CARDENOLIDES OF Digitalis ciliata

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In the isolation of digitoxin from the combined ether-soluble glycosides of the leaves of D. ciliata Trautv. by adsorption chromatography on alumina [1], a glycoside with the composition $C_{35}H_{54}O_{10} \cdot 3H_2O$ was obtained in the form of white acicular crystals with mp 185-186°C. This substance gives the reactions specific for the Digitalis glycosides: after treatment with the Svendsen–Jensen reagent in UV light the bright yellow fluorescence characteristic for derivatives of digitoxigenin appears. On paper chromatography in the systems methyl ethyl ketone–xylene (1:1)/formamide [2] and cyclohexane–tetrahydrofuran (3:2)/formamide [3] it is located just below the digitoxin. Acid hydrolysis gave digitoxigenin (mp 246-247°C) and digitoxose.

According to its physicochemical properties, the glycoside isolated corresponds to digitoxigenin 3-O-bisdigitoxoside, which has been described in the literature [3].

In the chromatographic separation of the combined secondary glycosides of the plant mentioned on a column of silica, we isolated α-acetyldigitoxin, digitoxin, a small amount of digitoxigenin bisdigitoxoside, α-acetylgitoxin, and gitoxin [4]. On further elution of the column, a fraction was obtained which consisted of four glycosides. The preparative separation of this mixture on a paper chromatogram in the methyl ethyl ketone–xylene (1:1)/formamide system yielded two individual cardenolides in the form of white tetragonal plates.

One of them, with mp 260°C, $[\alpha]_D^{20}+11.2°$ (c 0.42; pyridine) gave the reactions characteristic for digoxigenin and digitoxose derivatives: on a paper chromatogram it had the same mobility as authentic digoxin; the acid hydrolysis of the glycoside formed digoxigenin (mp 220°C) and digitoxose.

The second substance melted at 251-252°C, $[\alpha]_D^{20}+16.4°$ (c 0.32; methanol). In the Keller–Kiliani reaction, the layer of H_2SO_4 assumed a carmine red color (gitoxigenin), and the CH_3COOH layer was uncolored. The Pesez reaction was also negative. The substance gave the Kedde and Legal reaction. With the Svendsen–Jensen reagent in UV light it fluoresced bright blue. Its R_f value was identical with that of an authentic sample of strospeside and a mixture showed no depression of the melting point. On acid hydrolysis it was split into gitoxigenin (contaminated with dianhydrogitoxigenin) and digitalose.

On comparing the results obtained with literature information, it may be concluded that the first substance is digoxigenin 3-O-tridigitoxoside, or digoxin [5] and the second is gitoxigenin 3-O-monodigitaloside, or strospeside [6].

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