STEROID SAPONINS

III.* GLYCOSIDES A AND B FROM Yucca filamentosa

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The presence of steroid sapogenins is characteristic for plants of the family Liliaceae [1]. In particular, from the roots and leaves of Yucca filamentosa L. (Adam's needle yucca) and Y. gloriosa (moundlily yucca) sarsapogenin, hecogenin, tigogenin, and chlorogenin have been isolated, but their carbohydrate moieties have not been studied [2-4].

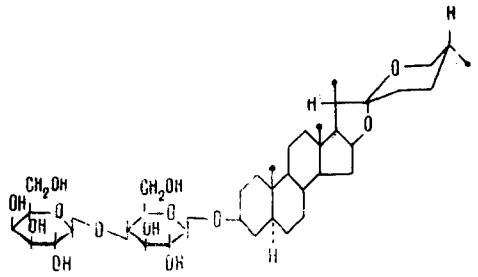
The present paper gives preliminary results of an investigation of the saponins of the roots of Yucca filamentosa collected in the Botanical Garden of the Academy of Sciences of the Moldavian SSR in the spring of 1971.

By qualitative tests in a thin layer of silica gel we showed that it contained not less than five substances. A methanolic extract, after concentration and dissolution in water, was separated with ethyl acetate and butanol into nonpolar and polar saponins. From the organic layer containing the nonpolar glycosides chromatography on silica gel yielded in the pure state two glycosides which have been called in increasing order of polarity substances A and B.

The first compound yielded as its aglycone a substance agreeing in melting point, specific rotation, and IR and mass spectra with an authentic sample of diosgenin. Glucose was found among the monosaccharides. The methylation of the glycoside by Hakomori's method [5] showed that the monosaccharide was in the pyranose form, which was additionally confirmed by the oxidation of substance A with sodium periodate. From its specific rotation and melting point, glycoside A was identified as trillin, isolated previously from Trillium erectum (purple trillium) [6].

Similar methods were used to determine the structure of substance B, which we have called yuccoside B. Acid cleavage of the saponin led to the formation of tigogenin, galactose, and glucose. The sequence of the monosaccharides and the type of bond between them in the saponin was shown by methylation, as a result of which 2,3,6-tri-O-methyl-D-glucose and 2,3,4,6-tetra-O-methyl-D-galactose were identified. On periodate oxidation, yuccoside B consumed about 3 moles of periodic acid and liberated 1 mole of formic acid. The substance gives a negative reaction with hydrazine hydrate [7], which confirms the pyranose form of the galactose. A calculation by Klyne's rule [8] showed the most probable existence of β-glycosidic bonds in the glycoside.

Thus, the structure of yuccoside B is as follows:



* For Communication II, see Khim. Prirodn. Soedin., 475 (1972).

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EXPERIMENTAL

Chromatography was performed on paper of the Leningrad mill, type S (medium) and silica gel of type KSK. Gas-liquid chromatography was performed on an LKhM-8M chromatograph with helium as the carrier gas and a flame-ionization detector at a temperature of 160° C using as the stationary phase 20% of Reoplex-400 on Chromosorb, 60-80 mesh, with a column 2 m long.

Isolation of the Total Saponins. The comminuted roots (1.5 kg) were extracted with 70% aqueous methanol. The extract was evaporated to dryness in a rotary evaporator at 50° C. Then the residue was dissolved in water and was extracted successively with ether, ethyl acetate, and butanol. The ethereal extracts were shown by thin-layer chromatography to contain sarsapogenin, hecogenin, tigogenin, and diosgenin. The ethyl acetate layer (3 g) consisted, according to thin-layer chromatography, predominantly of glycosides A and B. Other polar saponins were present in the butanol extract.

Substance A. The material from the ethyl acetate extract (1.5 g) was deposited on a column of silica gel and eluted with chloroform–methanol–ethyl acetate (3 : 1 : 1). This gave 300 mg of substance A with mp 265-276° C (from methanol), $[\alpha]_D^{20}$ –102° (c 1.3; pyridine) and 500 mg of yuccoside B with mp 285-286°C, $[\alpha]_D^{20}$ –19.5° (c 1.6; pyridine). Literature data for trillin: mp 269-271° C, $[\alpha]_D^{20}$ –103° (in dioxane).

The substance A (150 mg) was dissolved in 4 ml of methanol, and then 4 ml of 5% of H_2SO_4 was added and the mixture was heated at 100° C for 5 h. The precipitate that deposited was recrystallized twice from methanol. The aglycone so formed had mp 204-206° C, $[\alpha]_D^{20}$ –120°, mol. wt. 414. The mass and IR spectra of the aglycone coincided with those of diosgenin. Literature data for diosgenin: mp 205-206° C, $[\alpha]_D^{20}$ –121° [9].

Glycoside A (30 mg) was methylated by Hakamori's method. The products of methanolysis [72% $HClO_4$–methanol (1 : 10), 100° C, 3 h] were found by gas-liquid and thin-layer chromatography on silica gel in the benzene–acetone (2 : 1) system to contain 2,3,4,6-tetra-O-methyl-D-glucose. The saponin (20 mg) was oxidized with 40 mg of sodium periodate in 20 ml of methanol–water (1 : 1). After 48 h, 1.9 moles of $NaIO_4$ had been consumed per mole of substance.

Yuccoside B. Yuccoside B (150 mg) was hydrolyzed in the same way as glycoside A, giving 60 mg of an aglycone with mp 205-206° C, $[\alpha]_D^{20}$ –65° (c 1.5; chloroform), mol. wt. 416.

Tigogenin was identified by its chromatographic mobility in a thin layer of silica gel in the chloroform–methanol (12 : 1) system. The hydrolyzate after the separation of the precipitate was found by paper chromatography in the butanol–benzene–pyridine–water (5 : 1 : 3 : 3) system to contain galactose and glucose. As described above, 40 mg of yuccoside B was converted into the permethylated derivative. Among the cleavage products, 2,3,6-tri-O-methyl-D-glucose and 2,3,4,6-tetra-O-methyl-D-galactose were identified in the presence of synthetic samples.

Periodate Oxidation of Yuccoside B. A. Qualitative Characterization. To 20 mg of the saponin in methanol was added 50 mg of sodium periodate, and the mixture was left in the dark for two days. Then 1 ml of ethylene glycol was added and after an hour the solution was deionized. After concentration and hydrolysis no monosaccharides were found in the residue by chromatography.

B. Quantitative Determination. As for the case of glycoside A, it was found that the decomposition of glycoside B consumed 2.8 moles of oxidizing agent per mole of saponin.

SUMMARY

Two glycosides have been isolated from the roots of Yucca filamentosa L. One of them proved to be trillin, and the second – yuccoside B – 3-O-[galactopyranosyl-1(1→4)-glucopyranosyl]tigogenin.

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