By acid hydrolysis of the saponins we obtained a mixture of two aglycones. By chromatography in a thin layer of silica gel in the chloroform–ethanol (25 : 1) system, the aglycones were identified as oleanolic acid and hederagenin. Samples of the sapogenins were given to us by N. K. Abubakirov.

The main genin was isolated in the pure crystalline state with mp 303–307° C; its IR spectrum: 3360 cm^{-1} (hydroxyl); 1683 cm^{-1} (carbonyl of a carboxy group), which was identical with the IR spectrum of oleanolic acid.

Tschesche et al. [2], in studying another species of ivy—Hedera helix L.—found glycosides of the same sapogenins. We are continuing the study of the sapogenins of Hedera colchica.

REFERENCES

1. A. Ya. Khorlin, L. V. Bakinovskii, V. E. Vas'kovskii, et al., Izv. AN SSSR, ser. khim., 2008, 1963.
2. R. Tschesche, W. Schmidt, and G. Wulf, Z. Naturforch, no. 7, 20b, 708, 1965.

12 February 1968 Kutateladze Institute of Pharmacological Chemistry AS Georgian SSR

UDC 547.918

COMPOSITION OF THE GLYCOSIDIC FRACTION FROM STYCHOPUS JAPONICUS

G. B. Elyakov, T. A. Kuznetsova, and V. E. Vas'kovskii

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 4, pp. 253–254, 1968

In 1952, R. Nigrelli [1] showed that the holothuria Actinopyga agassizi contained a substance that was toxic for fishes and higher animals. He called it holothurin. On biological tests, the toxin was detected [2] in 30 species of holothuria belonging to four out of the five orders forming this class, including St. japonicus Selenka [3].

The results of a study of the chemical structure and biological properties of holothurin from A. agassizi have been given in the literature [1, 2, 4–6].

From Holothuria vagabunda, Japanese workers [7] isolated a glycoside which they also called holothurin.

We have studied the glycosides from a methanolic extract of the far eastern trepang (St. japonicus). "Sea ginseng," as the trepang is called, has long been used as a medicinal substance in eastern medicine. However, nothing has been known about the chemical properties of its active principles.

The chromatography of the methanolic extract in a thin layer of silica gel showed the presence of 10–12 substances in it.

As a result of the preparative purification of a methanolic extract obtained from 4.5 kg of raw trepangs by partition chromatography on alumina in the butanol–toluene–water system, 1.4 g (2.8%) of a glycosidic fraction was isolated, the hydrolysis of which was shown chromatographically to give the same mixture of monosaccharides as was obtained in the hydrolysis of holothurin from A. agassizi.

After partition chromatography of the total glycosides on silica gel, two chromatographically pure glycosides were isolated: stychoposide A and stychoposide C. Stychoposide A was purified twice on silica gel. A white amphorous substance with mp 215–217° C, $[\alpha]_D^{25}$ −62.3 ± 5° (c 5.01; pyridine) was obtained. IR spectrum: 3400–1745 cm^{-1}.

Found, %: C 58.87, 58.84; H 8.59, 8.60; S 2.08, 2.09.

Both glycosides differed from holothurin in their behavior on thin-layer chromatography in silica gel in the chloroform–methanol (2 : 1)/water system (revealing agent sulfuric acid). On hydrolysis, stychoposides A and C gave identical mixtures of products of the change of the aglycone which differed, however, from the analogous mixtures isolated in the hydrolysis of holothurin [chromatography in a thin layer on silica gel in the ethyl acetate–chloroform (3 : 2) system, revealing agent sulfuric acid]. The thin-layer chromatography of the mixture of monosaccharides [butanol–acetone–water (4 : 5 : 1) system] obtained in the hydrolysis of stychoposides A and C and of holothurin showed that stychoposide A and holothurin have an identical set of monosaccharides, among which it was possible to identify glucose, xylose, and 3-O-methylglucose, while stychoposide C also contained galactose.

The sample of holothurin was given to us by Prof. J. Chanley (New York, USA).

REFERENCES

1. R. F. Nigrelli, Zoologica, **37**, 89, 1952.

2. R. F. Nigrelli and S. Jakowska, Ann. N.Y. Acad. Sci., **90**, 884, 1960.

3. T. Jamanouchi, Publ. Seto Marine Biol. Lab., **4**, 184, 1955.

4. S. L. Friess, F. G. Standart, E. R. Whitcomb, R. F. Nigrelli, J. D. Chanley, and H. Sobotka, Ann. N.Y. Acad. Sci., **90**, 893, 1960.

5. R. F. Nigrelli, J. D. Chanley, S. K. Lohn, and H. Sobotka, Zoologica, **40**, 1, no. 4–5, 47, 1955.

6. J. D. Chanley, S. K. Kohn, R. F. Nigrelli, and H. Sobotka, Zoologica, **40**, 11, no. 9, 99, 1955; J. D. Chanley, R. Ledoon, J. Wax, R. F. Nigrelli, and H. Sobotka, J. Am. Chem. Soc., **81**, 5180, 1959; J. Chanley, J. Perlstein, R. F. Nigrelli, and H. Sobotka, Ann. N.Y. Acad. Sci., **90**, 902, 1960; J. D. Chanley, T. Mezzetti, and H. Sobotka, Tetrah., **22**, 1857, 1966.

7. T. Matsuno, and T. Jamanouchi, Nature, **191**, 75, 1961.

27 April 1967

Institute of Biologically Active Substances, Far Eastern Branch, Siberian Division AS USSR, Vladivostok

UDC 547.972

AN ISORHAMNETIN GLYCOSIDE FROM THE FLOWERS OF ASTRAGALUS NOVOASCANICUS

L. I. Deryugina, N. P. Maksyutina, and P. E. Krivenchuk

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 4, pp. 254–255, 1968

Continuing our investigation of the flavonoid composition of Astragalus novoascanicus Klok. [1], we have isolated a pure flavonol glycoside with a yield of 4.9%. The products of acid and enzymatic hydrolysis and of peroxide oxidation were studied by paper chromatography. It was found that the aglycone of this glycoside is identical with isorhamnetin. The sugars were compared with authentic samples of bioses and monoses, the spots being revealed with diphenylamine reagents [2]. From the colors of the spots on the chromatogram and from the R_f value it was shown that the sugar is a biose consisting of two molecules of glucose connected to one another in the 1–6 arrangement. The biose is, therefore, gentiobiose (O-6-β-D-glucosyl-D-glucose).

The position of the attachment of the gentiobiose to C-3 of the isorhamnetin was determined by UV spectroscopy using ionizing and complex-forming reagents and also by qualitative reactions with zirconyl nitrate and citric acid carried out on the aglycone, the bioside, and its monoside. Oxidative degradation with hydrogen peroxide selectively cleaves only C-3 glycosides [3].

Consequently, the flavonol bioside that we isolated is isorhamnetin 3-β-D-glucosyl-6-β-D-glucoside, which we isolated for the first time from the flowers of Astragalus pubiflorus D.C. and called astragaloside [4].

REFERENCES

1. L. I. Deryugina, Farm. zhurnal, **3**, 62, 1965.

2. R. W. Bailey, J. Chrom., **8**, 57, 1962.

3. B. V. Chandler and K. A. Harper, Austr. J. Chem., **14**, 586, 1961.

4. L. I. Deryugina, N. P. Maksyutina, and P. E. Krivenchuk, KhPS [Chemistry of Natural Compounds], **2**, 394, 1966.

9 January 1968

Zaporozh'e Pharmaceutical Institute

Kiev Institute for the Improvement of Medicine