

TRITERPENE GLYCOSIDES OF SAPINDUS MUKOROSI

III. Structure Of Sapindoside C

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In a further study of the chemical composition of the fruit of Sapindus mukorossi Gaerth. (Chinese soapberry) [1], from the mixture of saponins by chromatography on silica gel in a butan-1-ol-ethanol-ammonia (9 : 2 : 5) system we have isolated a triterpene glycoside, sapindoside C, with mp 235° C, $[\alpha]_D -5.5^\circ$ (c 7.2, methanol). The substance obtained is chromatographically homogeneous in a thin layer of silica gel in butan-1-ol-ethanol-water (10 : 2 : 5) and butan-1-ol-acetic acid-water (4 : 1 : 5) systems.

Like sapindosides A and B [2], sapindoside C contains the aglycone hederagenin and the monosaccharides glucose, arabinose, xylose, and rhamnose.

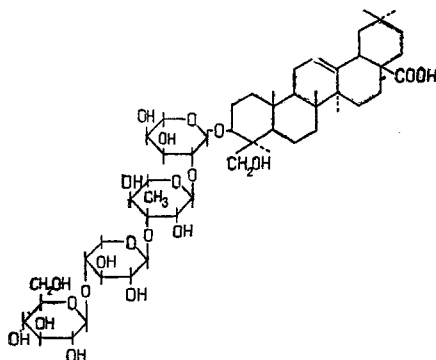
The hydrolytic cleavage of sapindoside C methylated with diazomethane leads to the formation of the methyl ester of hederagenin. This shows that the compound under study has no carbohydrate chain attached to the carboxyl group of the saponin.

To determine the nature of the linkages of the monosaccharides to one another, the glycoside was converted by Hakomori's method into the permethylated derivative [3]. On subsequent methanolysis of the glycoside, 2,3,4,6-tetra-O-methyl-D-glucose, 2,3-di-O-methyl-D-xylose, 2,4-di-O-methyl-L-rhamnose, and 3,4-di-O-methyl-L-arabinose were identified by gas-liquid chromatography and by thin-layer chromatography on silica gel in a benzene-acetone (2 : 1) system in the presence of markers. The methyl ester of 23-O-methylhederagenin was isolated as the aglycone [4]. These facts are confirmed by the degradation of sapindoside C by Smith's method [5], which showed that the rhamnose residue is not oxidized.

When the saponin was treated with a 10% solution of oxalic acid (80° C, 5 hr) the reaction mixture yielded hederagenin, hederagenin arabinoside, and sapindosides A and B, whose structures have been shown previously [2, 6].

The configurations of the glycoside centers in the saponin were determined from Klyne's rule [7] on the basis of the difference in the molecular rotations of sapindoside C and its progenins.

Thus, the final structure of this compound may be shown in the following manner.



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