SYNTHESIS OF GLYCOSIDES OF SOME STEROIDS

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We have used the orthoester method of glycosylation developed by N. K. Kochetkov et al. [1-3] for the synthesis of acetates of glycosides of β-sitosterol, lanosterol, panaxadiol, and 16-dehydropregnenolone [4]. In the present paper we give the results of the synthesis of acetates of maltosides of cholesterol, β-sitosterol, and 16-dehydropregnenolone. The glycosylation reaction was accompanied by the formation of ethers and of acetates of the aglycone which were easily separated from the glycosylation products [4].

When 2',3,3',4',6,6'-hexa-O-acetyl-1,2-(1-methylethylidene)-α-maltose [5] was condensed with steroid aglycones in boiling nitromethane in the presence of 0.02 mmole of $HgBr_2$, several compounds were isolated.

Compound (I). Cholesterol hepta-O-acetyl-β-maltoside with a yield of 42.7%, mp 179-182.5°C, $[\alpha]_D^{20}$ 36.6° (c 0.24; $CHCl_3$).

Found %: C 63.35; H 8.20. $C_{53}H_{80}O_{18}$. Calculated %: C 63.33; H 8.02.

Dicholesteryl ether, yield 16.2%, mp 199-200°C. A mixture with an authentic sample [6] gave no depression of the melting point.

Compound (II). β-Sitosterol hepta-O-acetyl-β-maltoside with a yield of 46.9%, mp 172-174°C, $[\alpha]_D^{20}$ +0.6° (c 0.24; $CHCl_3$).

Found %: C 63.85; H 8.34; $C_{55}H_{84}O_{18}$. Calculated %: C 64.09; H 8.19.

Di-β-sitosteryl ether, yield 14.8%, mp 190-191°C. A mixture with an authentic sample showed no depression of the melting point.

Compound (III). 16-Dehydropregnenolone hepta-O-acetyl-β-maltoside with a yield of 29.5%, mp 229.5-231.5°C $[\alpha]_D^{20}$ +8.6° (c 0.17; $CHCl_3$).

Found %: C 60.36; H 7.33. $C_{47}H_{65}O_{18}$. Calculated %: C 60.43; H 7.01.

16-Dehydropregnenolone acetate, yield 22.5%, mp 174-175°C, $[\alpha]_D^{20}$ −27.5° (c 0.98; $CHCl_3$). Literature data: mp 176°C, $[\alpha]_D^{20}$ −33° (C_2H_5OH) [7].

The configuration of the glycoside bond was determined by NMR spectroscopy. In the NMR spectra, the β anomer [8] is characterized by a doublet in the region δ 4.4-4.7 ppm with J=8 Hz due to the proton on the glycosidic carbon atom. This feature also appears in the spectra of the acetates of cholesterol, β-sitosterol, and 16-dehydropregnenolone acetates (δ 4.54 ppm, J=8.1 Hz; δ 4.54 ppm, J=8.0 Hz; and δ 4.63 ppm, J=7.6 Hz, respectively).

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