TRITERPENE GLYCOSIDES OF Gleditschia triacanthos

IV. THE STRUCTURE OF TRIACANTHOSIDES A_1 AND G

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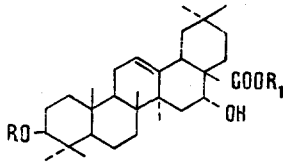
Continuing a study of the triterpene glycosides from the pericarps of Gleditschia triacanthos L. (family Leguminosae) [1], we have isolated triacanthoside A_1, composition $C_{46}H_{74}O_{17}$. According to acid hydrolysis and gas-liquid chromatography, triacanthoside A_1 contains D-glucose, L-arabinose, D-xylose, and echynocystic acid (I) in a ratio of 1:1:1:1. The glycoside is not saponified by alkali, which shows the absence of an acyloside carbohydrate chain in it. When triacanthoside A_1 (IV) was subjected to periodate oxidation, only the D-glucose remained unchanged. Exhaustive methylation of the glycoside followed by hydrolysis gave 2,3,4-tri-O-methyl-D-xylose, 2,3-di-O-methyl-L-arabinose, and 2,4,6-tri-O-methyl-D-glucose.

From the facts given, it can be seen that triacanthoside A_1 coincides in composition and properties with the trioside of echynocystic acid [2] obtained by the alkaline saponification of triacanthoside G (V), the structure of which has not yet been completely established.



I. $R=R_1=H$.

II. $R=\beta$—*D*—Glcp–; $R_1=H$.

III. $R=\alpha$—*L*—Arap (1→3)—β—*D*—Glcp–; $R_1=H$.

IV. $R=\beta$—*D*—Xylp (1→4)—α—*L*—Arap (1→3)—β—*D*—Glcp–; $R_1=H$.

V. $R=\beta$—*D*—Xylp (1→4)—α—*L*—Arap (1→3)—β—*D*—Glcp–:
R_1=*D*—Glcp (1→3)—*L*—Arap (1→4)—*L*—Rhap–.

In order to determine the structures of triacanthosides G (V) and A_1 (IV), we performed the stepwise hydrolysis of the trioside (the progenin of triacanthoside G) and of triacanthoside A_1 under similar conditions and obtained identical results. From the products of the hydrolysis of both the first and second glycoside we isolated a monoside of echynocystic acid, $C_{36}H_{58}O_9$ (II), and a bioside with the composition $C_{41}H_{66}O_{13}$ (III). The monosides from (IV) and from the progenin of triacanthoside G had identical properties and proved to be echynocystic acid 3-O-β-D-glucopyranoside. A study of the biosides from the same starting materials also showed that they were identical. Thus, the acid hydrolysis of both biosides performed under identical conditions gave D-glucose and L-arabinose. The exhaustive methylation of the biosides led to 2,3,4-tri-O-methyl-L-arabinose and 2,4,6-tri-O-methyl-D-glucose. Consequently, the bioside under investigation is echynocystic acid 3-O-[α-L-arabopyranosyl-(1→3)-O-β-D-glucopyranoside] (III). In this case, triacanthoside A_1 (the progenin of triacanthoside G) has the structure of echynocystic acid 3-O-[β-D-xylopyranosyl-(1→4)-O-α-L-arabopyranosyl-(1→3)-O-β-D-glucopyranoside] (IV). Triacanthoside G corresponds to structure V.

The configurations of the glycosidic bonds were determined from the differences in molecular rotations of (IV), (III), (II), and echynocystic acid.

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EXPERIMENTAL

Chromatography was performed on type KSK silica gel and on "M" ["slow"] paper of the Volodarskii Leningrad Mill. The following solvent systems were used: 1) chloroform–methanol–water (65 : 35 : 8); 2) chloroform–methanol (25 : 2); 3) butan-1-ol–pyridine–water (6 : 4 : 3); 4) benzene–acetone (2 : 1); and 5) methyl ethyl ketone saturated with water.

Isolation of Triacanthoside A_1. The fraction containing triacanthoside A_1 [1] was chromatographed on a column of silica gel (1 : 100) in system 1. The fractions were monitored by thin-layer chromatography in the same system. The fractions enriched in triacanthoside A_1 were combined and evaporated and rechromatographed on a column in system 1. The pure glycoside was isolated with mp 214-216°C (decomp.), $[\alpha]_D^{20}$ −16.8° (c 1.3; methanol). Its concentration in the raw material was 0.1%.

Action of Alkali on Triacanthoside A_1. A mixture of 10 mg of the glycoside and 2 ml of 10% caustic soda solution was heated at 90°C (5 h). After the cooling of the solution and the neutralization of the alkali thin-layer chromatography in system 1 showed the presence only of the initial glycoside.

Acid Hydrolysis of Triacanthoside A_1. A mixture of 50 mg of the glycoside and 10 ml of aqueous methanolic (1 : 1) sulfuric acid with a concentration of 5% was heated at 90°C (5 h). After recrystallization the precipitate that deposited had mp 304-306°C, $[\alpha]_D^{20}$ +31° (c 1.65; chloroform) and was identical with echynocystic acid in its chromatographic behavior in a thin layer of silica gel in system 2.

The aqueous part of the hydrolyzate was neutralized with barium carbonate, and paper chromatography in system 3 showed the presence of D-glucose, D-xylose, and L-arabinose.

Periodate Oxidation of Triacanthoside A_1. The oxidation of 50 mg of glycoside (IV) was performed under conditions similar to those for the oxidation of the trioside of echynocystic acid [2]. Only D-glucose was found among the residual sugars by chromatography in system 3.

Methylation of Triacanthoside A_1. The glycoside (IV) (50 mg) was methylated by Hakomori's method [3]. The products of the hydrolysis of the permethylate were shown by thin-layer chromatography in system 2 to contain 16-O-methylechynocystic acid and by paper chromatography in system 5 and thin-layer chromatography in system 4 with markers to contain 2,3,4-tri-O-methyl-D-xylose, 2,3-di-O-methyl-L-arabinose, and 2,4,6-tri-O-methyl-D-glucose.

Stepwise Hydrolysis of Triacanthoside A_1 and of the Progenin of Triacanthoside G. For each glycoside, 500 mg was heated in 30 ml of a 0.25% solution of sulfuric acid in aqueous methanol (1 : 1) at 90°C for 40 min. After cooling, the solutions were extracted with butan-1-ol, and the extracts were washed with water and evaporated to dryness. The hydrolysis products were separated by preparative thin-layer chromatography on 460× 350-mm plates in system 1. Apart from echynocystic acid and unchanged glycosides, in the one case 15 mg, and in the other case 12 mg, of the monoside of echynocystic acid (II) was isolated with mp 265-270°C (decomp.), $[\alpha]_D^{20}$ +17.9° (c 0.9; methanol) and 48 and 50 mg, respectively, of the bioside (III) with mp 220-224°C (decomp.), $[\alpha]_D^{20}$ −15.8° (c 12; methanol).

Hydrolysis of Echynocystic Acid β-D-Glucopyranoside. The monosides obtained in the preceding experiment (10 mg each) were hydrolyzed with 5% sulfuric acid at 90°C (5 h), each separately. Both hydrolyzates were shown by paper chromatography in system 3 to contain D-glucose and by thin-layer chromatography in system 2 to contain echynocystic acid (I).

Hydrolysis of the Echynocystic Acid Bioside (II). The biosides obtained in the stepwise hydrolysis of triacanthoside A_1 and of the progenin of triacanthoside G (15 mg in each case) were hydrolyzed separately as described above for the monosides. Paper chromatography in system 3 showed that the hydrolysis products contained D-glucose and L-arabinose, and thin-layer chromatography in system 2 showed the presence of echynocystic acid.

Methylation of the Biosides. The biosides from (IV) and (V) (30 mg each) were methylated by Hakomori's method [3]. The hydrolysis of each of the permethylates followed by paper chromatography in system 5 and thin-layer chromatography in system 4 with markers showed the formation of 2,3,4-tri-O-methyl-L-arabinose and 2,4,6-tri-O-methyl-D-glucose.

SUMMARY

The pericarps of Gleditschia triacanthos L. have yielded a new triterpene glycoside – triacanthoside A_1 – and it has been shown that it has the structure of echynocystic acid 3-O-[β-D-xylopyranosyl-(1→4)-α-L-arabopyranosyl-(1→3)-β-D-glucopyranoside].

It has been shown that the O-glycosidic moiety of triacanthoside G coincides in structure with triacanthoside A_1. The O-acyloside moiety of triacanthoside G contains the trisaccharide D-glucopyranosyl-(1→3)-O-L-arabopyranosyl-(1→4)-O-L-rhamnopyranose.

LITERATURE CITED

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