GLYCOSYLATED CARDENOLIDES.

VI. RIBOSIDES OF STROPHANTHIDIN AND DIGITOXIGENIN

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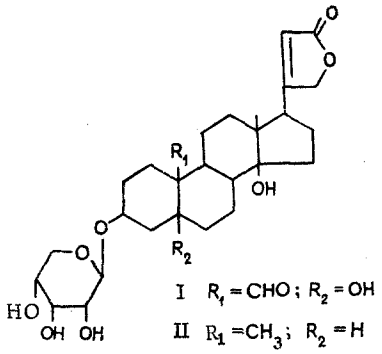
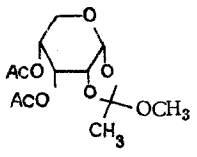
Partial syntheses of ribosides of strophanthidin (I) and digitoxigenin (II) have been carried out by the orthoester method [1] by analogy with previous work [2]. 3,4-Di-O-acetyl-α-D-ribopyranose 1,2-(methyl orthoacetate) (III) was obtained by the method of Mazurek and Perlin [3]. The orthoester (III), $C_{12}H_{18}O_8$, had mp 82-84°C (from diethyl ether—petroleum ether), $[\alpha]_D^{24}$ −7.7 ± 2° (c 1.78; chloroform). NMR spectrum ($CDCl_3$), ppm: 1.75 (3 H at CH_3, s), 2.10 (6 H at 2 Ac, s), 3.28 (3 H at OCH_3, s). The NMR spectrum shows the exo position of the OCH_3 group in compound (III) [3, 4].

The products of the interaction of the orthoester (III) with strophanthidin were saponified with a solution of ammonia in methanol. Subsequent chromatography on a column of SiO_2 gave a 75.0% yield (calculated on the strophanthidin) of strophanthidin β-D-riboside (I), $C_{28}H_{40}O_{10}$, mp 226-230°C (decomp.) [from benzene—chloroform—methanol (5:5:2)], $[\alpha]_D^{25}$ 0 ± 3° (c 1.18; methanol); $\lambda_{max}^{C_2H_5OH}$: 217 nm (log ε 4.18); ν_{max}^{KBr}, cm^{-1}: 3300-3500 (OH), 1780, 1740, 1720, 1632 (butenolide ring). NMR spectrum (C_5D_5N), ppm: 0.85 (3 H at C-18, s), 4.92, 5.21 (2 H at C-21, q, centers of doublets, J = 18 Hz), 5.25 (H at C-1', d, J = 5 Hz), 6.00 (H at C-22, br. s), 10.27 (H at C-19, s).



I $R_1 = CHO$; $R_2 = OH$

II $R_1 = CH_3$; $R_2 = H$



III

In a similar manner we obtained digitoxigenin β-D-riboside (II), $C_{28}H_{42}O_8$, mp 222°C (from methanol—ether), $[\alpha]_D^{25}$ −28.9 ± 3° (c 0.55; methanol), $\lambda_{max}^{C_2H_5OH}$: 218 nm (log ε 4.19); M^+ 506. ν_{max}^{KBr}, cm^{-1}: 3400-3500 (OH), 1785, 1750, 1625 (butenolide ring). NMR spectrum (C_5D_5N), ppm: 0.74 (3 H at C-18, s), 0.89 (3 H at C-19, s), 4.91, 5.21 (2 H at C-21, q, centers of doublets, J = 18 Hz), 5.12 (H at C-1', d, J = 5 Hz), 5.99 (H at C-22, br. s). The configurations of the glycosidic bonds in compounds (I) and (II) were determined by the method of molecular rotation differences [5].

The NMR spectra were taken on a JNM-4H-100 instrument (100 MHz, HMDS, δ scale, ppm).

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