GLUCOGITOROSIDE FROM Digitalis ciliata

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The combined primary glycosides of the leaves of Digitalis ciliata Trautv. isolated by extraction with a mixture of ethanol and chloroform [1] was separated by partition chromatography on silica gel [2] (with water as the stationary phase and ethyl acetate as the mobile phase). An individual glycoside was obtained with the composition $C_{35}H_{51}O_{13} \cdot H_2O$ (elementary analysis) depositing on recrystallization from methanol in the form of white acicular crystals with mp 240-241°C; $[\alpha]_D^{27}$ +12.57° (c 1.01; methanol). This glycoside gave the Legal, Raymond, Kedde, and Keller-Kiliani reactions. After treatment with the Svendsen-Jensen reagent, it fluoresced bright blue in UV light. With conc. H_2SO_4 it formed a coloration changing with time: 0 min, yellow-orange; 60 min, dark brown; 120 min, green; 180 min, bright green. Frerejacque's reaction [3] for an acetyl group was negative. The substance was not saponified with alkali. This again confirms that it does not contain an acetyl or a formyl group. The biological activity, determined by M. D. Gedevanishvili and Ts. P. Tkabladze, was 16,500 frog units.

The acid hydrolysis of the glycoside gave the aglycone, with mp 220-222°C, $[\alpha]_D^{25}$ +34.0° (c 1.02; methanol), which was identified as gitoxygenin. After the separation of the aglycone, the aqueous hydrolysate yielded digilanidobiose with mp 215-216°C. No other carbohydrates were found in the sugar moiety.

The enzymatic hydrolysis of the glycoside gave a monoglycoside and a monosaccharide. The monoglycoside had the composition $C_{29}H_{44}O_8$, mp 213-215°C, $[\alpha]_D^{27}$ +10.75° (c 1.265; methanol) and on a paper chromatogram it appeared between gitoxygenin and gitoxin. The information obtained indicates that this glycoside is a gitoxygenin digitoxoside or gitoroside [4-6]. The monosaccharide was characterized by the melting point and mobility in paper chromatography of the substance itself and of its osazone as D-glucose.

Thus, the glycoside that we isolated from D. ciliata is gitoxygenin digilanidobioside and its properties agree completely with the genuine glycoside glucogitoroside from the seeds of D. purpurea and from the leaves of D. lanata [7, 8].

The difficulty in performing acid hydrolysis shows the pyranose form of the carbohydrate part of the substance studied. An analysis of the molecular rotations of the diglycoside, the monoglycoside, and the aglycone in accordance with Klyne's rule [9] shows that the D-glucose and D-digitoxose are connected by β-glycosidic bonds. Consequently, the glucogitoroside obtained is gotoxygenin O-β-D-digitoxopyranosyl-β-D-glucopyranoside.

In view of the high content of glucogitoroside in the leaves of D. ciliata (0.15-0.20%) they may become an industrial raw material for the preparation of this glycoside.

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