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THE TRITERPENE GLYCOSIDE GYPSOSIDE FROM GYPSOPHILA BICOLOR

K. Amanmuradov and M. V. Gronovich

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The triterpene glycoside gypsoside was first isolated from Gypsophila pacifica [1] and then from other species of plants of the family Caryophyllaceae [2–4, 6, 7]. We have studied the triterpene glycosides of Gypsophila bicolor (Freyn et Sint.) Litv. gathered in the botanical garden of AS TurkmSSR. The seeds, previously treated with chloroform, together with the bracts, were first extracted with 96% and then with 50% aqueous ethanol with heating. By chromatography in a thin layer of silica gel in systems 1) [butan-1-ol–acetic acid–water (4 : 1 : 5)] and 2) [butan-1-ol–ethanol–25% ammonia (7 : 2 : 5)] the extract was shown to contain two triterpene glycosides. The extract was passed through a small layer of cellulose powder and washed with system 1. When the combined eluates were concentrated, a single glycoside precipitated which, after several reprecipitations from water-saturated butanol, had mp 218–222° C (decomp.), $[\alpha]_D^{20}$ +21 ± 2° (c 1; aqueous ethanol); acetate, mp 150–154° C, $[\alpha]_D^{20}$ +11 ± 2° (c 1.1; chloroform). The yield of pure glycosides was 2.5% of the weight of the air-dry seeds.

The constants of the glycoside under study and, particularly, of the acetate are low in comparison with literature data for gypsoside [1]. This discrepancy for the gypsoside isolated from other species has been mentioned previously [3, 4].

The glycoside and the gypsoside isolated from Acanthophyllum gypsophiloides [3] behaved identically when chromatographed on a thin layer of silica gel in systems 1 and 2.

On hydrolysis with 2% H_2SO_4, the glycoside gave vacaroside [5] while the hydrolysate, neutralized with the anion exchange EDE-10-P (OH^- form), was shown by two-dimensional paper chromatography in systems 1 and pyridine–butan-1-ol–water (4 : 6 : 3) to contain D-galactose, D-glucose, D-xylose, L-arabinose, D-fucose, and L-rhamnose.

Hydrolysis of the glycoside with 18% HCl gave the aglycone, gypsogenin, the physicochemical constants and IR spectrum of which agree well with the literature data. A mixture of the gypsogenin from G. bicolor and the gypsogenin from A. gypsophiloides [3] gave no depression of the melting point.

The second, less polar, glycoside was not studied because of its small amount.

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TRITERPENE GLYCOSIDES OF SAPINDUS MUKOROSSI

V. Ya. Chirva, P. K. Kintya, and V. A. Sosnovskii

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The information in the literature on the structure of the triterpene glycosides of Sapindus Mukorossi Gaertn. (Chinese soapberry) is contradictory and doubtful. Investigations carried out by Indian scientists were made without satisfactory chromatographic methods of purification and analysis [1]. However, other authors have found in hydrolysates of the individual substances several moles each of glucuronic acid and fructose [2]. The presence in triterpene glycosides of fructose residues must be carefully checked [3–7].

We have studied the fruit of the Chinese soapberry gathered in December, 1967 in the Batumi Botanical Garden. In a defatted methanolic extract, by chromatography in a thin layer of silica gel in several mixtures of solvents at various pH values we detected five compounds of a glycosidic nature, which we have called sapindosides A, B, C, D, and E.

In order to elucidate the nature of the aglycone, the combined saponins were subjected to acid hydrolysis. The genin obtained and its derivatives were identical in chromatographic behavior and mixed melting points with an authentic sample of hederagenin and its derivatives.

To isolate the individual glycosides, the mixture was chromatographed on silica gel in the butan-1-ol–ethanol–25% ammonia (9 : 2 : 5) system. Sapindosides C, D, and E were obtained in the individual state, and sapindosides A and B as a mixture. The final separation was achieved by means of chromatography on silica gel in ethyl acetate–methanol–water (10 : 2 : 1).

Paper chromatography in several systems showed that the sugar moiety of sapindosides C, D, and E contains glucose, arabinose, and rhamnose, that of sapindoside B arabinose, xylose, and rhamnose, and that of sapindoside A arabinose and rhamnose.

The presence of a O-acylglycosidic bond in the glycosides studied was shown by treating the combined saponins with an alcoholic solution of caustic potash. By analyzing the hydrolyzate in a thin layer of silica gel in the butan-1-ol–ethanol–ammonia (9 : 2 : 5) system it was possible to show that only sapindoside E is an O-acylglycoside. This conclusion was confirmed by methylation with diazomethane and subsequent acid hydrolysis. A chromatographic study of the hydrolyzates showed that sapindosides A, B, C, and D formed the methyl ester of hederagenin, while sapindoside E formed hederagenin itself.

Thus we have not confirmed the results of investigations of other authors [1–2]. This difference is apparently due to the dissimilar climatic conditions for the growth of the Chinese soapberry.

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TRITERPENE GLYCOSIDES OF DIPSACUS AZUREUS

M. M. Mukhamedziev and P. K. Alimbaeva

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Dipsacus azureus Schrenk, family Dipsacaceae, is a perennial plant widely distributed in the foothills of the Kirghiz Ala-Tau. The comminuted roots, gathered in the flowering period, were defatted with acetone and extracted with methanol. The methanolic extract was evaporated, and the saponins were precipitated with acetone. The yield was 18.9% of the weight of the air-dry raw material. A high hemolytic index (9.375) was found for the mixture of saponins. The combined saponins were chromatographed on a column of regenerated cellulose powder. The column was eluted with the organic phase of the solvent system butan-1-ol–acetic acid–water (4 : 1 : 5) (system 1). Two individual compounds were isolated which we called, in order of increasing polarity, dipsacosides A and B. A chromatogram on silica gel in system 1 showed the presence of a still more polar glycoside, C. The latter, however, could not be isolated because of its low concentration.