THE STRUCTURE OF XANTHOCERAS SAPONIN

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UDC 547.913+547.917

Of the plants of the family Sapindaceae that have been studied in our laboratory, Xanthoceras sorbifolium (shinyleaf yellowhorn) is widely distributed in Moldavia. In contrast to the soap trees Sapindus mukorossi and Koelreuteria paniculata, there is no literature information at all on the chemical composition of this representative.

In qualitative tests, a methanolic extract gave a positive reaction for triterpene glycosides and, according to thin-layer chromatography on silica gel, it contained one substance – xanthoceras saponin (I). It was isolated in the pure state by column chromatography on alumina.

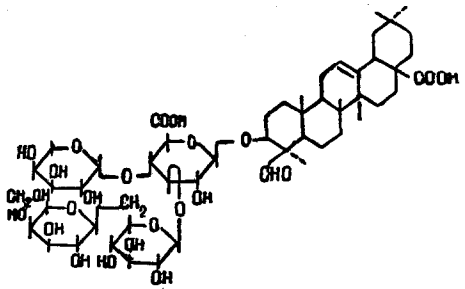
In spite of the fact that the compound obtained has the same chromatographic mobility and the same aglycone as and very similar physical constants to koelreuteria saponin B [1], the composition of its carbohydrate moiety differs somewhat from that of the latter. Thus, the acid hydrolysis of (I) with Kiliani's mixture [2] forms glucuronic acid, arabinose, glucose, and galactose.

By analogy with other gypsogenin glycosides [3, 4], the 3-O-β-glucuronoside of this aglycone was isolated.

The structure of the carbohydrate component of the saponin was shown by comparing the results obtained by the use of a number of known methods. Thus, on methylation by Hakomori's method [5] and subsequent hydrolysis with perchloric acid, methyl 2-O-methyl-D-glucuronate, 2,3,4-tri-O-methyl-L-arabinose, 2,3,4,6-tetra-O-methyl-D-galactose, and 2,3,4-tri-O-methyl-D-glucose were identified.

When the glycoside was oxidized by Smith's method [6], only the glucuronic acid residue was unaffected. Further information on the structure of the sugar chain was obtained by treating the saponin with oxalic acid, as a result of which a bioside was isolated which contained glucuronic acid and glucose. The action of sodium periodate on this progenin did not affect the glucuronic acid, which shows a 1 → 3 bond between the monosaccharides. Only the question of the order of attachment of the terminal galactose and arabinose residues remained obscure. This problem was solved by studying the other progenin arising together with the gypsogenin bioside. When it was hydrolyzed, glucuronic acid, glucose, and arabinose were obtained. Consequently, the terminal arabinose residue is attached directly to the glucose, and the galactose is attached to the hydroxyl at C_4 of the glucuronic acid.

The study of these progenins enabled us to establish not only the sequence of the monosaccharides in the carbohydrate chain of (I) but also the configuration of the glycosidic centers, which were determined by molecular rotation differences. Thus, the final structure of xanthoceras saponin has the form



Institute of Chemistry, Academy of Sciences of the Moldavian SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 442-444, July-August, 1971. Original article submitted February 16, 1971.

EXPERIMENTAL

Chromatography was performed with paper of type "S" ["medium"] of the Volodarskii Leningrad Mill, with KSK silica gel, and with neutral alumina. Gas-liquid chromatography was performed on a KhT-63 chromatograph with a katharometer detector using helium as the carrier gas at a rate of flow of 60 ml/min; the temperature of chromatography was 156° C and the liquid phase was a silicone oil and the solid phase Celite-540 (100-120 mesh). The following solvent systems were used: 1) butan-1-ol–ethanol–water (10 : 2 : 5); 2) butan-1-ol–ethanol–25% ammonia (9 : 2 : 5); 3) butan-1-ol–benzene–pyridine–water (5 : 1 : 3 : 3); 4) chloroform–ethyl acetate (3 : 1); 5) benzene–acetone (2 : 1); and 6) toluene–ethanol (9 : 1).

Isolation of Xanthoceras Saponin. The fruit of the soap tree Xanthoceras sorbifolium (2.5 kg) was extracted with aqueous methanol. The extract was evaporated to dryness and then the powder was dissolved in 1 liter of water and exhaustively extracted with diethyl ether, after which the aqueous layer was washed with butan-1-ol. The weight of the butanolic fraction was 125 g. The substance (10 g) was dissolved in system 1 and transferred to a column (60 × 3 cm) containing alumina and was eluted with the same mixture. This gave 2.4 g of xanthoceras saponin (I) with mp 152-154° C, $[\alpha]_D^{20}$ – 23° (c 1.77; methanol).

Acid Hydrolysis of Xanthoceras Saponin. Compound (I) (100 mg) was hydrolyzed with 10 ml of Kiliani's mixture at 110° C for 5 h. Then the hydrolysate was diluted with 10 ml of water and extracted with ether. This gave 45 mg of a substance with mp 263-265° C, $[\alpha]_D^{20}$ + 85° (c 1.8; ethanol). From its chromatographic mobility in system 4, the compound was identical with gypsogenin. The aqueous layer obtained by the action of Kiliani's mixture was treated with KU-2 and AV-17 ion-exchange resins and evaporated. Paper chromatography in system 3 revealed glucuronic acid, arabinose, glucose and galactose.

Preparation of Gypsogenin Glucuronoside. A mixture of 0.5 g of (I) and 20 ml of 2% H_2SO_4 was heated at 80° C for 5 h, giving 0.23 g of a compound with mp 201-203° C, $[\alpha]_D^{20}$ + 21° (c 1.2; ethanol). Literature data: mp 203-205° C, $[\alpha]_D^{20}$ + 16.2° (c 1.4; ethanol). In its chromatographic behavior in system 4, the substance agreed with gypsogenin 3-O-β-glucuronoside.

Smith Degradation of Xanthoceras Saponin. A solution of 100 mg of the saponin in 40 ml of aqueous methanol was treated with a solution of 250 mg of sodium metaperiodate in 70 ml of water, and the mixture was left in the dark at room temperature. After two days, the solution was deionized and evaporated to small volume. A day after the addition of $NaBH_4$ the polyol was cleaved in the same way as the gypsogenin glucuronoside. Glucuronic acid was identified by paper chromatography in system 3.

Full Methyl Ether of Xanthoceras Saponin. The methylation of 1 g of (I) was performed by Hakomori's method. This gave 0.8 g of permethylate, which was cleaved with perchloric acid, and by gas-liquid and thin-layer chromatography in system 5 methyl 2-O-methyl-D-glucuronate, 2,3,4-tri-O-methyl-L-arabinose and 2,3,4,6-tetra-O-methyl-D-galactose were identified.

Alkaline Saponification of Xanthoceras Saponin. A mixture of 50 mg of (I) and 10 ml of 10% aqueous ethanolic caustic potash was heated at 80° C for 5 h. After extraction with isoamyl alcohol, the initial substance was detected in the organic extract by thin-layer chromatography.

Partial Hydrolysis of Xanthoceras Saponin. A mixture of 2 g of (I) and 200 ml of 10% oxalic acid was heated at 75° C for 10 h. After extraction with butan-1-ol, the organic extract was evaporated and the residue was chromatographed on a column in system 2. This gave 0.2 g of a substance with $[\alpha]_D^{20}$ + 21° (c 1.2; ethanol), 36 mg of compound (II) with $[\alpha]_D^{20}$ – 67° (c 1.2; methanol), and 39 mg of the derivative (III) with $[\alpha]_D^{20}$ – 20.5° (c 1.95; methanol).

Acid Hydrolysis of the Progenins. When 20 mg of (II) was hydrolyzed with 2% H_2SO_4, glucuronic acid and glucose were identified, and in the case of (III) glucuronic acid, glucose, and arabinose. When (II) was oxidized under the conditions given above, glucuronic acid was identified.

SUMMARY

It has been established that xanthoceras saponin is O-β-arabopyranosyl-(1 → 4)-[O-β-galactopyranosyl-(1 → 6)-O-β-glucopyranosyl-(1 → 3)]-O-β-glucuronopyranosyl-(1 → 3)-gypsogenin.

LITERATURE CITED

1. V. Ya. Chirva, P. K. Kintya, and V. A. Sosnovskii, Khim. Prirodn. Soedin., 6, 328 (1970).
2. H. Kiliani, Ber., 2866 (1930).
3. N. K. Abubakirov and K. A. Amanmuradov, Zh. Obshch. Khim., 34, 1661 (1964).
4. N. K. Kochetkov, A. Ya. Khorlin, and Yu. S. Ovodov, Izv. Akad. Nauk SSSR, Ser. Khim., 1436 (1964).
5. S. Hakomori, J. Biochem. (Tokyo), 55, 205 (1964).
6. M. Abdel-Akher, J. K. Hamilton, R. Montgomery, and F. Smith, J. Amer. Chem. Soc., 74, 4970 (1952).