanol (from 5 to 30% of ethanol). As a result, the ethyl acetate extract yielded two (I and II) and the aqueous extract yielded three (III-V) flavonoid glycosides.

Substance (I) — $C_{22}H_{22}O_{12}$, mp 192-198°C, $[\alpha]_D^{21}$ — 56° (DMFA). On hydrolysis with grapesnail enzyme [3], it split into the aglycon isorhamnetin [4] and D-glucose. The β -configuration of the glycosidic bond of the carbohydrate component and its position at C_3 of the aglycon were established by UV spectroscopy with diagnostic reagents [5] and by a comparison of the molecular rotation of the substance with those of phenyl O- α - and - β -D-glucopyranosides [6]. Substance (I) was identical with the isorhamnetin 3-O- β -D-glucopyranoside isolated previously from sea buckthorn [7].

Substance (II) — $C_{21}H_{20}O_{19}$, mp 192-194°C, $[\alpha]_D^{20}$ — 30° (ethanol). On hydrolysis with 3% sulfuric acid it split into the aglycon kaempferol and D-galactose. Its further study was carried out in a similar manner to that of substance (I). It was found that compound (II) was kaempferol 3-0- β -D-galactopyranoside (trifolin), which has been obtained previously from Astragalus galegiformis.

Substance (III) — $C_{33}H_{40}O_{19}$, mp 187-189°C, $[\alpha]_D^{21}$ — 83.5° (ethanol—DMFA (8:2). Enzymatic hydrolysis with rhamnodiastase [7] split the glycoside into kaempferol 7-0- α -L-rhamnoside $[C_{22}H_{20}O_{10}$, mp 227-229°C, $[\alpha]_D^{20}$ — 128° (ethanol)] and robinobiose. UV spectroscopy with diagnostic additives showed that the robinobiose was attached at the C_3 position of the kaempferol. A comparison of the cleavage products, UV spectra, and physicochemical properties of substance (III) and robinin showed their identity was established [8].

Substance (IV) — $C_{28}H_{32}O_{16}$, mp 220-223°C, $[\alpha]_D^{2\circ}$ — 104° (ethanol). On hydrolysis with 3% sulfuric acid, it split into the aglycon isorhamnetin and two sugars: D-glucose and L-rhamnose. However, on enzymatic hydrolysis with rhamnodiastase only D-glucose was split off and not rutinose, as is observed for rutinosides [7]. The substance formed as the result of enzymatic hydrolysis $[C_{22}H_{22}O_{11}$, mp 118-119°C, $[\alpha]_D^{2^1}$ — 122° (ethanol)] was identical with isorhamnetin 7-0- α -L-rhamnopyranoside [7]. A comparison of the properties of compound (IV) with an authentic sample of isorhamnetin 3-0- β -D-glucopyranoside 7-0- α -L-rhamnopyranoside showed their identity [7].

Substance (V) — $C_{27}H_{30}O_{15}$, mp 204-208°C, $[\alpha]_D^{20}$ — 24° (ethanol) was split by rhamnodiastase into kaempferol and rutinose. The position of attachment of the biose to the aglycon determined by UV spectroscopy with diagnostic additives was C_3 . A comparison of the properties of substance (V) with an authentic sample of kaempferol 3-0-rutinoside [8] showed their identity.

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Thus, from Astragalus adsurgens we have isolated kaempferol glycosides - trifolin, kaempferol rutinoside, and robinin — and also two isorhamnetin glycosides — isorhamnetin 3-0- β -Dglucopyranoside and an isorhamnetin 3-glucoside 7-rhamnoside.

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SWERTIAJAPONIN FROM Iris lactea

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In an investigation of the ethyl acetate fraction obtained by treating an ethanolic extract from the epigeal part of Iris lactea Pall. we have isolated apigenin C-glycosides and two luteolin glycosides [1-3].

Continuing an investigation of the same fraction, by chromatography on a column of silica gel and polyamide with elution by ethanol—chloroform (90:10) and ethanol—water (20:80) mixtures we have isolated a substance (VI). It was a light yellow crystalline powder with mp 264-265°C (50% ethanol); $[\alpha]_D^{22}$ - 55° (c 0.1; ethanol), R_f 0.37 (15% acetic acid), 0.56 (butan-l-ol-acetic acid-water (4:1:2).

The full acetate of substance (VI) had mp 153-155°C.

The prolonged heating of (VI) with dilute acid did not lead to the formation of an aglycon and a carbohydrate component, but on paper chromatograms in the 15% acetic acid system a new substance with a lower Rf value (0.31) was detected which gave an equilibrium system with the initial compound. The formation of the latter is characteristic for 6-C-glycosides. Hydrolysis with hydriodic acid gave the aglycon luteolin, and D-glucose was detected as the carbohydrate component.

The IR spectrum of substance (VI) had absorption bands at (cm^{-1}) 3440-3020 (phenolic hydroxyls), 1650 (C=0 of a γ -pyrone ring), 1600, 1540, 1480 (conjugated double bonds); 1305 (methoxy group); and 1020-1050 (pyranose form of a sugar). UV spectrum, λC_2H_5OH , nm: 245, max 275, 350, + NaOEt 267, 404; + NaOAc 269, 355, + NaOAc/H₃BO₃ 266, 370; + A1CI₃/HCl 279, 355. Analysis of the results of UV spectroscopy showed the presence of free hydroxy groups in positions 3', 4', and 5, and substitution at C_7 .

A physicochemical study of substance (VI) and a comparison of the results obtained with those given in the literature permitted the compound isolated to be characterized as $6-C-\beta-$ D-glucopyranosyl-7-0-methylluteolin or swertiajaponin. This is the first time that swertiajaponin has been isolated from representatives of species of the Iris genus [5, 6].

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