

Studies on Digitalis Glycoside. Acetyldigitoxin- α from Digitoxin.

In the previous papers¹⁾ we reported the partial synthesis of acetylgitoxin- α from gitoxin. Later, we prepared acetyldigitoxin- α by a similar method from digitoxin.

Digitoxin was acetylated for 16 hrs. with equimolar amount of acetic anhydride in pyridine solution at room temperature and the crude acetate was submitted to alumina chromatography. The main fraction eluted with $\text{CHCl}_3:\text{MeOH}=100:1$ was recrystallized from $\text{CHCl}_3\text{-Et}_2\text{O}$ and acetone- Et_2O to colorless plates, m.p. $153\sim 180^\circ/217\sim 223^\circ$. Analysis gave values which agreed well with the formula of digitoxin-monoacetate (*Anal.* Calcd. for $\text{C}_{48}\text{H}_{66}\text{O}_{14}\cdot\text{H}_2\text{O}$: C, 62.60; H, 8.31; COCH_3 , 5.22. Found: C, 62.65, H, 8.53, COCH_3 , 5.51). A comparison of this product with authentic sample of acetyldigitoxin- α , kindly furnished by Prof. A. Stoll, proved the identity of the two acetates as follows:

	Acetyldigitoxin- α (Stoll)	Monoacetyldigitoxin obtained here	Mixture
m.p. ($^\circ\text{C}$)	155~180/217~224	153~180/217~223	154~180/217~223
$[\alpha]_{\text{D}}^{25}$ (MeOH)	+24.5 ²⁾	+25.9 ^o	
Rf (HCONH_2 , xylene : $\text{MeCOEt}=3:1$)	0.72	0.72	0.72
(HCONH_2 , xylene : dioxane=1:1)	0.61	0.62	0.62

The infrared spectra of the two substances also agreed well.

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- 1) D. Satoh, Y. Oyama, H. Ishii: This Bulletin, 5, 493(1957). The melting points of acetylgitoxin- α which was furnished by Prof. A. Stoll and that obtained by us were reported as $190\sim 203^\circ/245\sim 248^\circ$ and $190\sim 202^\circ/246\sim 249^\circ$, respectively. According to a later study, it was found that these products were contaminated with a small amount of acetylgitoxin- β . After purification of our product by the method of Stoll,²⁾ the pure acetylgitoxin- α showed m.p. $190\sim 203^\circ$. The sample of acetylgitoxin- α newly furnished by J. Renz showed m.p. $184\sim 202^\circ$ and no depression of the melting point was observed on mixed fusion.
- 2) A. Stoll, W. Kreis: Helv. Chim. Acta, 35, 1318(1952).