TRITERPENE GLYCOSIDES OF ACANTHOPHYLLUM GYPSOPHILOIDES

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The isolation from Acanthophyllum gypsophiloides Rgl. of a glycoside which, on the basis of the qualitative composition of the sugars and the common aglycone, and also its chromatographic behavior, was identified as gypsoside, a triterpene glycoside from Gypsophilla pacifica [2], has been reported previously [1].

However, even then we showed that some of the physicochemical properties were different. In this paper we give information showing quite unambiguously that the compound from Acanthophyllum gypsophiloides has a structure differing from that of gypsoside.

In a detailed study of a methanolic extract of the roots of the plant by thin-layer chromatography (TLC) on KSK silica gel in system 1 [butan-1-ol–ethanol–25% ammonia (7 : 2 : 5)], in addition to the main glycoside we found a small amount of another less polar glycoside. In order of increasing polarity, we have called this glycoside "acanthophylloside" A and the main glycoside acanthophylloside B.

Acanthophylloside B was oxidized with 1% sodium periodate solution in the cold. After the decomposition of the excess periodate with ethylene glycol, the oxidation product of the glycoside was hydrolyzed by being heated with 5% H_2SO_4 for 6 hr. In the purified hydrolysate by paper chromatography in system 2 [butan-1-ol–acetic acid–water (4 : 1 : 5)] we identified D-glucuronic acid, D-fucose, and D-xylose. When gypsoside was oxidized under the same conditions, in addition to these sugars L-rhamnose was found [2]. Therefore, even if gypsoside and acanthophylloside B have the same quantitative sugar composition, their carbohydrate chains have different structures.

In order to elucidate the qualitative composition of the sugars in the acyloside part of the molecule and in the chain attached to the hydroxyl at C_3, we subjected acanthophylloside B to alkaline hydrolysis by heating it in 10% NaOH for 6 hr. The hydrolysate was neutralized with dil H_2SO_4 and extracted with butanol. The butanol extracts were evaporated and chromatographed on a column of KSK silica gel in system 3 [butan-1-ol–ethanol–water (10 : 2 : 5)]. The fractions containing the saponified glycoside (the fractions being monitored by TLC on silica gel in the same system) were evaporated and hydrolyzed with 5% H_2SO_4 with heating for 6 hr. The hydrolysate was shown by chromatography in system 2 to contain D-galactose, L-arabinose, and D-glucuronic acid. Consequently, these sugars, present in the carbohydrate chain of acanthophylloside B, are attached to the hydroxyl at C_3, in contrast to gypsoside in which the same chain also contains D-glucose.

The aqueous part of the alkaline hydrolysate, freed from glycosides, was also hydrolyzed with 5% H_2SO_4 and then chromatographed on paper in system 2. D-Glucose, D-xylose, and L-rhamnose were found. The absence of D-fucose can be explained by assuming that it is attached directly to the carboxyl group of the gypsogenin and was decomposed under the alkaline hydrolysis conditions. This means that the acyloside carbohydrate chain of acanthophylloside B is not identical with the corresponding chain of gypsoside either, in view of the presence of D-glucose and the fact that it is D-fucose and not L-rhamnose that is attached directly to the aglycone.

Thus, acanthophylloside B differs from gypsoside by the composition and structure of the two carbohydrate chains and is a new triterpene glycoside which has not been previously described in the literature.

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