TRITERPENE GLYCOSIDES OF Acanthophyllum paniculata

II. STRUCTURE OF PANICULATOSIDE C

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As reported previously [1], from the roots of Acanthophyllum paniculata L. we have obtained the total triterpene glyclosides, including paniculatosides A, B, C, D, E, and F with the common aglycone gypsogenin.

However, subsequently, after preparative reduction with sodium tetrahydroborate [2] of the combined glycosides and acid hydrolysis, gypsogenic acid was found chromatographically, in addition to hederagenin.

When the combined glycosides were separated on a column of silica gel in the chloroform–methanol–water (65 : 35 : 8) system, a glycoside of gypsogenic acid – paniculatoside C – with the composition $C_{54}H_{86}O_{25}$, mp 220-230°C (decomp.), $[\alpha]_D^{20}$ + 5.3° (c 1.49; water) was isolated.

The hydrolysis of paniculatoside C with 5% H_2SO_4 for 7 h with heating gave an aglycone with mp > 350°C (decomp.), $[\alpha]_D^{20}$ + 97.6° (c 1.29; dioxane), which was identified through its physicochemical properties as gypsogenic acid [3]; it gave no depression of the melting point in admixture with an authentic sample.

Thin-layer chromatography (TLC) of the hydrolyzate, after neutralization with $BaCO_3$, in a layer of silica gel impregnated with a 0.3 M solution of NaH_2PO_4 in the butan-1-ol–methanol–water (5 : 3 : 1) system showed the presence of D-glucose. Alkaline hydrolysis of the glycoside with a 10% aqueous solution of KOH on the boiling water for 6 h gave gypsogenic acid, which shows the presence of only an acyloside carbohydrate chain in the glycoside. An attempt at the lactonization of paniculatoside C [4] did not lead to the formation of gypsogenic acid lactone, which shows the attachment of the carbohydrate chain to the carboxy group at C_{17} of the aglycone.

The product of the Hakamori methylation of the glycoside was hydrolyzed with 5% H_2SO_4, and the reaction products were found by TLC with markers in the benzene–acetone (2 : 1) system to contain 2,3-di-O-methyl-D-glucose, 2,3,4-tri-O-methyl-D-glucose, and 2,3,4,6-tetra-O-methyl-D-glucose, the spot of the last being twice as intense as the spots of the first two methylated sugars. Consequently, paniculatoside C contains four glucose molecules.

It follows from the presence of 2,3-di-O-methyl-D-glucose that this molecule of D-glucose is a center of branching.

The acid hydrolysis of the permethylate of paniculatoside C with subsequent acid hydrolysis of the oligosugar split out gave only 2,3,4-tri-O-methyl-D-glucose and 2,3,4,6-tetra-O-methyl-D-glucose. The absence of 2,3-di-O-methyl-D-glucose can be explained only by the assumption that it was attached directly to the carboxyl of the aglycone and underwent degradation in the process of alkaline hydrolysis.

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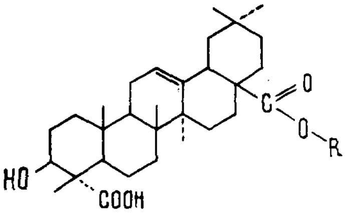

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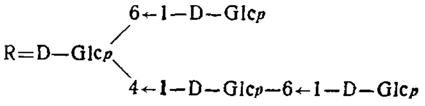
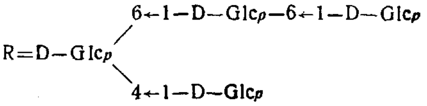


$$R=\text{D—Glc}p\begin{array}{l}\diagup\, 6\leftarrow 1\text{—D—Glc}p\\ \diagdown\, 4\leftarrow 1\text{—D—Glc}p\text{—}6\leftarrow 1\text{—D—Glc}p\end{array}$$

II,



$$R=\text{D—Glc}p\begin{array}{l}\diagup\, 6\leftarrow 1\text{—D—Glc}p\text{—}6\leftarrow 1\text{—D—Glc}p\\ \diagdown\, 4\leftarrow 1\text{—D—Glc}p\end{array}$$

Thus, one of two variants of the above structure may be proposed for paniculatoside C.

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