TRITERPENE GLYCOSIDES OF SAPINDUS MUKOROSSI

V. Structure of Sapindoside E

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Sapindoside E (I) is the only glycoside of Sapindus mukorossi (Chinese soapberry) belonging to the acylosides [1]. Acid hydrolysis has shown that it consists of hederagenin, D-glucose, L-arabinose, D-xylose, and L-rhamnose (1 : 2 : 2 : 2 : 3).

In order to simplify the proof of the structure of the glycoside I and simultaneously to elucidate the composition of its acyl moiety, we saponified the ester bond with caustic potash. The resulting glycoside was identical in chromatographic mobility and monomeric composition with sapindoside B [2]. The oligosaccharide (II) was found to contain glucose, xylose, and rhamnose.

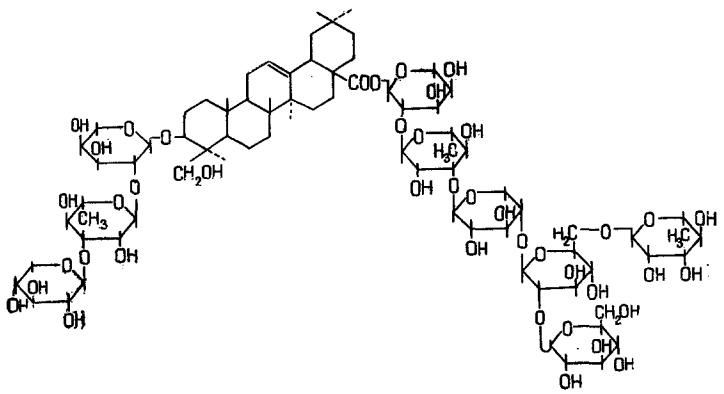
To determine the type of bonds between the monosaccharides, sapindoside E was converted into the permethylated derivative and then treated with lithium aluminum hydride. In the reduced glycoside 3,4-di-O-methyl-L-arabinose, 2,4-di-O-methyl-L-rhamnose, and 2,3,4-tri-O-methyl-D-xylose were identified by thin-layer and gas-liquid chromatography in the presence of markers, and in the reduced oligosaccharide 3,4-di-O-methyl-L-arabitol, 2,4-di-O-methyl-L-rhamnose, 2,3-di-O-methyl-D-xylose, 3,4-di-O-methyl-D-glucose, 2,3,4-tri-O-methyl-L-rhamnose, and 2,3,4,6-tetra-O-methyl-D-glucose. When the saponin was cleaved by Smith's method [3], rhamnose and glycerol were found.

The results of methylation and of periodate oxidation show that the acyl moiety of sapindoside E has a structure which is the same, or similar, to the carbohydrate component on C_3 of the aglycone of sapindoside D [4]. To determine the sequence of the monosaccharides attached to the carboxyl group in the glycoside I we used partial hydrolysis, which, however, did not give satisfactory results.

The action of diastase on the oligosaccharide II gave a new oligosaccharide III which, on acid hydrolysis, split into glucose, rhamnose, and xylose and had a xylose residue at the reducing end. According to the R_f value and the methylation products, this compound was identical with the oligosaccharide arising in the diastase cleavage of sapindoside D and having the following structure.

$$\alpha\text{-L-Rha}_p 1 \begin{matrix} \nearrow 6 \\ \searrow 2 \end{matrix} \text{G}_p \text{ 1-4 Xyl}_p$$
$$\alpha\text{-D-G}_p \text{ 1}$$

Thus, the most probable structure for sapindoside E can be expressed by formula I.



EXPERIMENTAL

Chromatography was carried out with type C paper of the Volodarskii Leningrad 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) butan-1-ol–benzene–pyridine–water (5 : 1 : 3 : 3), 4) benzene–acetone (2 : 1), and 5) chloroform–ethyl acetate (3 : 1). The sugars were developed with aniline phthalate and the glycosides with antimony trichloride in chloroform and with H_2SO_4.

Isolation of sapindoside E. The total saponins (12 g) were chromatographed several times on silica gel in system 1. This gave 4 g of an individual substance with mp 164–166° C, $[\alpha]_D^{20}$ −45.4° (C 1.76, methanol).

Hydrolysis of sapindoside E. A mixture of 100 mg of sapindoside E and 10 ml of 2% H_2SO_4 was heated in a sealed tube at 110° C for 5 hr. Then the hydrolysate was diluted with 15 ml of water and extracted with ether. After concentration of the organic layer, the residue was recrystallized from methanol. This gave 25 mg of a substance with mp 226–228° C, $[\alpha]_D^{20}$ +79° (C 2.0, chloroform). From its chromatographic mobility in a thin layer of silica gel in system 5, the compound was identical with hederagenin. By paper chromatography in system 3, arabinose, xylose, rhamnose, and glucose were found in the aqueous solution after neutralization with EDE-10P resin (OH-form).

Methylation of sapindoside E. The saponin (100 mg) was methylated by Hakomori's method [5], yielding 100 mg of permethylated product. A mixture of 40 mg of the fully methylated substance and 0.1 ml of 72% perchloric acid in 1 ml of methanol was heated in a sealed tube at 100° C for 5 hr. After the reaction ceased, the mixture was diluted with water and the precipitate was filtered off. After neutralization of the filtrate the following sugar derivatives were identified in a thin layer of silica gel in system 4: 3,4-di-O-methyl-L-arabinose, 2,4-di-O-methyl-L-rhamnose, 2, 3-di-O-methyl-D-xylose, 3,4-di-O-methyl-D-glucose, 2,3,4-tri-O-methyl-D-xylose, 2,3,4-tri-O-methyl-L-rhamnose, and 2,3,4,6-tetra-O-methyl-D-glucose.

Aluminum hydride cleavage of the methylated sapindoside E. A solution of 0.6 g of the methylated saponin in 60 ml of absolute tetrahydrofuran was treated with 0.2 g of lithium aluminum hydride. The mixture was heated at the boil for 10 hr. A reduced glycoside and an oligosaccharide were obtained. By methanolysis and subsequent separation of the methyl glycosides in a thin layer of silica gel and also by gas-liquid chromatography the reduced glycoside was found to contain 3,4-di-O-methyl-L-arabinose, 2,4-di-O-methyl-L-rhamnose, and 2,3,4-tri-O-methyl-D-xylose, and the oligosaccharide 2,3-di-O-methyl-D-xylose, 2,4-di-O-methyl-L-rhamnose, 3,4-di-O-methyl-D-glucose, 2,3,4-tri-O-methyl-L-rhamnose, 2,3,4,6-tetra-O-methyl-D-glucose, and 3,4-di-O-methylarabitol.

Alkaline saponification of sapindoside E. A mixture of 1 g of the substance and 50 ml of 10% aqueous ethanolic caustic potash was heated at 80° C for 5 hr. After the elimination of the alkali, the solution was extracted repeatedly with isoamyl alcohol. The organic layer was evaporated and, after chromatographic purification in system 1, the substance was hydrolyzed with 2% H_2SO_4. Arabinose, rhamnose, and xylose were detected. The aqueous layer was evaporated and hydrolyzed under the conditions described above. Glucose, rhamnose, and xylose were identified.

Partial hydrolysis of sapindoside E. A mixture of 1 g of the saponin and 30 ml of 10% oxalic acid was heated at 78° C for 10 hr. Then the reaction mixture was diluted with water and extracted with isoamyl alcohol. After concentration, the extracts were chromatographed in system 2. This yielded 0.1 g of hederagenin, 0.16 g of a monoside with mp 226–228° C, $[\alpha]_D^{20}$ +58.2° (C 2.6, methanol), 0.28 g of sapindoside A with mp 214–216° C, $[\alpha]_D^{20}$ +16.5° (C 4.85, methanol), and 0.37 g of sapindoside B with mp 276–278° C, $[\alpha]_D^{20}$ +17.5° (C 2.85, methanol).

Smith degradation of sapindoside E. A solution of 1.2 g of sodium metaperiodate in 350 ml of water was added to 0.5 g of the glycoside in 75 ml of water. After the consumption of the oxidizing agent had become constant, the solution was deionized and evaporated. The residue was dissolved in 25 ml of water and 0.25 g of sodium borohydride was added. After a day, the solution was neutralized and the eluate was evaporated. The resulting polyol was hydrolyzed, and rhamnose and glycerol were found by paper chromatography.

Enzymatic hydrolysis of the saponified oligosaccharide using diastase. A few milligrams of diastase was added to 0.3 g of the oligosaccharide in 100 ml of phosphate buffer, and the mixture was thermostated at 35° C. Then a less polar oligosaccharide was found in the substrate. The substance was obtained in the individual state by paper chromatography. The oligosaccharide (10 mg) was hydrolyzed with 2% H_2SO_4, and xylose, glucose, and rhamnose were identified. The same oligosaccharide (10 mg) was reduced with sodium borohydride and hydrolyzed as described above. Xylitol, glucose, and rhamnose were identified by paper chromatography.

CONCLUSIONS

The structure of sapindoside E, a nonaoside of hederagenin,has been established.

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