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.

REFERENCES

1. R. L. Ramachandra and C. Rukmini, Indian J. Chem., **4**, No. 1, 36, 1966.
2. N. Ya. Zykova and P. E. Krivenchuk, Farmatsevtich. zh., no. 1, 66, no. 4, 27, 1965; no. 3, 51, 1966.
3. S. C. Bhattacharyya and B. Lythgoe, Nature, **163**, 259, 1949.
4. S. C. Bhattacharyya, J. Indian Chem. Soc., **33**, 579, 630, 1956.
5. L. Kitasato and Ch. Sone, Acta phytochim., (Tokyo), **6**, 179, 1932.
6. I. P. Varsney, Ch. Sonnie, and C. R. Hebd, Seances Acad. Sci., 242, 2393, 1956.
7. A. Winterstein, J. Meyes, and Hoppe-Seylers, Z. physiol. Chem., 199, 37, 1931.

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TRITERPENE GLYCOSIDES OF DIPSACUS AZUREUS

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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.

Dipsacoside A, $C_{41}H_{66}O_{12} \cdot H_2O$ (elementary analysis), is a diglycoside with mp 240–245° C (from ethanol), $[\alpha]_D^{20}$ +12.5 ± 3° (c 2.40; ethanol). On being heated in a mixture of 6% H_2SO_4 and methanol (1 : 1) it hydrolyzed, giving an aglycone with mp 324–326° C (from ethanol), $[\alpha]_D^{20}$ +75.5 ± 2° (2.96; pyridine) and two monosaccharides, identified by paper chromatography in system 1 as L-arabinose and L-rhamnose. The diacetate of the aglycone had mp 164–166° C (from aqueous ethanol) and $[\alpha]_D^{20}$ +65.5 ± 2° (c 3.27; chloroform). A chromatogram on silica gel in chloroform–ethanol (10 : 1) (system 2) and in ether–benzene (34 : 1) (system 3) showed the identity of the sapogenin of dipsacoside A and hederagenin obtained by the hydrolysis of the glycosides of Leontice eversmanii [1]. The IR spectra of the compounds compared coincided. From the composition of the aglycone and the sugars, dipsacoside A is similar to kalopanax saponin A [2], but possibly differs from it in the arrangement of the bonds between the monosaccharides.

The bulk of the combined saponins consisted of the amorphous but chromatographically homogeneous dipsacoside B with mp 198–202° C, $[\alpha]_D^{22}$ +11 ± 3° (c 0.20; water). The glycoside gave an amorphous polyacetate with mp 140–144° C (from benzene–petroleum ether). From the behavior of the substance on silica gel in systems 2 and 3 it may be concluded that dipsacoside B is an acyloside [1]. When the glycoside was hydrolyzed with 6% H_2SO_4, hederagenin, L-arabinose, L-rhamnose, and D-glucose were obtained. Alkaline hydrolysis on the anion-exchanger AV-17 (OH form), carried out under the conditions for the hydrolytic cleavage of patrinoside C [3], led to dipsacoside A, identified chromatographically on silica gel in the butan-1-ol–ethanol–25% ammonia (10 : 2 : 5) system and on paper in system 1. D-Glucose was detected in the sugar fraction after acid hydrolysis. Consequently, dipsacoside B differs from dipsacoside A by the presence of an acylglycosidic moiety consisting of one or more molecules of D-glucose.

REFERENCES

1. L. G. Mzhel'skaya, V. K. Yatsyn, and N. K. Abubakirov, KhPS [Chemistry of Natural Compounds], 2, 421, 1966; 3, 101, 218, 1967; 4, 153, 216, 1968.

2. A. Ya. Khorlin, A. G. Ven'yaminova, and N. K. Kochetkov, Izv. AN SSSR, ser. khim., 1447, 1964; DAN SSSR, 155, 619, 1964.

3. V. G. Bukharov, V. V. Karlin, and V. A. Talan, KhPS [Chemistry of Natural Compounds], 3, 17, 1967.

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SOME RESULTS ON THE STRUCTURE OF THE GENIN OF THE GLYCOSIDE OF POLEMONIUM COERULEUM

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On hydrolysis, polemoniosides B and C formed one and the same aglycone. Since in this process the product underwent pronounced resinification, it was converted into the acetyl derivative, which was purified on silica gel and was then deacetylated by being heated with alkali. The genin obtained in this way with mp 198–200° C and $[\alpha]_D$ +50° (c 1; ethanol) had a neutral character and was soluble in only chloroform, ethyl acetate, and ethanol. According to the elementary analysis, the substance contained no nitrogen and its most probable empirical formula was $C_{30}H_{48}O_5$. The IR spectrum exhibited strong absorption maxima in the 1650, 1725, and 3300–3500 cm^{-1} regions. The band at 1725 cm^{-1} shows the presence of a carbonyl group of some kind. This is not an aldehyde group, since there are no characteristic frequencies in the 2700–2730 cm^{-1} region and the NMR spectrum has no signals of protons at 9–10 ppm. The aglycone gave a crystalline 2,4-dinitrophenylhydrazone $C_{36}H_{54}O_8N_4$ with mp 155–157° C.

When the aglycone was hydrogenated over Raney Ni in acetic acid, it consumed 1 mole of hydrogen. When the IR spectrum of the product was obtained, with mp 181-183°C, and $[\alpha]_D$ +40° (c 1; ethanol), the carbonly absorption band had disappeared.

The genin gave a positive color reaction with tetranitromethane and it added bromine in chloroform solution forming a crystalline dibromide [acetyl derivative $C_{36}H_{58}O_8Br_2$, mp 102–105° C, $[\alpha]_D$ +30° (c 1; ethyl acetate)].

The double bond is apparently tetrasubstituted, since the NMR spectrum lacks signals of protons in the 5–6.8 ppm region and the substance does not hydrogenate over PtO_2 in acetic acid. When the aglycone was boiled with lithium