TRITERPENE GLYCOSIDES OF SAPINDUS MUKOROSSI

II. The Structure of Sapindosides A and B

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In a preceding communication [1] we reported the isolation from the fruit of Sapindus mukorossi Gaertn. (Chinese soapberry) of five triterpene glycosides called sapindosides A, B, C, D, and E.

It was shown that the first two compounds are glycosides of hederagenin and that the carbohydrate moiety of sapindoside A contained arabinose and rhamnose and that of sapindoside B arabinose, xylose, and rhamnose, and that the glycosides have no O-acyl glycosidic bond.

The present paper gives data on the structures of sapindosides A and B. To show the absence of furanose forms of the sugars in the glycosides, we heated the sapindosides with dilute oxalic acid (under these conditions furanoside bonds generally undergo cleavage). The glycosides were recovered unchanged.

The general features of the structure of sapindoside A were found by its oxidation by Smith's method [2]. This showed that neither of the monosaccharides was retained, so that this excludes a 1 → 3 bond between them. In addition, only ethylene glycol was identified in the hydrolysate and consequently a 1 → 4 bond between the monosaccharides is impossible.

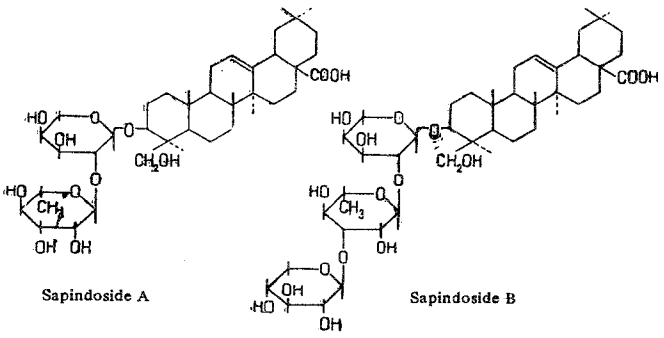
The Smith oxidation of sapindoside B yielded ethylene glycol and rhamnose, which shows the presence of 1 → 2 and 1 → 3 bonds in the glycoside.

The results were then confirmed by methylation [3, 4], as a result of which 3, 4-di-O-methyl-L-arabopyranose and 2, 3, 4-tri-O-methyl-L-rhamnopyranose were identified in the case of sapindoside A, and 3, 4-di-O-methyl-L-arabopyranose, 2, 3, 4-tri-O-methyl-D-xylopyranose, and 2, 4-di-O-methyl-L-rhamnopyranose in the case of sapindoside B. The methylated sugars were identified by paper, thin-layer, and gas-liquid chromatography in the presence of authentic samples.

Methanolysis of the permethylated sapindosides gave a crystalline substance similar in melting point and specific rotation to the methyl ester of 2,3-O-methylhederagenin [5]. This shows that in the glycosides the carbohydrate moiety is attached to the secondary hydroxyl at $C_{(3)}$ of the aglycone.

To determine the nature of the glycosidic centers and the sequence of the monosaccharides in the carbohydrate chain, we performed partial hydrolysis with oxalic acid. Both glycosides yielded hederagenin arabopyranoside. In addition, sapindoside B gave a bioside consisting of hederagenin, arabinose, and rhamnose.

On the basis of these results, the structures of sapindosides A and B can be represented in the following way:



The configurations of the glycosidic bonds were determined from Klyne's rule [6] (table).

Table

Glycosides of the monosaccharides	$[M]_D^{20}$ deg		Glycosides	$[M]_D^{20}$ deg	Δc	Form of the bond
	α	β				
Methyl D-sylopyranoside	+253	—108	Trioside	+165	+ 35	β
Methyl L-rhamnopyranoside	—111	+170	Bioside	+130	—225	α
		+402	Monooside	+355		
Methyl L-arabinoside	± 28		Hederagenin	+368	— 13	α

Thus, sapindoside A is identical with kalopanax saponin A [7].

EXPERIMENTAL

Chromatography was carried out with type KSK silica gel and type "M" paper of the Volodarskii Leningrad Mill. The following systems of solvents were used: 1) butan-1-ol–ethanol–25% ammonia (9 : 2 : 5), 2) toluene–ethanol (9 : 1), 3) butan-1-ol–pyridine–benzene–water (5 : 3 : 1 : 3), and 4) ethyl acetate–methanol–water (10 : 2 : 5). The sugars were revealed on the chromatograms with aniline phthalate and potassium periodatocuprate and the glycosides with a solution of $SbCl_3$ containing 5% of $SbCl_5$ in chloroform or with conc H_2SO_4.

Sapindosides A and B. Four grams of a mixture of sapindosides A and B was repeatedly separated on silica gel in system 1. The yield of sapindoside A was 1 g and of sapindoside B 3 g. The melting points of the sapindosides were: A 214–216° C, B 276–278° C, and their rotations A $[\alpha]_D^{20}$ +16.5° (c 4.85; methanol) and B $[\alpha]_D^{20}$ +17.5° (c 2.85; methanol).

Smith degradation of sapindosides A and B. A solution of 50 mg of sapindoside A in 20 ml of water was left in the dark at room temperature. After 3 days the solution was deionized by means of KU-2 (H^+ form) and AV-17 (OH^- form) resins, and the solution was evaporated to a volume of 15 ml and treated with 30 mg of $NaBH_4$. After a day, the reducing agent was eliminated and the polyol was heated with 10 ml of 1 N H_2SO_4 for 5 hr. A chromatogram in system 3 showed the presence of ethylene glycol. The similar treatment of sapindoside B gave ethylene glycol and rhamnose.

Methylation of sapindosides A and B. In a minimum volume of dimethyl sulfoxide, 0.5 g of the substance was dissolved and 15 ml of methylsulfinyl carbanion was added. The mixture was stirred in a current of argon at room temperature for 10 min, after which an excess of methyl iodide was added and stirring was continued for another 20 min. Then the reaction mixture was diluted with water and exhaustively extracted with chloroform. The yield of fully methylated product was 0.45 g. The completeness of methylation was checked by chromatography on alumina in system 2 and by IR spectroscopy in the 3400 cm^{-1} region.

Then, 0.5 g of the permethylated substance was treated with 5 ml of absolute methanol and 0.5 ml of 72% perchloric acid and, after being heated on the water bath, the solution was diluted with water, and the aglycone was filtered off and recrystallized from ethanol. This gave a substance with mp 218–220° C (from ethanol), $[\alpha]_D^{20}$ +69° (c 1.5; chloroform). The filtrate was neutralized with AV-17 ion-exchanger (OH^- form). The hydrolysate of sapindoside A was shown by paper, thin-layer, and gas-liquid chromatography with reference samples to contain 2, 3, 4-tri-O-methyl-L-rhamnopyranose and 3, 4-di-O-methyl-L-arabinose with $[\alpha]_D^{20}$ +118° (c 3.62; methanol). The hydrolysate of spindoside B was found to contain 3, 4-di-O-methyl-L-arabopyranose, 2, 4-di-O-methyl-L-rhamnose with $[\alpha]_D^{20}$ +65° (c 2.45; methanol) and 2, 3, 4-tri-O-methyl-D-xylopyranose. The presence of 3, 4-di-O-methylarabinose was shown by mass spectrometry*.

Partial hydrolysis of sapindosides A and B. A mixture of 1 g of sapindoside A and 30 ml of 10% oxalic acid was heated at 78° C for 10 hr. The reaction mixture was diluted with water and exhaustively extracted with isoamyl alcohol. After concentration, the extract was chromatographed on silica gel in system 4, which gave us 0.25 g of hederagenin, monooside [mp 226–228° C, $[\alpha]_D^{20}$ +58.2 (c 2.6; methanol)], and 0.15 g of the initial glycoside.

On acid hydrolysis of the hederagenin monooside, paper chromatography showed the presence of arabinose.

*The mass spectra were taken by B. M. Zolotarev in the laboratory of Physical Methods of Investigation (IOKh [Institute of Organic Chemistry], Moscow).

Under similar conditions, 1 g of sapindoside B gave 0.2 g of hederagenin, 0.22 g of a monooside and 0.20 g of a bioside of hederagenin, and 0.1 g of the initial glycoside. Acid hydrolysis of the monooside formed arabinose and that of the bioside formed arabinose and rhamnose.

CONCLUSIONS

The structure of two triterpene glycosides from Sapindus mukorossi Gaertn. has been established. It has been shown that sapindoside A is hederagenin 3-O-α-L-arabinosyl-(2 → 1)-α-L-rhamnopyranoside and sapindoside B is the 3-O-α-L-arabopyranosyl-(2 → 1)-O-α-L-rhamnopyranosyl-(3 → 1)-β-D-xylopyranoside.

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