GLYCOSYLATION OF CARDENOLIDES.

II. STROPHANTHIDIN 3β-(METHYL GLUCOSIDURONATE)

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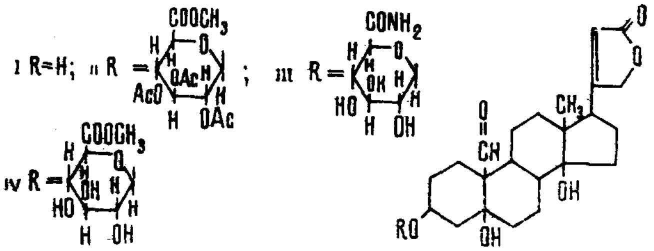
An investigation has been made of the preparation of glycosides of cardenolides with uronic acids [1].

The synthesis of strophanthidin (methyl glucosiduronate) (IV) was performed by the Koenigs–Knorr method [2]. The reaction of methyl 2,3,4-tri-O-acetyl-1-bromo-1-deoxy-α-D-glucuronate [3] with strophanthidin (I) gave a 61.2% yield of strophanthidin 3β-O-(methyl 2',3',4'-tri-O-acetyl-β-D-glucosiduronate) (II), $C_{36}H_{48}O_{15}$, crystals from ethanol with mp 212/228-231°C (decomp.), $[\alpha]_D^{22}$ −3,4 ± 3° (c 1.16; chloroform); $\lambda_{max}^{C_2H_5OH}$ 218 nm (log ε 4.23); ν_{max}^{KBr} 3550 cm^{-1} (OH), 2760 cm^{-1} (CHO), 1750-1760, 1715 cm^{-1} (C=O group), 1630 cm^{-1} (C=C), 1225 cm^{-1} (C–O–C); NMR spectrum of (II) ($CDCl_3$) (δ, ppm): 0.82 (3H at C_{18}, s); 1.98 (9H in 3Ac), 3.71 (3H in OCH_3, s); 4.10 (H at $C_{5'}$, d); 4.15 (H at C_3, m); 4.68 (H at $C_{5'}$, d, J = 8 Hz — β configuration of the glycosidic bond [4]); 4.85 (2H at C_{21}, q); 5.10-5.30 (3H at $C_{2'}$, $C_{3'}$, and $C_{4'}$, m); 5.85 (H at C_{22}, s); 9.93 (H of the aldehyde group and C_{19}, s).



The treatment of compound (II) with a solution of ammonia in absolute methanol at room temperature gave an 87.5% yield (as crude product) of strophanthidin 3β-O-(β-D-6'-glucosiduronamide) (III), $C_{29}H_{42}NO_{11}$; crystals from acetone with mp 224-228°C (decomp.), $[\alpha]_D^{22}$ + 5.2 ± 3° (c 0.88; methanol); $\lambda_{max}^{C_2H_5OH}$ 218 nm (log ε 4.24); ν_{max}^{KBr} 3480 cm^{-1} (OH), 2760 cm^{-1} (CHO), 1760-1720 cm^{-1} (C=O), 1665 cm^{-1} ($CONH_2$), 1635 cm^{-1} (C=C).

The saponification of the triacetate (II) with a catalytic amount of sodium methoxide in absolute methanol gave a 64.5% yield of chromatographically homogeneous but amorphous strophanthidin 3β-O-(methyl β-D-glucopyranosiduronate) (IV), $C_{30}H_{42}O_{12}$, $[\alpha]_D^{20}$ −7.3 ± 3° (c 0.83; methanol); $\lambda_{max}^{C_2H_5OH}$ 218 nm, (log ε 4.16), ν_{max}^{KBr} 3490 cm^{-1} (OH), 2770 cm^{-1} (CHO), 1750 cm^{-1} (C=O), 1630 cm (C=C); NMR spectrum (C_5D_5N), δ, ppm: 0.88 (3H at C_{18}, s), 3.56 (3H at OCH_3, s), 5.05 (2H at C_{21}, q); 6.00 (H at C_{22}, s); 10.28 (H at C_{19}, s).

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

LITERATURE CITED

1. N. S. Pal'yants, M. B. Gorovits, and N. K. Abubakirov, Khim. Prirodn. Soedin., 263 (1975).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 522-523, July-August, 1975. Original article submitted March 18, 1975.

2. W. Konings and E. Knorr, Ber., 34, 957 (1901).
3. G. N. Bollenback, J. W. Long, D. G. Benjamin, and J. A. Lindquist, J. Amer. Chem. Soc., 77, 3310 (1955).
4. M. Mamsui and M. Okada, Chem. Pharm. Bull., 19, 395 (1971).