BRIEF COMMUNICATIONS

SYNTHESIS OF β-D-GLUCOPYRANOSIDES OF TRANSFORMED STEROIDS

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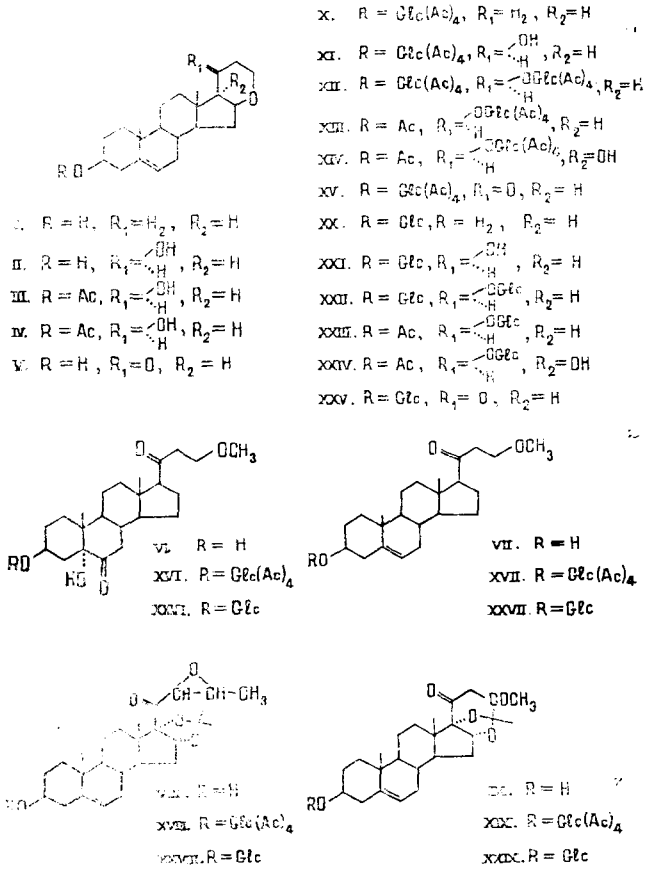
UDC: 547.918+547.920+542.91

Transformed steroids [1] and their derivatives (acetates and glucosides) [2] exert an inhibiting action on Na^+, K^+-ATPase the degree of which depends on the structure of the molecule and the nature of its substituents. To investigate this dependence glucoside derivatives of the steroid derivatives (I-IX) have been synthesized [3-5].



The glycosylation of (I) and (IX) was effected with α-acetobromoglucose in the presence of cadmium carbonate [6] and 4 Å molecular sieves in toluene with azeotropic distillation, and that of (II)-(VIII) in the presence of mercury cyanide [7] in absolute nitromethane at room temperature. The reaction was performed until the initial alcohol had disappeared, its course being monitored with the aid of TLC on silica gel in the hexane–acetone (3:1) and benzene–chloroform–methanol (6:4:1) systems. The acetylated glucosides (X-XIX) were isolated by column chromatography on silica gel in the hexane–acetone system. The results of elementary analysis for all the newly obtained compounds corresponded to the calculated figures. The β configurations of the glycosidic bonds of comounds (X-XII) and (XV-XIX) were confirmed by the presence in the ^1H NMR spectra of the signals of the anomeric protons of the carbohydrate component at C-3 in the 4.53-4.59 ppm region ($J_{1,2}$ = 7.3-7.5 Hz) and for the carbohydrate component at C-20 in the 4.65 ppm region ($J_{1,2}$ = 7.5 Hz) for compounds (XII-XIV).

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Scientific Center, Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 832-833, November-December, 1985. Original article submitted March 13, 1985.

 0009-3130/85/2106-0792$09.50

Compound X — $C_{36}H_{52}O_{11}$, Yield 61%, mp 180—183° (methanol), $[\alpha]_D^{20}$ —33,3° (*c* 0,79; $CHCl_3$).

Compound XI — $C_{36}H_{52}O_{12}$, Yield 42%, mp 162—165° (methanol) $[\alpha]_D^{20}$ — 55° (*c* 1; $CHCl_3$).

Compound XII — $C_{50}H_{70}O_{21}$, Yield 32%, mp 230—231° (methanol) $[\alpha]_D^{20}$ — 47° (*c* 1; $CHCl_3$).

Compound XIII — $C_{38}H_{54}O_{13}$, Yield 60%, mp 143—145° (methanol) $[\alpha]_D^{20}$ — 34° (*c* 0,8; $CHCl_3$).

Compound XIV — $C_{38}H_{54}O_{14}$, Yield 63%, mp 177—179° (methanol) $[\alpha]_D^{20}$ — 48° (*c* 1; $CHCl_3$).

Compound XV — $C_{36}H_{51}O_{12}$, Yield 60%, amorphous

Compound XVI — $C_{37}H_{50}O_{15}$, Yield 51%, mp 238—239° (ethanol)

Compound XVII — $C_{37}H_{52}O_{13}$, Yield 75%, mp 190—191° (hexane) $[\alpha]_D^{20}$ — 22° (*c* 0,94; chloroform)

Compound XVIII — $C_{40}H_{56}O_{14}$, Yield 51%, mp 208—210° (ethanol)

Compound XIX — $C_{40}H_{56}O_{14}$, Yield 51%, mp 186—189° (methanol) $[\alpha]_D^{20}$ — 53° (*c* 1; chloroform)

The saponification of the acetates (X-XIX) with a 0.1 N solution of sodium methanolate in methanol gave the corresponding free glucosides (XX-XXIX) with yields of 80-95%.

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