# ACETYLGITOXIN-α AND GITOXIN FROM Digitalis ciliata

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The combined secondary glycosides of the leaves of Digitalis ciliata Trautv. (ethereal fraction) [1] were separated by partition chromatography on a column of cellulose (with ethylene glycol as the stationary phase and toluene and toluene–acetone as the mobile phases). Elution with toluene gave acetyldigitoxin-α, while a mixture of toluene and acetone (94 : 6) gave digitoxin, which we have described previously [1, 2]. From the fractions eluted by toluene–acetone (85 : 15), an individual compound was obtained which crystallized from ethylene glycol and from a mixture of chloroform and ether in the form of elongated rectangular white plates, and from methanol and acetone in the form of acicular crystals with mp 200-202°C; $[\alpha]_D^{18}$ +25.3° (c 0.96; methanol). It dissolved in 70 parts of methanol and 280 parts of acetone. On paper chromatography in the methyl ethyl ketone–xylene–formamide system [3], it appeared slightly below gitaloxin, with $R_f$ 0.50. It gave the Legal, Raimond, Kedde, Pesez, and Keller–Kiliani reactions. After treatment with the Svendsen–Jensen reagent, it showed a bright blue fluorescence in UV light. The reaction for an acetyl group was positive. Under the action of alkali it saponified, forming gitoxin. On acid hydrolysis the glycoside yielded the aglycone gitoxigenin (mp 220-223°C) and digitoxose.

The physicochemical properties of the glycoside isolated corresponded to those of acetylgitoxin-α as given in the literature [4].

In the isolation of the acetylgitoxin-α, a substance extremely sparingly soluble in acetone precipitated in the form of white acicular crystals with mp 254-256°C having the same mobility on a paper chromatogram as acetylgitoxin-α, but because of its small amount it could not be characterized. It is possible that this substance is the β form of acetylgitoxin.

The subsequent fractions obtained in the washing of the column with toluene–acetone (70 : 30) yielded an individual glycoside with mp 268-270°C, $[\alpha]_D^{18}$ +4.3° (c 0.68; pyridine). This substance precipitated from ethylene glycol in the form of white acicular crystals and from methanol–chloroform as elongated rectangular crystals. It was almost insoluble in ethanol, methanol, acetone, chloroform, and ethyl ether, and dissolved in chloroform–methanol and pyridine. On a paper chromatogram [3] it was located at the level of an authentic sample of gitoxin. It gave no depression of the temperature with gitoxin. It gave all the reactions characteristic of derivatives of gitoxigenin and deoxy sugars. The reactions for acetyl and formyl groups were negative. Acid hydrolysis gave gitoxigenin with mp 223-225°C and digitoxose.

The results that we obtained and literature information [5] permit the conclusion that the substance studied was gitoxin.

## LITERATURE CITED

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