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Preliminary communication

Oxirane–oxetane–1,4-dioxane anhydro-ring migration in sucrose derivatives*

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Treatment of a methanolic solution of octa-*O*-acetylsucrose with aluminum oxide impregnated with potassium carbonate[1] gave a mixture of *O*-acetylsucroses having various degrees of acetylation[2]. Column chromatography (chloroform–ethanol, 100:2) of the penta-*O*-acetylsucrose fraction on silica gel gave 2,3,4,6,1′- (**1**), 3,4,6,1′,6′- (**2**), and 2,3,4,6,6′-penta-*O*-acetylsucrose† (**3**) in the ratios 3:1:7. Treatment of **3** {$[\alpha]_D$ +60° (chloroform)} with 2 equiv. of toluene-*p*-sulfonyl chloride in pyridine (64 h) at room temperature followed by column chromatography (benzene–acetone, 85:15) of the product gave, in addition to the 1′,3′,4′-tritosylate **4** (11.5%) and 1′-tosylate **5** (29.2%), the 1′,3′- {**6** (23.9%), $[\alpha]_D$ +37° (chloroform)} and 1′,4′-ditosylate {**7** (24.3%), $[\alpha]_D$ +64° (chloroform)}. Reaction of the 1′,3′-ditosylate **6** with sodium methoxide under conditions *A* (refluxing methanolic M sodium methoxide for 2 min, which converted[3] **22** into **9** and **10**) or *B* [refluxing M sodium methoxide for 24 h (ref. 4)] gave, after column chromatography on silica gel (benzene–acetone, 9:1), 32% of the dianhydro derivative **8** (ref. 5) and 55% of the anhydro derivative **9** (refs. 3 and 5) or 52% of **8** and 38% of **9**, respectively. Under conditions *A*, the 1′,4′-ditosylate **7** gave 60% of the anhydro derivative **10** (refs. 3 and 5–7) {m.p. 116°, $[\alpha]_D$ +72° (chloroform)} and, under conditions *B*, 60% of the 4′-*O*-methyl-2,1′-anhydro derivative **11** {m.p. 109–111°, $[\alpha]_D$ +53° (chloroform)}; (deacetylation of **11** and **23** (ref. 4) followed by methylation furnished the same hexa-*O*-methyl derivative **24**) and a mixture of **12** and **13**. Re-chromatography (benzene–acetone, 9:1) of this mixture gave the sorbose derivative **12** {$[\alpha]_D$ +69° (chloroform)} and 4′-*O*-methylsucrose heptaacetate {**13**, $[\alpha]_D$ +46° (chloroform)}, in yields of 16 and 13%, respectively (the same reaction sequence with **13** gave octa-*O*-methylsucrose[8]). Compounds **12** and

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†All new compounds gave satisfactory elemental analyses.

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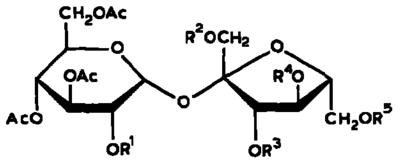
13 were also obtained by reaction of the anhydro derivative **10** under conditions *B*, in yields of 40 and 36%, respectively.

Thus, oxirane ring formation occurs under conditions *B* with the ditosylates **6** and **7** to give **14** and **15**, respectively. However, **14** is then transformed into **16** and **17** with retention of the oxirane ring, probably owing to the poor accessibility of position 4′ for the methoxide ion[9]. In contrast, the oxirane ring in **15** is easily opened by methoxide ion and recyclisation then gives **18**. Furthermore, some of **15** is solvolysed to give the anhydro derivative **19**, the oxirane ring of which is probably opened by the assistance of HO-1′. The oxetane ring of the postulated (*cf.* ref. 10) intermediate **20** is then attacked by HO-2 to give the sorbofuranose derivative **21**. In accord with this mechanism, hydrolysis of the oxirane ring in the dianhydro derivative **16** under more drastic conditions (42-h reflux with M sodium hydroxide) gave, after acetylation, 70% of **12**.

N.m.r. data*: **3**, ^{1}H, δ 2.02, 2.04, 2.11 (3 s, 3, 3, and 9 H, 5 Ac), 4.92 (dd, 1 H, $J_{1,2}$ 3.9, $J_{2,3}$ 9.8 Hz, H-2), 5.05 (dd, 1 H, $J_{3,4}$ 9.8, $J_{4,5}$ 9.3 Hz, H-4), 5.51 (t, 1 H, H-3), 5.62 (d, 1 H, H-1); ^{13}C, δ 20.4 (q, 5 C), 62.0 (t), 63.4 (t), 64.2 (t), 67.8 (d), 68.2 (d), 69.9 (d), 70.1 (d), 74.9 (d), 77.5 (d), 78.6 (d), 88.8 (d), 104.1 (s), 169.3 (s), 169.6 (s), 170.4 (s), 170.8 (s), 171.0 (s); **6**, ^{1}H, δ 1.94, 2.01, 2.03, 2.06, 2.10 (5 s, 3, 3, 3, 3, and 3 H, 5 Ac), 2.48 (s, 6 H), 4.74 (d, 1 H, $J_{3',4'}$ 8.8 Hz, H-3′), 4.78 (dd, 1 H, $J_{1,2}$ 3.9, $J_{2,3}$ 10.3 Hz, H-2), 5.04 (dd, 1 H, $J_{3,4}$ 9.7, $J_{4,5}$ 9.3 Hz, H-4), 5.38 (dd, 1 H, H-3), 5.68 (d, 1 H, H-1), 7.39–7.81 (m, 8 H); ^{13}C, δ 20.47 (q), 20.55 (q), 20.63 (q), 20.71 (q, 2 C), 21.68 (q), 21.77 (q), 61.6 (t), 61.7 (t), 68.1 (d), 68.4 (t), 68.5 (d), 69.9 (d), 70.0 (d), 71.2 (d), 78.4 (d), 81.5 (d), 88.3 (d), 101.2 (s), 128.0 (d, 2 C), 128.3 (d, 2 C), 130.0 (d, 2 C), 130.4 (d, 2 C), 131.7 (s), 132.5 (s), 145.3 (s), 146.2 (s), 169.6 (s), 169.7 (s), 170.0 (s), 170.6 (s), 170.9 (s); **7**, ^{1}H, δ 1.982, 2.010, 2.031, 2.034, 2.107 (5 s, 3, 3, 3, 3, and 3 H, 5 Ac), 2.468 (s, 6 H), 3.168 (d, 1 H, $J_{3',OH}$ 6.8 Hz, HO-3′), 3.913 (d, 1 H, $J_{1'a,1'b}$ 10.7 Hz, H-1′b), 4.090 (d, 1 H, H-1′a), 4.192 (dd, 1 H, $J_{5,6a}$ 4.8, $J_{6a,6b}$ 13.2 Hz, H-6a), 4.317 (ddd, 1 H, $J_{4,5}$ 10.3, $J_{5,6b}$ 2.4 Hz, H-5), 4.418 (dd, 1 H, $J_{3',4'}$ 8.0 Hz, H-3′), 4.834 (dd, 1 H, $J_{1,2}$ 3.9, $J_{2,3}$ 10.4 Hz, H-2), 4.870 (dd, 1 H, $J_{4',5'}$ 7.7 Hz, H-4′), 5.065 (dd, 1 H, $J_{3,4}$ 9.4 Hz, H-4), 5.392 (dd, 1 H, H-3), 5.668 (d, 1 H, H-1), 7.368 and 7.830 (AA′BB′, 4 H, $J_{AB} + J_{AB'}$ = 8.25 Hz), 7.384 and 7.805 (AA′BB′, 4 H, $J_{AB} + J_{AB'}$ = 8.25 Hz); ^{13}C, δ 20.7 (q, 5 C), 21.8 (q, 2 C), 61.7 (t), 62.1 (t), 68.1 (t), 68.5 (d), 68.7 (d), 69.7 (d), 69.9 (d), 75.0 (d), 76.7 (d), 80.4 (d), 89.0 (d), 103.3 (s), 128.1 (d, 4 C), 130.2 (d, 4 C), 132.3 (s), 134.6 (s), 145.7 (s, 2 C), 169.2 (s), 169.7 (s), 170.1 (s, 3 C); **11**, ^{1}H, δ 2.05, 2.06, 2.09, 2.13, 2.22 (5 s, 3, 3, 3, 3, and 3 H, 5 Ac), 3.40 (s, 3 H), 3.47 (d, 1 H, $J_{1'a,1'b}$ 13.4 Hz, H-1′b), 3.78 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 10.0 Hz, H-2), 3.98 (d, 1 H, H-1′a), 5.06 (dd, 1 H, $J_{3,4}$ 9.3, $J_{4,5}$ 9.8 Hz, H-4), 5.11 (d, 1 H, $J_{3',4'}$ 6.1 Hz, H-3′), 5.49 (d, 1 H, H-1), 5.60 (dd, 1 H, H-3); ^{13}C, δ 20.7 (q, 5 C), 58.2 (q), 61.7 (t), 61.8 (t), 64.3 (t), 66.1 (d), 67.6 (d), 69.7 (d), 71.8 (d), 77.1 (d), 79.7 (d), 82.8 (d), 90.5 (d), 103.7 (s), 169.4 (s), 169.8 (s), 170.2 (s), 170.6 (s), 170.8 (s); **12**, ^{1}H, δ 2.05,

*Obtained with Jeol FX-60 (59.797 and 15.036 MHz) and Varian X1-200 (200 MHz) spectrometers.



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2 $R^2 = R^5 = Ac, R^1 = R^3 = R^4 = H$
3 $R^1 = R^5 = Ac, R^2 = R^3 = R^4 = H$
4 $R^1 = R^5 = Ac, R^2 = R^3 = R^4 = Ts$
5 $R^1 = R^5 = Ac, R^2 = Ts, R^3 = R^4 = H$
6 $R^1 = R^5 = Ac, R^2 = R^3 = Ts, R^4 = H$
7 $R^1 = R^5 = Ac, R^2 = R^4 = Ts, R^3 = H$
13 $R^1 = R^2 = R^3 = R^5 = Ac, R^4 = CH_3$
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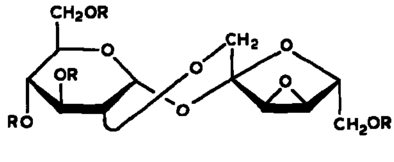

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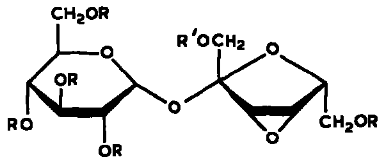

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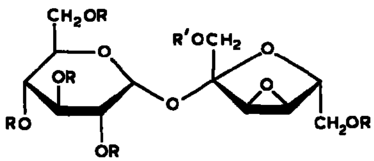

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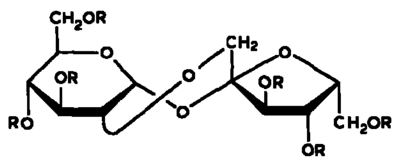

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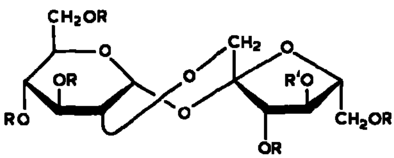

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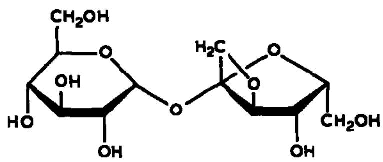
18 R = H, R′ = CH_3
23 R = R′ = Ac
24 R = R′ = CH_3



20

2.08, 2.11, 2.13 (4 s, 3, 9, 3, and 3 H, 6 Ac), 3.50 (d, 1 H, $J_{1'a,1'b}$ 12.2 Hz, H-1′b), 3.81 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.2 Hz, H-2), 3.88 (d, 1 H, H-1′a), 5.07 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.2 Hz, H-4), 5.36 (m, 2 H, H-3′,4′), 5.50 (d, 1 H, H-1), 5.64 (t, 1 H, H-3); ^{13}C, δ 20.6 (q, 2 C), 20.7 (q, 4 C), 60.8 (t), 61.7 (t), 62.6 (t), 66.4 (d), 67.4 (d), 69.7 (d), 71.9 (d), 75.6 (d), 78.5 (d), 81.0 (d), 90.3 (d), 106.2 (s), 169.5 (s), 170.2 (s), 170.6 (s, 2 C), 170.9 (s), 171.0 (s); **13**, ^{1}H, δ 2.01, 2.04, 2.08, 2.10, 2.11, 2.19 (6 s, 3, 3, 3, 6, 3, and 3 H, 7 Ac), 3.41 (s, 3 H), 3.88 (t, 1 H, $J_{3',4'} = J_{4',5'}$ = 5.5 Hz, H-4'), 4.84 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.8 Hz, H-2), 5.07 (t, $J_{3,4} = J_{4,5}$ = 9.2 Hz, H-4), 5.38 (d, 1 H, H-3'), 5.47 (dd, 1 H, H-3), 5.64 (d, 1 H, H-1); ^{13}C, δ 20.7 (q, 7 C), 58.2 (q), 61.9 (t), 63.5 (t), 64.1 (t), 68.4 (d, 2 C), 69.7 (d), 70.4 (d), 76.6 (d), 79.5 (d), 83.2 (d), 89.8 (d), 104.0 (s), 169.5 (s), 170.4 (s, 3 C), 170.6 (s, 4 C).

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