DIGITALINUM VERUM AND LANATOSIDE A FROM Digitalis ciliata

É. P. Kemertelidze

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Upon chromatography of the combined primary glycosides from the leaves of Digitalis ciliata Trautv. on a column of Sephadex G-75, we obtained lanatoside C and lanatoside B [1], and also glucogitoroside, which we had isolated previously by partition chromatography on silica gel [2]. Later, from the same column yet another individual glycoside was isolated which, on paper chromatography in various solvent systems [3-5], appeared at the level of an authentic sample of digitalinum verum. From aqueous methanol it formed white acicular crystals with mp 240°C. It gave the specific reactions for the glycosides of the foxglove. The Pesez reaction was negative. After treatment with the Svendsen–Jensen reagent, it showed the bright blue fluorescence characteristic for gitoxigenin derivatives. With conc. H_2SO_4 it formed a coloration changing with time: 0 min – yellow; 5 min – yellow-orange; 30 min – orange-red; 100 min – brown-green; 160 min – green. The reactions for acetyl and formyl groups were negative, and alkali did not saponify the compound. In the IR spectrum it had the absorption bands characteristic of the foxglove glycosides.

Acid hydrolysis yielded gitoxigenin, digitalose, and glucose. It underwent enzymatic hydrolysis by the enzyme of the grape snail with difficulty: on prolonged fermentation the substance decomposed partially with the formation of strospeside and glucose.

In its physicochemical properties, the glucoside isolated corresponds to gitoxigenin digitaloside-glucoside, or digitalinum verum [4, 5, 7].

The chloroform-soluble combined glycosides from the leaves of D. ciliata were separated by partition chromatography on a cellulose column (stationary phase water, mobile phase toluene–butanol). An individual glycoside deposited in the form of white acicular crystals with mp 245-246°C from acetone–ether $[\alpha]_D^{18}$ +30.8° (c 0.78; ethanol). On a paper chromatogram it had the same mobility as a standard sample of lanatoside A. It gave no depression of the melting point. It exhibited the reactions characteristic for derivatives of digitoxigenin and digitoxose. With conc. H_2SO_4 it formed a coloration changing with time: 0 min – dark brown; 20 min – brown-red-green; 60 min – bright brown; 120 min – brown-violet; 180 min – violet. The reaction for an acetyl group was positive. On saponification with alkali, it formed a glycoside which appeared on a paper chromatogram in the region of desacetyllanatoside A. The acid hydrolysis of the latter gave digitoxigenin (mp 251-252°C), digitoxose, and digilanidobiose. On enzymatic hydrolysis with the enzyme of the grape snail, digitoxin (mp 242-243°C) and D-glucose were isolated. The IR spectrum coincided completely with that for lanatoside A [8].

On the basis of the above facts, the substance studied has been characterized as lanatoside A [9, 10], which is the main genuine glycoside of the leaves of Digitalis ciliata.

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I. G. Kutateladze Institute of Pharmaceutical Chemistry, Academy of Sciences of the Georgian SSR.
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