TRITERPENE GLYCOSIDES OF SAPINDUS MUKOROSSI

V. The Structure Of Sapindoside D

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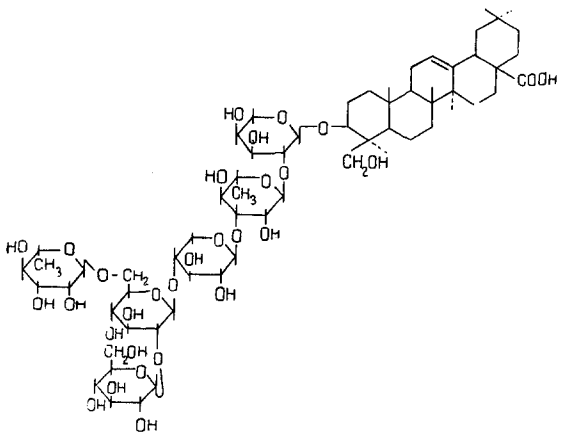
Having investigated the triterpene glycosides of Sapindus mukorossi (Chinese soapberry) [1-4], from a methanolic extract of the fruit of this plant we have obtained sapindoside D by chromatography on silica gel. Below we give a proof of its structure.

As previously, sapindoside D contains hederagenin as the aglycone, and the carbohydrate moiety contains glucose (2 moles), arabinose (1 mole), xylose (1 mole), and rhamnose (2 moles).

The main features of the structure of the glycosides were elucidated by studying the products of the cleavage of permethylated sapindoside D. The isolation of the methyl ester of 23-O-methylhederagenin shows that the single carbohydrate chain is attached to the hydroxyl group at C_3 of the aglycone. Among the methylated monosaccharides the following were detected and identified in the presence of reference samples: 3, 4-di-O-methyl-L-arabinose; 2, 4-di-O-methyl-L-rhamnose; 2, 3, 4-tri-O-methyl-L-rhamnose; 2, 3, 4, 6-tetra-O-methyl-D-glucose; and 2, 3-di-O-methyl-D-xylose. 3, 4-Di-O-methyl-D-glucose was also obtained, its structure being shown in the following way. By means of deuteromethyl iodide it was converted into the completely substituted derivative. The presence in its mass spectrum of peaks with m/e 76, 78, 88, 91, 104, and 179 shows the positions of the trideuteromethyl groups to be on the second and sixth carbon atoms, which enables the monosaccharide to be ascribed unambiguously the structure of 3, 4-di-O-methyl-D-glucopyranose [5]. Among the methylated sugars Bonner's reagent showed the presence of glucose and arabinose [6].

We obtained further information on the structure of sapindoside D by partial hydrolysis. Using preparative chromatography on silica gel, sapindosides A, B, and C and an arabinoside and a pentaoside of hederagenin were isolated from the reaction mixture and were identified by their melting points and monosaccharide composition. The carbohydrate part of the last progenin contained arabinose, xylose, rhamnose, and glucose. Thin-layer chromatography showed the presence in a hydrolysate of the permethylated substance of 2, 3, 4-tri-O-methyl-D-glucose, in addition to 2, 4-di-O-methyl-L-rhamnose, 3, 4-di-O-methyl-L-arabinose, 2, 3-di-O-methyl-D-xylose, and 2, 3, 4-tri-O-methyl-L-rhamnose. This result is an additional confirmation of the structure of 3, 4-di-O-methyl-D-glucose, and also of the fact that the branching in the carbohydrate chain of the initial glycoside is due to a terminal glucose residue attached to the C_2OH group of the nonterminal glucose. Thus, we give the final form of the sapindoside as follows:



Calculations of the configurations of the glycoside centers in the saponin are shown in the table.

Glycosides of the monosaccharides	$[M]_D^{20}$, deg.		Glycosides	$[M]_D^{20}$, deg.	ΔC	Form of the bond
	α	β				
Methyl D-glucopyranoside [8]	+309	— 66	Sapindoside D	+616	—	—
			Pentaoside	−448	+1064	α
Methyl L-rhamnopyranoside [7]	−111	+170	Pentaoside	−448	—	—
			Tetraoside*	— 58	— 390	α

*We have previously determined the configuration of the glycosidic centers of the monosaccharides of the tetraoside of sapindoside C [1].

EXPERIMENTAL

Chromatography was carried out with type S paper of the Leningrad Volodarskii Mill and with KSK silica gel, using the following solvent systems: 1) butan-1-ol–ethanol–25% ammonia (9 : 2 : 5), 2) ethyl acetate–methanol–water (10 : 2 : 3), 3) butanol–benzene–pyridine–water (5 : 1 : 3 : 3), 4) benzene–acetone (2 : 1), 5) chloroform–ethyl acetate (3 : 1). The sugars were revealed with aniline phthalate, and the glycosides with antimony trichloride in chloroform and with conc H_2SO_4.

Isolation of sapindoside D. A 5-g quantity of the combined saponins was chromatographed on silica gel in system 1. After repeated separations, 0.8 g of a pure substance with mp 100–102° C, $[\alpha]_D^{20}$ +44° (*c* 1.3, methanol) was obtained.

Methylation of sapindoside D. Sapindoside D, 100 mg, was methylated by Hakomori's method [9]. This gave 100 mg of the permethylated product, 50 mg of which was treated with 0.1 ml of 72% perchloric acid and 1 ml of methanol, and the mixture was heated in a sealed tube at 100° C for 5 hr. Then it was diluted with water and the resulting precipitate was found in system 5, in the presence of markers, to contain the methyl ester of 23-O-methylhederagenin; and the filtrate was found by chromatography in system 4 to contain 3,4-di-O-methyl-L-arabinose, 2,3-di-O-methyl-D-xylose, 2,4-di-O-methyl-L-rhamnose, 2,3,4-tri-O-methyl-L-rhamnose, and 2,3,4,6-tetra-O-methyl-D-glucose.

Stepwise hydrolysis of sapindoside D. A mixture of 2 g of sapindoside D and 60 ml of 10% oxalic acid was heated at 78° C for 10 hr. After dilution with water, the reaction mixture was exhaustively extracted with isopentyl alcohol. Then the extract was concentrated and separated on silica gel in system 2. This gave 0.2 g of hederagenin, 0.3 g of a monooside with mp 226–228° C, $[\alpha]_D^{20}$ +58.2° (*c* 2.6, methanol); 0.5 g of a bioside of hederagenin with mp 214–216° C, $[\alpha]_D^{20}$ +16.5° (c 4.85, methanol); 0.15 g of a trioside with mp 276–278° C, $[\alpha]_D^{20}$ +17.5° (*c* 2.85, methanol); 0.2 g of a tetraoside of hederagenin with mp 235–236° C, $[\alpha]_D^{20}$ −5.5° (*c* 7.2, methanol); and 0.3 g of a pentaoside with $[\alpha]_D^{20}$ −35° (*c* 0.57, methanol).

The acid hydrolysis of the monooside of hederagenin gave, as shown by paper chromatography in system 3, arabinose; that of the bioside gave arabinose and rhamnose, that of the trioside gave arabinose, rhamnose, and xylose; and those of the tetraoside and pentaoside gave arabinose, rhamnose, xylose, and glucose.

Periodate oxidation of sapindoside D. A solution of 100 mg of the saponin in 40 ml of aqueous methanol was treated with 250 ml of sodium metaperiodate dissolved in 70 ml of water and the mixture was left to stand at room temperature in the dark for 3 days. Then it was deionized with KU-2 and AV-17 resins (H^+ and OH^- forms, respectively). The eluate was evaporated and rhamnose and glucose were identified by paper chromatography in system 3.

Methylation of the hederagenin pentaoside. A 75-mg quantity of the substance was methylated in a manner similar to that described above. After the separation of the permethylated pentaoside by thin-layer and gas-liquid chromatography, 3,4-di-O-methyl-L-arabinose, 2,3-di-O-methyl-D-xylose, 2,4-di-O-methyl-L-rhamnose, 2,3,4-tri-O-methyl-L-rhamnose, and 2,3,4-tri-O-methyl-D-glucose were detected.

CONCLUSIONS

The structure of sapindoside D, which is a hexaoside of hederagenin, has been shown.

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