TRITERPENE GLYCOSIDES OF Gleditschia triacanthos

VI. THE STRUCTURE OF TRIACANTHOSIDE F

T. A. Badalbaeva, E. S. Kandratenko, and N. K. Abubakirov

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In a further separation of the mixture of triterpene glycosides from the pericarps of Gleditschia triacanthos [1] we have isolated triacanthoside F, in addition to triacanthosides A_1, C, and G. The new glycoside has the composition $C_{63}H_{102}O_{30}$, mp 208-218°C (decomp.) $[\alpha]_D^{20}$ −12.3° (c 1.55; 70% methanol).

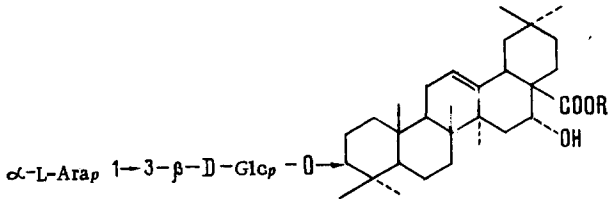
As a result of the hydrolysis of triacanthoside F with 5% sulfuric acid, echinocystic acid, D-glucose, D-xylose, L-rhamnose, and L-arabinose were identified.

Triacanthoside F was saponified with 10% caustic potash solution. A progenin was obtained which, according to its physical constants [mp 216-225°C (decomp.), $[\alpha]_D^{20}$ − 15° (c 1.25; methanol)], chromatographic behavior, and the results of periodate oxidation and exhaustive methylation, was identical with echinocystic acid 3-O-[α-L-arabopyranosyl-(1 → 3)-β-D-glucopyranoside]., i.e., gleditschoside E [2].

Acid hydrolysis of the oligosaccharide split-off gave D-glucose and D-xylose. The absence of L-rhamnose shows that it was directly attached to the carboxyl of the aglycone and was destroyed on alkaline hydrolysis. When triacanthoside F was subjected to periodate oxidation, only the D-glucose remained unaffected.

Hydrolysis of the permethylate of triacanthoside F, obtained by Hakamori's method yielded 2,3,4-tri-O-methyl-D-xylose, 2,3,4-tri-O-methyl-L-arabinose, 2,4,6-tri-O-methyl-D-glucose, 2,3-di-O-methyl-D-xylose, 2,3-di-O-methyl-L-rhamnose, and 16-O-methylechinocystic acid.

Consequently, the acyloside chain is attached to the carboxyl of the aglycone through the L-rhamnose. The sequence of the other two sugars (D-xylose and D-glucose) between the L-rhamnose and the terminal D-xylose remains obscure, although it has been established that the intermediate D-xylose is attached to the next sugar through the fourth and the D-glucose through the third hydroxyl. The L-rhamnose is attached to the following trisaccharide through the C_4 hydroxyl.



I. $R = L-Rhap\,4 \leftarrow 1-D-Xylp\,4 \leftarrow 1-D-Glcp\,3 \leftarrow 1-D-Xylp$

II. $R = L-Rhap\,4 \leftarrow 1-D-Glcp\,3 \leftarrow 1-D-Xylp\,4 \leftarrow 1-D-Xylp$

On the basis of the results given, one of the above two possible variants of the structure may be proposed for triacanthoside F.

LITERATURE CITED

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