THE STRUCTURE OF SAPONIN A FROM *Naumburgia thyrsiflora*

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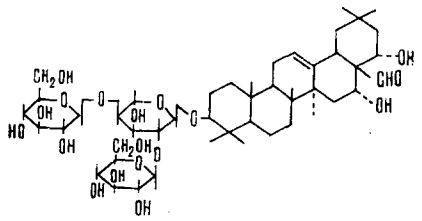
Naumburgia thyrsiflora (L) Rchb., family Primulaceae is a perennial herbaceous plant with a height of about 60 cm. It is widely distributed along the banks of the rivers, lakes, and marshes in the temperate zone. There is no information whatever on the chemical composition of *N. thyrisflora* in the literature. It has been established by the usual qualitative reactions [1] that the plant contains flavonoids saponins, and ascorbic acid.

By chromatography on silica gel in several solvent systems we have found six glycosides in it. Four saponins of low polarity were present in very small amounts and we have therefore not studied them. Two glycosides, with R_f 0.27 and 0.20, which we have called saponins A and B, amounted to about 80 % of the total saponins. These substances were isolated in the pure form by column chromatography on alumina, Sephadex, and silica gel.

When saponin A was subjected to acid hydrolysis, paper chromatography and thin-layer chromatography on silica gel and on "Silufol" plates with markers showed the presence of the aglycone priverogenin A, glucose, and arabinose. The melting points, specific rotations, and IR spectra of priverogenin A* and the aglycone obtained from saponin A coincided.

The results of a quantitative determination of the acetates of the aldononitrile derivatives of glucose and arabinose by gas–liquid chromatography (GLC) showed that their ratio was 2:1. The structure of the carbohydrate component of saponin A was demonstrated by comparing the results obtained by using a series of known methods. Thus, Kuhn methylation [2] followed by the hydrolysis of the permethylate of the saponin and the study of the resulting products by GLC led to the identification among the monosaccharides of 2,3,4,6-tetra-O-methyl-D-glucose and 3-O-methyl-L-arabinose. When saponin A was subjected to periodate oxidation, only the arabinose remained unchanged. By partial hydrolysis of the initial saponin we isolated priverogenin A arabinoside. The position of the carbohydrate chain was not determined, and its site of attachment is based on analogies with other glycosides of the β-amyrin series.

Thus, the structure of saponin A can be represented by the following formula:



*Priverogenin A and some other markers consisting of pure substances from the group of sapogenins of plants of the family Primulaceae were given to us by Prof. G. Wulff (University of Bonn, GRF).

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EXPERIMENTAL METHOD

Chromatography was performed on type S [medium] paper of the Volodarskii Leningrad Mill, type KSK silica gel, "Silufol" plates, neutral alumina, and Sephadex using the following solvent systems: 1) butan-1-ol–ethanol–water (10 : 2 : 5); 2) chloroform–methanol–water (65 : 35 : 19); 3) butan-1-ol–benzene–pyridine–water (5 : 1 : 3 : 3); 4) chloroform–methanol (9 : 1); 5) benzene–ethanol (9 : 1); and 6) butan-1-ol–acetic acid–water (4 : 1 : 5). The sugars were revealed with aniline phthalate and the glycosides and aglycones with antimony trichloride in chloroform and with a 25% ethanolic solution of phosphotungstic acid.

Isolation of the Saponins. The air-dry comminuted raw material (the whole plant) (1 kg) was exhaustively extracted with 70% ethanol. The combined extracts were evaporated to dryness. The residue was dissolved in hot water and was successively treated repeatedly with ether, ethyl acetate, and butan-1-ol. The butanolic extracts were combined and evaporated. This gave 120 g of total saponins, which were additonally purified on a column (25 × 8 cm) of neutral alumina with elution in system 1. The eluates were evaporated, and then the total material was freed from sugars by passing it through a column (50 × 3 cm) of Sephadex G-25 and washing with water. The fractions containing the saponins were collected. The yield was 72 g.

Isolation of Saponin A. The purified total saponins (2 g) were deposited on a dry column (30 × 3 cm) of silica gel. Elution was performed in system 1, giving 1.3 g of saponin A (I) with mp 248-258°C, $[\alpha]_D^{20}$ –8.0° (c 10; methanol). The individuality of the glycoside was checked by chromatography on plates in systems 2 and 6.

Acid Hydrolysis of Saponin A. The hydrolysis of 500 mg of (I) was performed with 2% sulfuric acid in dioxane–benzene at 110° C for 12 h. This yielded 230 mg of a substance with mp 196-198° C, $[\alpha]_D^{20}$ –6.5° (c 1.0; chloroform). Literature date for priverogenin A – mp 198-202° C, $[\alpha]_D^{20}$ –4.2° (c 0.9; chloroform) [3, 4].

From its chromatographic mobility in system 4, the substance obtained was identical with priverogenin A. In addition, the IR spectra of priverogenin A and of the aglycone obtained coincided completely.

The hydrolyzate was shown by paper chromatography in system 3 to contain glucose and arabinose. According to the GLC of the acetates of the aldononitrile derivatievs of the sugars obtained, their ratio was 2:1.

Smith Degradation of Saponin A [5]. A solution of 100 mg of (I) in 50 ml of water was treated with 250 mg of sodium metaperiodate and the mixture was left in the refrigerator for 48 h. Then 1-2 drops of ethylene glycol was added to the solution and it was left for 1 h, after which sodium tetrahydroborate was added. The product obtained after reduction was hydrolyzed with 2% H_2SO_4. Arabinose and glycerol were identified by paper chromatography in system 3.

Full Methyl Ether of Saponin A. Compound (I) (1 g) was methylated by Kuhn's method. This gave 0.75 g of a permethylate, which was cleaved with 7% perchloric acid in methanol. After additional hydrolysis, 2,3,4,6-tetra-O-methyl-D-glucose and 3-O-methyl-L-arabinose were identified by gas–liquid chromatography and by thin-layer chromatography in system 5. The methyl monomethylarabinoside gave a negative reaction with the Bonner reagent [6] but a positive one after the removal of the methyl group at the C_1 atom of arabinose with 2% H_2SO_4 (100° C, 3 h).

SUMMARY

Triterpene glycosides have been isolated from Naumburgia thyrsiflora (L.) Rchb. for the first time. It has been established that saponin A is a trioside of priverogenin A.

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