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Studies on Digitalis Glycoside. Acetyldigitoxin-α from Digitoxin.

In the previous papers[1] 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 $CHCl_3$:MeOH=100:1 was recrystallized from $CHCl_3$–Et_2O and acetone–Et_2O to colorless plates, m.p. 153～180°/217～223°. Analysis gave values which agreed well with the formula of digitoxin-monoacetate (*Anal.* Calcd. for $C_{43}H_{66}O_{14}\cdot H_2O$: 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. (°C)	155～180/217～224	153～180/217～223	154～180/217～223
$[\alpha]_D^{25°}$ (MeOH)	+24.5°[2]	+25.9°	
Rf ($HCONH_2$, xylene : 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 190～203°/245～248° and 190～202°/246～249°, 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. 190～203°. The sample of acetylgitoxin-α newly furnished by J. Renz showed m.p. 184～202° and no depression of the melting point was observed on mixed fusion.

2) A. Stoll, W. Kreis : Helv. Chim. Acta, **35**, 1318(1952).