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GLYCOSYLATION OF CYCLOSIEVERSIOSIDES A AND H

N. Sh. Pal'yants, R. U. Umarova, M. B. Gorovits and N. K. Abubakirov

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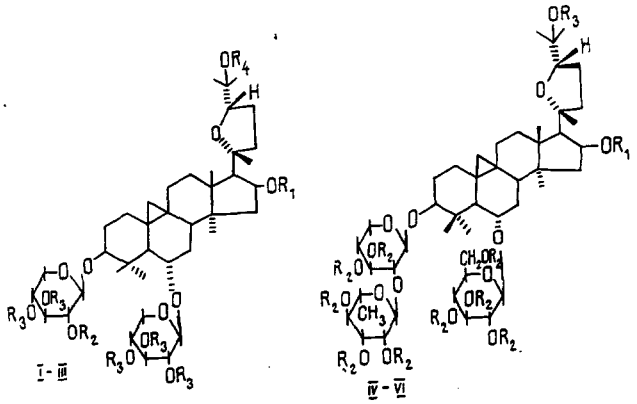
Continuing work on the glycosylation of cycloartane glycosides [1], we have achieved a partial synthesis of rhamnosides of the 16-O-acetates of cyclosieversiosides A and H [2—4].

The acetylation of cyclosieversioside A (I) with acetic anhydride in pyridine followed by chromatography on a column of SiO_2 in the chloroform—methanol (40:1) system gave the hexaacetate of cyclosieversioside A (II) with the composition $C_{55}H_{82}O_{21}$, mp 130—132°C (from methanol); $[\alpha]_D^{22}$ 104.4 ± 2°C (*c* 0.90; chloroform) ν_{max}^{KBr}, cm^{-1} 3550—3400 (OH), 3060 (CH_2 of a cyclopropane ring), 1760, 1240 (acetyl). The presence in the mass spectrum of compound (II) of an ion with m/z 143 ($C_8H_{15}O_2$) showed a free hydroxy group at C-25 [5].



I. R_1=R_3=R_4=H; R_2=Ac
II. R_1=R_2=R_3=Ac; R_4=H
III. R_1=Ac; R_2=R_3=H; R_4=α-*L*-Rhap
IV. R_1=R_2=R_3=H
V. R_1=R_2=Ac; R_3=H
VI. R_1=Ac; R_2=H; R_3=α-L-Rhap

The interaction of (II) with acetobromorhamnose in dichloroethane in the presence of mercury cyanide and 4Å molecular sieve in a current of nitrogen, followed by acetylation of the reaction products with a 1% methanolic solution of KOH led to the 3,6-di-(O-β-D-xylopyranoside) 25-O-α-L-rhamnopyranoside of cyclosieversigenin (III) with a yield of 78%. Product (III) had the composition $C_{50}H_{80}O_{19}$, mp 275°C (from methanol), $[\alpha]_D^{22}$ +10.9 ± 2° (c 1.01; pyridine); ν_{max}^{KBr}, cm^{-1}: 3550-3250 (OH); 3050 (CH_2 of a cyclopropane ring), 1740, 1250 (acetyl). PMR (C_5D_5N), δ, ppm, 0 — TMS: 0.49 (1H, d, ^2J = Hz, H-19); 0.96; 1.17; 1.22; 1.76 (21H, s, 7 × CH_3); 1.50 (3H, d, ^3J = 5 Hz; CH_3 of rhamnose); 1.94 (3H, s, 16-O-Ac); 4.66, 4.72 (each 1H, d, ^3J = 6 Hz, anomeric protons of xylose); 5.40 (1H, d, H-16; 5.53 (1H, br.s; anomeric proton of rhamnose).

The acetylation of cyclosieversioside H (IV) under the same conditions gave cyclosieversioside H decaacetate (V). Compound (V) had the composition $C_{67}H_{98}O_{28}$, mp 208—210°C (from methanol); $[\alpha]_D^{22}$ +13.3 ± 2° (c 0.75; methanol). The ion with m/z 143 ($C_8H_{15}O_2$) observed in the mass spectrum of compound (V) indicated a free hydroxy group at C-25 [5].

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The interaction of compound (V) with acetobromorhamnose, followed by saponification of the reaction products was carried out similarly to the procedure described above. This gave the 3-O-[α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranoside] 6-O-β-D-glucopyranoside 25-O-α-L-rhamnopyranoside of cyclosieversigenin (VI) with a yield of 72%. Substance (VI) had the composition $C_{55}H_{90}O_{23}$, mp 259—260°C (from a mixture of methanol and ether): $[\alpha]_D^2$ +12.9 ± 2° (c 0.77; methanol); ν_{max}^{KBr}, cm^{-1}: 3550-3250 (OH); 3040 (CH_2 of a cyclopropane ring), 1740, 1250 (acetyl). PMR (C_5D_5N, δ, ppm, 0 — TMS): 0.49 (1H, d, ^2J = 4 Hz, H-19), 1.05; 1.15; 1.25; 1.64 (21H, s, $7CH_3$); 1.50, 1.55 (3H, d, ^3J = 5 Hz, $2CH_3$ rhamnose); 1.96 (3H, s, 16-O-c); 4.65 (2H, m, anomeric protons of xylose); 5.45 (1H, m, H-16); 5.50, 6.32 (1H, br.s, anomeric protons rhamnose).

The signal of the anomeric carbon atom of the rhamnose at C-25 in the 96.0 ppm region of the ^{13}C NMR spectrum showed the α-configuration of the glycosidic bond under consideration in compounds (III) and (VI) [6].

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