Carbohydrate Research, 65 (1978) 99–108

SYNTHESIS OF SUCROSE EPOXIDES, PARTIAL DE-ESTERIFICATION OF 1′,2:4,6-DI-*O*-ISOPROPYLIDENESUCROSE TETRA-ACETATE, AND SELECTIVE TOSYLATION OF 3,6′-DI-*O*-ACETYL-1′,2:4,6-DI-*O*-ISOPROPYLIDENESUCROSE*

RIAZ KHAN, MICHAEL R. JENNER, AND HARALD LINDSETH
Tate & Lyle Limited, Group Research and Development, Philip Lyle Memorial Research Laboratory, University of Reading, P.O. Box 68, Reading RG6 2BX (Great Britain)

(Received August 24th, 1977; accepted for publication, October 3rd, 1977)

ABSTRACT

Selective de-esterification of 1′,2:4,6-di-*O*-isopropylidenesucrose tetra-acetate[2] (**1**) with methanolic ammonia at −10° gave an inseparable mixture (**2**+**3**) of the 3,4′,6′- and 3,3′,6′-triacetates and also the 4,6′-diacetate **4**. When the reaction was performed at 5°, it gave **4**, the 4-acetate **8**, and the parent diacetal **9**. These derivatives allow selective reaction at hydroxyl groups in sucrose, in particular at HO-3′ and HO-4′, not hitherto possible. Mesylation of **4** gave the 3′,4′-dimesylate **7**, which, on treatment with aqueous acetic acid followed by acetylation, afforded 3′,4′-di-*O*-mesylsucrose hexa-acetate (**11**). Treatment of **11** with sodium methoxide in methanol at 70° for 1 min gave the *ribo*-3′,4′-epoxide **12** as the minor, and the *lyxo*-3′,4′-epoxide **13** as the major, product. Selective tosylation of **4** gave the 3′,4′-ditosylate **14** (3.7%), 4′-tosylate **15** (3.1%), and 3′-tosylate **16** (31%), indicating the order of reactivity HO-3′>HO-4′ in **4**. De-acetalation of **15** and **16** followed by acetylation gave the hepta-acetates of 4′- and 3′-*O*-tosylsucrose, respectively, which were converted into the respective epoxides, **13** and **12**, by methanolic sodium methoxide.

INTRODUCTION

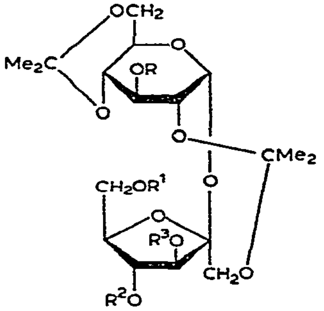
The value of sugar epoxides as synthetic intermediates is well-recognised[3]. 4,6-Dichloro-4,6-dideoxy-2,3-di-*O*-sulpho-α-D-galactopyranosyl 3,4-anhydro-1,6-dichloro-1,6-dideoxy-β-D-*ribo*-hexulofuranoside was formed during the reaction of sucrose with sulphuryl chloride[4], but a deliberate synthesis of a sucrose epoxide has not hitherto been reported. We now describe selective de-esterification reactions of 1′,2:4,6-di-*O*-isopropylidenesucrose tetra-acetate (**1**), total and partial sulphonylation of 3,6′-di-*O*-acetyl-1′,2:4,6-di-*O*-isopropylidenesucrose (**4**), and syntheses of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl 1,6-di-*O*-acetyl-3,4-anhydro-β-D-*ribo*- (**12**) and -β-D-*lyxo*-hexulofuranoside (**13**).

---

*Sucrochemistry: Part XXIV. For Part XXIII, see Ref. 1.

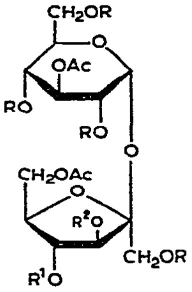
RESULTS AND DISCUSSION

Reaction of **1**[2] with methanolic ammonia at −10° for 15 min, followed by chromatography on silica gel, gave **1** (24%), an inseparable mixture of two monohydroxy compounds (32%), and **4** (30%). The ^{1}H-n.m.r. spectrum of the mixture of monohydroxy compounds revealed a low-field triplet (τ 3.91, 1:2:1) due to overlapping doublets of the anomeric protons. One of the H-3′ resonances appeared at τ 5.14, thereby suggesting that one of the compounds [3,4′,6′-tri-*O*-acetyl-1′,2:4,6-di-*O*-isopropylidenesucrose (**2**)] had the hydroxyl group at C-3′. Based on the structure of **4**, which is discussed below, the other component of the mixture was assumed to be the 4′-hydroxy compound 3,3′,6′-tri-*O*-acetyl-1′,2:4,6-di-*O* isopropylidenesucrose (**3**). On addition of trichloroacetyl isocyanate to a solution of **2**+**3** in deuteriochloroform, two singlets appeared at τ 1.34 and 1.52, integration of which and of the H-1 triplet (1:2:1) indicated an equimolar mixture.

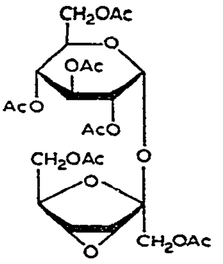


1 $R = R^1 = R^2 = R^3 = Ac$
2 $R = R^1 = R^2 = Ac, R^3 = H$
3 $R = R^1 = R^3 = Ac, R^2 = H$
4 $R = R^1 = Ac, R^2 = R^3 = H$
5 $R = R^1 = R^2 = Ac, R^3 = Ms$
6 $R = R^1 = R^3 = Ac, R^2 = Ms$
7 $R = R^1 = Ac, R^2 = R^3 = Ms$

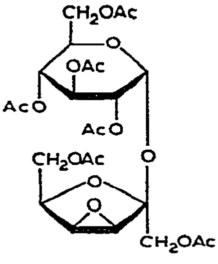
8 $R = Ac, R^1 = R^2 = R^3 = H$
9 $R = R^1 = R^2 = R^3 = H$
14 $R = R^1 = Ac, R^2 = R^3 = Ts$
15 $R = R^1 = Ac, R^2 = Ts, R^3 = H$
16 $R = R^1 = Ac, R^2 = H, R^3 = Ts$
17 $R = R^1 = R^2 = Ac, R^3 = Ts$



10 $R = H, R^1 = R^2 = Ms$
11 $R = Ac, R^1 = R^2 = Ms$
18 $R = Ac, R^1 = R^2 = Ts$
19 $R = R^2 = Ac, R^1 = Ts$
20 $R = R^1 = Ac, R^2 = Ts$



12



13

In order to confirm the structures of **2** and **3**, the mixture was mesylated and the products were subjected to chromatography on silica gel. Only small amounts of pure 3'-mesylate **5** and 4'-mesylate **6** were obtained, the major fraction being a mixture of **5** and **6**. The ^{1}H-n.m.r. spectrum of **5**+**6** contained, *inter alia*, a triplet at τ 3.94 due to overlapping doublets of H-1, an H-3' resonance at τ 5.13, and singlets for the two mesylate groups at τ 6.74 and 6.94, integration of which indicated an approximately equimolar ratio. In the ^{1}H-n.m.r. spectrum of **5**, the resonances due to H-1,2,3,3',4' were assigned on a first-order basis and confirmed by spin-decoupling experiments. The resonance due to H-3' appeared at a higher field (τ 5.12) than the corresponding resonance (τ 4.76i) in the spectrum of **1**, indicating the presence of a MsO-3' group. Similarly, for the 4'-mesylate **6**, the presence of a MsO-4' group was supported by the fact that the signals due to H-4' appeared at a higher field (τ 4.82) than the corresponding resonance (τ 4.53) for **1**.

The structure **4** was supported by its ^{1}H-n.m.r. spectrum. Although the signals due to H-3' and H-4' were not allocated, their appearance in the region τ 5.55–6.55 confirmed the presence of the hydroxyl groups at C-3' and C-4'. Addition of trichloroacetyl isocyanate to a solution of **4** in deuteriochloroform generated two singlets at τ 1.03 and 1.21, and also caused the appearance of the signals due to H-3' and H-4' at τ 4.78 and 4.55, respectively. Conventional mesylation of **4** gave the corresponding 3',4'-dimesylate **7**, the ^{1}H-n.m.r. spectrum of which contained, as expected, the H-3' and H-4' resonances at τ 5.00 and 4.79, respectively.

Treatment of **1** with methanolic ammonia initially at −10° for 0.5 h and then at 5° for 3.5 h, followed by chromatography of the products on silica gel, gave **4** (35%), the 3',4',6'-triol **8** (44.5%), and the diacetal **9** (5.2%). The structure of **8** was supported by its ^{1}H-n.m.r. spectrum. The resonance of H-3 at τ 4.72 is typical of acetylated derivatives of sucrose, and confirmed the presence of an AcO-3 group. The shift of resonances due to H-3' and H-4' from the region τ 4.5–4.8 to τ 5.31–6.57 indicated that HO-3' and HO-4' were unsubstituted. On addition of trichloroacetyl isocyanate to a solution of **8** in deuteriochloroform, three singlets appeared at τ 0.71, 1.1, and 1.35, thus confirming the presence of three hydroxyl groups, and signals due to H-3' and H-4' at τ 4.73 and 4.55, respectively, appeared, confirming the presence of the two hydroxyl groups in **8** at C-3' and C-4'. The third hydroxyl group in **8** must therefore be located at C-6'.

In the ^{1}H-n.m.r. spectrum of **9**, the signals for all the ring protons, except H-1 (τ 3.75), appeared in the region τ 5.32–6.60. Although those for H-3,3',4' were not allocated, their shift to higher field confirmed the presence of hydroxyl groups at positions 3, 3', and 4'. The absence of signals due to acetyl protons and the presence of resonances due to the protons of the two acetal groups provided additional evidence for the structure of **9**.

On the basis of the foregoing results, it is suggested that the rate of hydrolysis of the acetyl groups in **1** is in the order of O-3' $\approx$ O-4' $>$ O-6' $>$ O-3. The low reactivity of AcO-3 is probably due to steric hindrance by the 4,6- and 1',2-acetal groups.

3',4'-Di-*O*-mesylsucrose hexa-acetate (**11**), a precursor of the epoxides **12** and **13**, was obtained by treatment of **7** with boiling, aqueous acetic acid to give **10**, followed by acetylation. The structures of **10** and **11** were supported by their ^{1}H-n.m.r. spectra and (for **11**) by the mass spectrum. Treatment of **11** with methanolic M sodium methoxide at 70° for 1 min, followed by acetylation and chromatography on silica gel, gave the *ribo*-epoxide **12** (12.4%) and *lyxo*-epoxide **13** (73.3%). The fact that **13** preponderated suggested that MsO-3′ was more readily attacked by methoxide ion than MsO-4′. In the ^{1}H-n.m.r. spectrum of **12**, the resonances for H-3′,4′ were present as an AB-like quartet (J 2.5 Hz), the higher field doublet at τ 6.15 being assigned to H-4′ because it showed further splittings of 1.0 Hz due to coupling with the *trans* proton H-5′. The pattern of the resonances H-3′ and H-4′, their chemical shifts, and their coupling constants were typical of protons attached to an epoxide ring fused to a larger ring[5–7]. The mass spectrum of **12** revealed oxycarbonium ions at *m/e* 331 and 229 due to hexopyranosyl and ketofuranosyl cations, respectively.

The ^{1}H-n.m.r. spectrum of **13** also revealed an AB-like quartet due to H-3′ and H-4′ (J 3.0 Hz). The lower field doublet, which had further fine splittings of 0.5 Hz, was assigned to H-4′. The mass spectrum of **13** contained peaks for ions at *m/e* 331 and 229, corresponding to the hexopyranosyl and ketofuranosyl cations, respectively.

The structure of **12** and **13** were confirmed by unambiguous syntheses. The 3′-sulphonate **20** and the 4′-sulphonate **19**, precursors of the *ribo*-expoxide **12** and the *lyxo*-epoxide **13**, respectively, were synthesised by partial tosylation of the 3′,4′-diol **4**. Treatment of **4** with 1.3 mol. of tosyl chloride in pyridine at room temperature for 3 h, followed by chromatography on silica gel, gave the 3′,4′-ditosylate **14** (3.7%), the 4′-tosylate **15** (31%), and the 3′-tosylate **16** (31%), indicating the reactivity sequence HO-3′>HO-4′ in **4**.

The structures of **14–16** were established by chemical transformations, and by ^{1}H-n.m.r. and mass spectrometry. Although the resonances due to H-3′ and H-4′ were not allocated in the ^{1}H-n.m.r. spectrum of **14**, they were shown by spin-decoupling experiments to be in the region τ 5.0–5.3. Treatment of **14** with boiling aqueous acetic acid followed by acetylation gave 3′,4′-di-*O*-tosylsucrose hexa-acetate (**18**, 81%). The ^{1}H-n.m.r. spectrum of **18** showed two methyl peaks at τ 7.54 and 7.55, the rest of the spectrum being similar to that of sucrose octa-acetate, except for a small, relative upfield shift of ~0.2 p.p.m. for the signals due to H-3′ and H-4′, indicating that the tosyl groups were located at C-3′ and C-4′. The structure of **18** was also supported by its mass spectrum, which showed peaks for ions at *m/e* 331 and 555 due to hexopyranosyl and ketofuranosyl cations, respectively.

In the ^{1}H-n.m.r. spectrum of the 4′-tosylate **15**, the resonances due to H-3′ appeared at a relatively high field (τ 5.8), indicating the presence of a hydroxyl group at C-3′. This assignment was confirmed by the observation of a low-field singlet at τ 1.33, due to an imino proton, following the addition of trichloroacetyl isocyanate to the n.m.r. solution. Simultaneously, the signals due to H-3′ appeared at τ 4.9. Deacetalation of **15** followed by acetylation gave 4′-*O*-tosylsucrose hepta-acetate (**19**), the structure of which was ascertained on the basis of its ^{1}H-n.m.r. spectrum. In relation to the ^{1}H-n.m.r. spectrum of sucrose octa-acetate, the resonances due to H-4′ appeared at a slightly higher field (τ 4.91), indicating the presence of the tosyl group at C-4′. The mass spectrum of **19** revealed the presence of the tosyl group in the ketofuranosyl cation (ion at *m/e* 443).

The structure of the 3′-tosylate **16** was supported by its ^{1}H-n.m.r. spectrum. Although the resonances due to H-2,4,4′ were not allocated, they were shown by spin-decoupling experiments to be in the region τ 5.4–6.9. Addition of trichloroacetyl isocyanate to a solution of **16** in deuteriochloroform caused the appearance of a low-field imino-proton singlet at τ 1.31, and also signals due to H-4′ at τ 4.57, thereby confirming the presence of a hydroxyl group in **16** at C-4′. Conventional acetylation of **16** gave the corresponding acetate **17**, the structure of which was supported by its ^{1}H-n.m.r. spectrum. Treatment of **16** with boiling, aqueous acetic acid followed by acetylation afforded 3′-*O*-tosylsucrose hepta-acetate (**20**), the structure of which was supported by its ^{1}H-n.m.r. and mass spectra.

Treatment of the 3′-tosylate **20** with methanolic sodium methoxide at 70° for 1 min followed by acetylation gave the 3′,4′-*ribo*-epoxide **12** (96%), and similar treatment of the 4′-tosylate **19** gave the expected 3′,4′-*lyxo*-epoxide **13** (82%).

When the 3′,4′-ditosylate **18** was treated with sodium methoxide, as described for the 3′,4′-dimesylate **11**, it gave, after acetylation and chromatography, the expected epoxides **12** (12%) and **13** (76%). These results confirm the earlier observation that the initial attack by methoxide ion occurs mainly on MsO-3′.

EXPERIMENTAL

General methods. — All evaporations were carried out under reduced pressure. Melting points were measured on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer 141 polarimeter in 1-dm tubes. Column chromatography on silica gel was carried out at room temperature with Kieselgel (Merck 70–230 mesh). T.l.c. was performed at room temperature on silica gel 60 F-254 (Merck), with detection by charring with sulphuric acid. N.m.r. spectra (100 MHz) were measured for solutions in $CDCl_3$ (internal Me_4Si) and, wherever possible, spin-decoupling experiments were carried out to confirm the assignments. Mass spectra (70 eV) were recorded on an A.E.I. MS 12/DS 30 system with a source temperature of 200° and a heated direct-insertion probe.

*Reaction of 1′,2:4,6-di-*O*-isopropylidenesucrose tetra-acetate*[2] (**1**) *with methanolic ammonia at −10° for 15* min. — A solution of **1** (3.7 g) in dry methanol (40 ml) was treated with ammonia gas at −10° for 15 min. T.l.c. (ether–acetone 4:0.5) then showed a mixture of three components in the ratios ~1:1:1. The solution was concentrated to a syrup (3.3 g) and eluted from a column of silica gel (100 g) with ether–light petroleum (1:1) to afford the following products.

1′,2:4,6-Di-*O*-isopropylidenesucrose tetra-acetate (**1**; 0.9 g, 24.3%), m.p. and mixture m.p. 135–137° (previously reported[2] in error as m.p. 85–87°). The n.m.r. spectrum was identical to that of an authentic sample.

A mixture (1.1 g, 32.1%) of 3,4′,6′-tri-*O*-acetyl-1′,2:4,6-di-*O*-isopropylidenesucrose (**2**) and 3,3′,6′-tri-*O*-acetyl-1′,2:4,6-di-*O*-isopropylidenesucrose (**3**). N.m.r.

data: τ 3.91 (t, $J_{1,2}$ 3.0 Hz, H-1), 5.14 (d, $J_{3',4'}$ 6.5 Hz, H-3'), 7.7–8.0 (Ac), and 8.55–8.72 (Me).

Anal. Calc. for $C_{24}H_{36}O_{14}$: C, 52.6; H, 6.6. Found: C, 53.2; H, 6.8.

3,6'-Di-*O*-acetyl-1',2:4,6-di-*O*-isopropylidenesucrose (**4**) as a syrup (960 mg, 30.3%), $[\alpha]_D$ +49.5° (*c* 1, chloroform). N.m.r. data: τ 3.88 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 6.17 (q, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.71 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 7.83, 7.93 (2 s, 6 H, 2 Ac), and 8.54–8.68 (4 s, 12 H, 4 Me).

Anal. Calc. for $C_{22}H_{34}O_{13}$: C, 52.2; H, 6.8. Found: C, 52.4; H, 7.0.

Mesylation of the mixture **2**+**3**. — A solution of the foregoing mixture (0.4 g) in pyridine (40 ml) was treated with methanesulphonyl chloride (1 ml) at 0°. The solution was stored at room temperature for 24 h, and t.l.c. (ether–light petroleum, 6:1) then revealed two fast-moving spots of equal intensity. The mixture was poured into ice–water and extracted with dichloromethane, and the extract was washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and concentrated. The syrupy residue was eluted from a column of silica gel with ether–light petroleum (1:3) to afford the following products.

3,4',6'-Tri-*O*-acetyl-1',2:4,6-di-*O*-isopropylidene-3'-*O*-mesylsucrose (**5**; 25 mg, 5.5%), $[\alpha]_D$ +15° (*c* 1.1, chloroform). N.m.r. data: τ 3.92 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 6.2 (q, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.8 (q, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 5.12 (d, 1 H, $J_{3',4'}$ 6.5 Hz, H-3'), 4.64 (q, 1 H, $J_{4',5'}$ 4.5 Hz, H-4'), 6.74 (s, 3 H, Ms), 7.90–7.99 (9 H, 3 Ac); 8.56, 8.61, 8.73, and 8.77 (4 s, 12 H, 4 Me).

Anal. Calc. for $C_{25}H_{38}O_{16}S$: C, 47.9; H, 6.1; S, 5.12. Found: C, 49.2; H, 6.4; S, 4.94.

3,3',6'-Tri-*O*-acetyl-1',2:4,6-di-*O*-isopropylidene-4'-*O*-mesylsucrose (**6**; 60 mg, 13.1%), $[\alpha]_D$ +1.5° (*c* 1.3, chloroform). N.m.r. data: τ 3.97 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 6.22 (q, 1 H, $J_{2,3}$ 9.0 Hz, H-2), 4.8 (t, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 4.82 (t, 1 H, $J_{4',5'}$ 4.0 Hz, H-4'), 6.22 (s, 3 H, Ms), 7.75–8.0 (9 H, 3 Ac), and 8.55–8.79 (12 H, 4 Me).

Anal. Calc. for $C_{25}H_{38}O_{16}S$: C, 47.9; H, 6.1; S, 5.12. Found: C, 49.1; H, 6.5; S, 5.34.

A mixture containing **5** and **6** (350 mg, 76.6%), $[\alpha]_D$ +8° (*c* 1.1, chloroform). N.m.r. data: τ 3.94 (t, $J_{1,2}$ 3.5 Hz, H-1), 5.13 (d, $J_{4,4}$ 6.5 Hz, H-3'), 6.74, 6.94 (2 m, 2 Me), 7.7–8.04 (Ac), and 8.45–8.87 (Me).

Reaction of **1** *with methanolic ammonia at 5° for 3.5 h.* — A solution of **1** (8 g) in dry methanol was treated with ammonia gas at −10° for 30 min. The reaction mixture was stored at 5° for 3.5 h, and t.l.c. (dichloromethane–methanol, 5:1) then revealed two slow-moving, major products). The solution was concentrated, and the syrupy residue was eluted from a column of silica gel with dichloromethane–acetone (6:1) to give the following products.

3,6'-Di-*O*-acetyl-1',2:4,6-di-*O*-isopropylidenesucrose (**4**; 2.4 g, 35%), $[\alpha]_D$ +49.5° (*c* 1, chloroform). The n.m.r. spectrum was identical with that of the previously prepared sample.

3-*O*-Acetyl-1',2:4,6-di-*O*-isopropylidenesucrose (**8**; 2.8 g, 44.5%), $[\alpha]_D$ +28°

(*c* 1.18, chloroform). N.m.r. data ($CDCl_3$): τ 3.80 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.72 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 7.96 (s, 3 H, Ac), and 8.54–8.65 (12 H, 4 Me).

Anal. Calc. for $C_{20}H_{32}O_{12}$: C, 51.7; H, 6.9. Found: C, 51.1; H, 7.0.

1′,2:4,6-Di-*O*-isopropylidenesucrose (**9**; 300 mg, 5.2%), m.p. 164–166° (from acetone–ether), $[\alpha]_D$ +38° (*c* 1.11, pyridine). N.m.r. data ($CDCl_3$): τ 3.52 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.0–6.5 (m, 13 H), and 8.55–8.74 (12 H, 4 Me).

Anal. Calc. for $C_{18}H_{30}O_{11}$: C, 51.2; H, 7.2. Found: C, 51.0; H, 7.8.

3,6′-Di-O-acetyl-1′,2:4,6-di-O-isopropylidene-3′,4′-di-O-mesylsucrose (**7**). — A solution of **4** (4 g) in pyridine (50 ml) was treated with mesyl chloride (3 ml) at −5° for 2 h. The mixture was stored at room temperature for 24 h and then worked-up as described previously. The syrupy product was eluted from a column of silica gel with ether–light petroleum (9:1) to give **7** (3.8 g, 72.6%), $[\alpha]_D$ +14° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): τ 3.87 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 6.15 (q, 1 H, $J_{2,3}$ 9.0 Hz, H-2), 4.77 (t, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 5.00 (d, 1 H, $J_{4',5'}$ 5.0 Hz, H-4′), 6.62, 6.8 (s, 6 H, 2 Ac), and 8.51–8.67 (4 s, 12 H, 4 Me).

Anal. Calc. for $C_{24}H_{38}O_{17}S_2$: C, 43.5; H, 5.8; S, 9.7. Found: C, 44.3; H, 6.0; S, 9.3.

3,6′-Di-O-acetyl-3′,4′-di-O-mesylsucrose (**10**). — A solution of **7** (3.8 g) in 60% aqueous acetic acid (40 ml) was kept at 100° for 15 min and then concentrated to give **10** (3 g, 89.8%), m.p. 152–154°, $[\alpha]_D$ +54° (*c* 1.1, water). N.m.r. data (C_5D_5N): τ 3.96 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.05 (t, 1 H, $J_{2,3}$ 10.0 Hz, H-3), 4.04 (d, 1 H, $J_{3',4'}$ 6.5 Hz, H-3′), 4.22 (t, 1 H, $J_{4',5'}$ 6.5 Hz, H-4′), 6.46, 6.62 (2 s, 6 H, 2 Ms), 8.04 and 8.13 (2 s, 6 H, 2 Ac).

Anal. Calc. for $C_{18}H_{30}O_{17}S_2$: C, 37.1; H, 5.2; S, 11.0 Found: C, 37.2; H, 5.1; S, 11.2.

3′,4′-Di-O-mesylsucrose hexa-acetate (**11**). — A solution of **10** (5 g) in pyridine (50 ml) was treated with acetic anhydride (5 ml) at room temperature for 24 h. T.l.c. (ether–acetone, 4:1) then showed a fast-moving product. The solution was concentrated to give **11** (6.3 g, 98%), $[\alpha]_D$ +47° (*c* 1.23, chloroform). N.m.r. data ($CDCl_3$): τ 4.31 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.09 (q, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.65 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 4.94 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.66 (d, 1 H, $J_{3',4'}$ 7.0 Hz, H-3′), 4.73 (t, 1 H, $J_{4',5'}$ 7.0 Hz, H-4′), 6.76, 6.9 (2 s, 6 H, 2 Ms), and 7.85–8.0 (m, 18 H, 6 Ac). Mass spectrum [(a) indicates hexopyranosyl and (b) ketofuranosyl cations]: *m/e* 403(b), 331(a), 271(a), 247(b), 211(a), 169(a), 127(a), and 109(a).

Anal. Calc. for $C_{26}H_{38}O_{21}S_2$: C, 41.6; H, 5.1; S, 8.5. Found: C, 42.0; H, 5.2; S, 8.2.

Reaction of **11** *with sodium methoxide.* — A solution of **11** (11 g) in methanolic M sodium methoxide (200 ml) was heated to 70° for 2 min, and then concentrated, and the residue was treated with acetic anhydride (50 ml) and pyridine (300 ml) at room temperature for 24 h. T.l.c. (ether–acetone, 4:1) then showed two fast-moving products. The mixture was poured into ice–water and extracted into dichloromethane, and the extract was washed successively with water, aqueous sodium hydrogen carbonate, and water, dried (Na_2SO_4), and concentrated. The residue was eluted from a column of silica gel (300 g) with ether–light petroleum (9:1) to give the following epoxides.

2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl 1,6-di-*O*-acetyl-3,4-anhydro-β-D-*ribo*-hexulofuranoside (**12**; 1.1 g, 12.4%), $[\alpha]_D$ +59° (*c* 0.6, chloroform). N.m.r. data ($CDCl_3$): τ 4.39 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.13 (q, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.53 (q, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 4.94 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 6.12 (d, 1 H, $J_{3',4'}$ 2.5 Hz, H-3'), 6.15 (q, 1 H, $J_{4',5'}$ 1.0 Hz, H-4'), and 7.86–8.0 (18 H, 6 Ac). Mass spectrum [(a) indicates hexopyranosyl and (b) ketofuranosyl cations]: *m/e* 331(a), 271(a), 229(b) 211(a), 169, 127(b), and 109.

Anal. Calc. for $C_{24}H_{32}O_{16}$: C, 50.0; H, 5.6. Found: C, 50.0; H, 5.7.

2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl 1,6-di-*O*-acetyl-3,4-anhydro-β-D-*lyxo*-hexulofuranoside (**13**; 6.2 g, 73.3%), $[\alpha]_D$ +59° (*c* 0.6, chloroform). N.m.r. data ($CDCl_3$): τ 4.23 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.21 (q, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.55 (q, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 4.96 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 6.32 (d, 1 H, $J_{3',4'}$ 3.0 Hz, H-3'), 6.25 (q, 1 H, $J_{4',5'}$ 0.5 Hz, H-4'), and 7.88–7.99 (m, 18 H, 6 Ac).

Anal. Calc. for $C_{24}H_{32}O_{16}$: C, 50.0; H, 5.6. Found: C, 50.1; H, 5.7.

Selective tosylation of **4**. — A solution of **4** (10 g) in pyridine (200 ml) was treated with tosyl chloride (5 g, 1.3 mol.) at −10°. The mixture was allowed to attain room temperature slowly, and then stirred for 3 h. T.l.c. (ether–acetone, 10:1) revealed **4** and three fast-moving products. The reaction was worked-up as described above, and the syrupy residue was eluted from a column of silica gel (400 g) with ether–light petroleum (1:1) to afford the following products.

3,6'-Di-*O*-acetyl-1',2:4,6-di-*O*-isopropylidene-3',4'-di-*O*-tosylsucrose (**14**; 600 mg, 3.7%), $[\alpha]_D$ −13° (*c* 1.0, chloroform). N.m.r. data ($CDCl_3$): τ 4.05 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.8 (t, 1 H, $J_{2,3}$ 9.5 Hz, H-3), 7.93, 7.96 (2 s, 6 H, 2 Ac), 7.53, 7.59, (2 s, 6 H, 2 Ts), 8.55–8.62 (12 H, 4 Me), and 2.13–2.68 (4 H, Ts).

Anal. Calc. for $C_{36}H_{46}O_{17}S_2$: C, 53.1; H, 5.7; S, 7.9. Found: C, 53.6; H, 6.0; S, 7.4.

3,6'-Di-*O*-acetyl-1',2:4,6-di-*O*-isopropylidene-4'-*O*-tosylsucrose (**15**; 400 mg, 3.1%), $[\alpha]_D$ +2° (*c* 0.6, chloroform). N.m.r. data ($CDCl_3$): τ 3.96 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.81 (t, 1 H, $J_{2,3}$ 7.5 Hz, H-3), 5.29 (q, 1 H, $J_{3',4'}$ 5.0, $J_{4',5'}$ 6.0 Hz, H-4'), 7.54 (s, 3 H, Ts). 7.95, 7.96 (2 s, 6 H, 2 Ac), 8.54–8.73 (12 H, 4 Me), and 2.15–2.7 (4 H, Ts).

Anal. Calc. for $C_{29}H_{40}O_{15}S$: C, 52.7; H, 6.1; S, 4.9. Found: C, 53.6; H, 6.3; S, 4.6.

3,6'-Di-*O*-acetyl-1',2:4,6-di-*O*-isopropylidene-3'-*O*-tosylsucrose (**16**; 4.1 g, 31%), m.p. 158–160° (from ether), $[\alpha]_D$ +9° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): τ 4.03 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.78 (t, 1 H, $J_{2,3}$ 9.0 Hz, H-3), 7.58 (s, 3 H, Ts), 7.84, 7.87 (2 s, 6 H, 2 Ac), 8.56–8.93 (12 H, 4 Me), 2.06, 2.14, 2.56, and 2.64 (4 s, 4 H, Ts).

Anal. Calc. for $C_{29}H_{40}O_{15}S$: C, 52.7; H, 6.1; S, 4.9. Found: C, 52.7; H, 6.1; S, 4.8.

Conventional acetylation of **16** (200 mg), with acetic anhydride (0.5 ml) and pyridine (5 ml), gave **17** (200 mg, 94%), m.p. 161–163° (from ether), $[\alpha]_D$ +8° (*c* 0.7, chloroform). N.m.r. data ($CDCl_3$): τ 4.00 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), (q, 1 H, $J_{4',5'}$ 4.0 Hz, H-4'), 7.58 (s, 3 H, Ts), 7.93–7.99 (9 H, 3 Ac), 2.09, 2.16, 2.57, and 2.65 (4 s, 4 H, Ts).

Anal. Calc. for $C_{31}H_{42}O_{16}S$: C, 53.0; H, 6.0; S, 4.6. Found: C, 52.8; H, 6.1; S, 4.5.

3',4'-Di-O-tosylsucrose hexa-acetate (**18**). — A solution of **14** (400 mg) in 60% aqueous acetic acid (10 ml) was heated at 100° for 8 min, and then concentrated to dryness. Conventional acetylation of the residue gave **18** (360 mg, 81%), m.p. 150–152° (from ether), $[\alpha]_D$ +54° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): τ 4.36 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.18 (q, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.63 (q, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 4.97 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.83 (d, 1 H, $J_{3',4'}$ 5.5 Hz, H-3'), 4.81 (q, 1 H, $J_{4',5'}$ 8.0 Hz, H-4'), 7.54, 7.55 (2 s, 6 H, 2 Ts), and 2.2–2.71 (8 H, 2 Ts).

Anal. Calc. for $C_{38}H_{46}O_{21}S_2$: C, 50.6; H, 5.1; S, 7.1. Found: C, 50.4; H, 5.1; S, 7.0.

4'-O-Tosylsucrose hepta-acetate (**19**). — A solution of **15** (400 mg) in aqueous acetic acid (10 ml) was heated at 100° for 8 min and then concentrated, and the residue was acetylated with acetic anhydride and pyridine, as described previously, to afford **19** (310 mg, 65%) as a syrup, $[\alpha]_D$ +49° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): τ 4.37 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.17 (q, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.61 (q, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 4.95 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.47 (d, 1 H, $J_{3',4'}$ 6.5 Hz, H-3'), 4.91 (t, 1 H, $J_{4',5'}$ 6.5 Hz, H-4'), 7.55 (s, 3 H Ts), 7.87–8.00 (21 H, 7 Ac), 2.20, 2.28, 2.63, and 2.71 (4 s, 4 H, Ts).

Anal. Calc. for $C_{33}H_{42}O_{20}S$: C, 50.1; H, 5.4; S, 4.1. Found: C, 50.5; H, 5.5; S, 4.1.

3'-O-Tosylsucrose hepta-acetate (**20**). — A solution of **16** (1.8 g) was treated with 60% aqueous acetic acid, as described in the preparation of **19**, and then concentrated. The residue was acetylated to give **20** (1.8 g, 84%), m.p. 180–181° (from ether), $[\alpha]_D$ +51° (*c* 1.1, chloroform). N.m.r. data ($CDCl_3$): τ 4.36 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.13 (q, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.60 (q, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 4.98 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.84 (d, 1 H, $J_{3',4'}$ 8.0 Hz, H-3'), 4.44 (t, 1 H, $J_{4',5'}$ 8.0 Hz, H-4'), 7.54 (s, 3 H, Ts), 7.89–8.02 (21 H, 7 Ac), 2.17, 2.25, 2.57, and 2.71 (4 s, 4 H, Ts).

Anal. Calc. for $C_{33}H_{42}O_{20}S$: C, 50.1; H, 5.4; S, 4.1. Found: C, 49.9; H, 5.2; S, 4.0.

Reaction of **20** *and* **19** *with sodium methoxide.* — Treatment of the 3'-tosylate **20** (100 mg) with methanolic M sodium methoxide (1 ml) at 70° for 1 min, followed by concentration and conventional acetylation of the product, gave the *ribo*-epoxide **12** (70 mg, 96%). The $[\alpha]_D$, ^{1}H-n.m.r., and mass-spectral data were indistinguishable from those of the sample prepared previously.

Similar treatment of **19** (100 mg) afforded the *lyxo*-epoxide **13** (60 mg, 82%). The $[\alpha]_D$, ^{1}H-n.m.r., and mass-spectral data were identical with those of the standard sample.

ACKNOWLEDGMENTS

We thank Professor A. J. Vlitos, Chief Executive of the Tate and Lyle Research Centre, for his interest and support, Dr. K. J. Parker for helpful discussions, and R. W. Butters for providing the mass spectra.

REFERENCES

1 R. Khan, M. R. Jenner, and H. F. Jones, *Carbohydr. Res.*, 49 (1976) 259–265.

2 R. Khan and K. S. Mufti, *Carbohydr. Res.*, 43 (1975) 247–253.

3 F. H. Newth, *Q. Rev.*, (1959) 30–47; R. E. Parker and N. S. Isaacs, *Chem. Rev.*, 59 (1959) 737–799; N. R. Williams, *Adv. Carbohydr. Chem. Biochem.*, 25 (1970) 109–179.

4 J. M. Ballard, L. Hough, and A. C. Richardson, *Chem. Commun.*, (1972) 1097–1098.

5 J. M. Ballard, L. Hough, A. C. Richardson, and P. H. Fairclough, *J. Chem. Soc., Perkin Trans. I*, (1973) 1524–1528.

6 D. H. Buss, L. Hough, L. D. Hall, and J. F. Manville, *Tetrahedron*, 21 (1965) 69–74.

7 L. Hough, P. A. Monroe, and A. C. Richardson, *J. Chem. Soc., C*, (1971) 1090–1094.