Carbohydrate Research, 43 (1975) 247–253

SYNTHESIS AND REACTIONS OF 1′,2:4,6-DI-*O*-ISOPROPYLIDENE-SUCROSE*

RIAZ KHAN AND KHIZAR S. MUFTI

Tate & Lyle Ltd., Group Research & Development, Philip Lyle Memorial Research Laboratory, University of Reading, P.O. Box 68, Reading RG6 2BX (Great Britain)

(Received February 14th, 1975; accepted for publication, February 24th, 1975)

ABSTRACT

The reaction of sucrose with a combination of 2,2-dimethoxypropane, *N*,*N*-dimethylformamide, and toluene-*p*-sulphonic acid (reagent *A*) gave, after acetylation followed by chromatography, 1′,2:4,6-di-*O*-isopropylidenesucrose tetra-acetate (**1**) in 15% yield. The structure of **1** was determined on the basis of p.m.r. and mass spectrometry, and by chemical transformations. Treatment of **1** with aqueous acetic acid afforded sucrose 3,3′,4′,6′-tetra-acetate **2**. Reacetalation of **2** using reagent *A* gave **1** in 80% yield. The p.m.r. spectrum of **2** confirmed the presence of hydroxyl groups at C-2 and C-4. The following sequence of reactions showed that the remaining two hydroxyl groups were located at C-6 and C-1′. Selective tritylation of **2** gave 1′,6-di-*O*-tritylsucrose 3,3′,4′,6′-tetra-acetate (**3**) as the minor, and 6-*O*-tritylsucrose 3,3′,4′,6′-tetra-acetate (**4**) as the major, product. When tritylation was carried out under forcing conditions, **2** gave **3** as the major product. Acetylation of **4** afforded 6-*O*-tritylsucrose hepta-acetate. Mesylation of **2** gave the tetramethanesulphonate **5**, which afforded the 6-deoxy-6-iodo derivative **6** on treatment with a refluxing solution of sodium iodide in butanone. Treatment of **3** with methanesulphonyl chloride in pyridine gave the disulphonate **7**, which on detritylation followed by acetylation gave 2,4-di-*O*-methanesulphonylsucrose hexa-acetate (**9**). Treatment of **9** with sodium benzoate in hexamethylphosphoric triamide displaced the 4-sulphonate, with inversion of configuration, to give the *galacto* derivative **10**.

INTRODUCTION

In continuation of our studies on the synthesis of acetal derivatives of sucrose, we have used the combination (reagent *A*) of 2,2-dimethoxypropane, *N*,*N*-dimethylformamide, and toluene-*p*-sulphonic acid as an acetalating reagent. The unique acetalating properties of reagent *A* have been recognised and demonstrated to give strained and otherwise inaccessible cyclic acetal derivatives of sugars[2–5]. In our previous study of this reaction with sucrose, the expected 4,6-*O*-isopropylidenesucrose

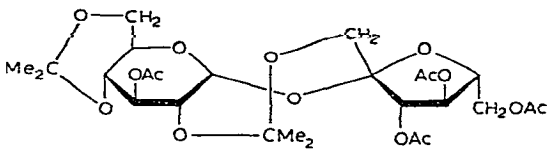
*Sucrochemistry: Part XVII. For Part XVI, see Ref. 1.

was obtained in 55% yield[6]. We now report the synthesis of a dicyclic acetal derivative of sucrose containing a six-membered (4,6-*O*-) and an eight-membered (1′,2-*O*-) cyclic acetal linkage. Apparently, an eight-membered cyclic acetal ring has not, hitherto, been reported in carbohydrate chemistry. The flexibility of the eight-membered ring parallels that of the 1,3-dioxepane ring in the 3,4-*O*-benzylidene or 3,4-*O*-isopropylidene derivatives of 1,6-di-*O*-benzoyl-2,5-*O*-methylene-D-mannitol, which is flexible enough to accommodate torsional angles between projected *trans* C–O bonds of 41° or less[7]. The structure of the diacetal derivative of sucrose has been confirmed by p.m.r. and mass spectrometry, and by chemical transformations.

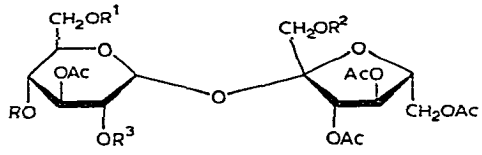
RESULTS AND DISCUSSION

Treatment of sucrose with reagent *A* afforded a mixture which, after treatment with acetic anhydride and pyridine followed by chromatography on silica gel, gave the crystalline 1′,2:4,6-diacetal **1** in 15% yield. In the p.m.r. spectrum of **1**, the signals due to H-2 and H-4 appeared at relatively high field (τ 6.15 and 6.25, respectively). The signals for these protons usually appear in the region τ 4.5–5.4 for acetylated derivatives of sucrose. The shift to higher field therefore suggested that C-4 and C-2 were involved in the presumed acetal linkages. The p.m.r. spectrum of **1** showed four methyl peaks at τ 8.56, 8.64, 8.77, and 8.85 due to two isopropylidene groups. Further proof of the presence of two cyclic acetal groups in **1** was supplied by the formation of the tetra-acetate **2** on treatment with 60% acetic acid at 90° for 10 min. Although the signals due to H-2 and H-4 were not allocated in the p.m.r. spectrum of **2**, they were shown by spin-decoupling experiments to be in the region of τ 5.55–6.5 in deuteriochloroform and τ 5.2–5.5 in deuteriobenzene. The shift of these signals to higher field would be expected if C-2 and C-4 carried free hydroxyl instead of acetoxyl groups. Addition of trichloroacetyl isocyanate to a solution of **2** in deuteriochloroform generated in the p.m.r. spectrum four singlets at τ 0.59, 0.85, 1.12, and 1.26 due to imino protons. It also caused the reappearance of signals for H-2 and H-4 at τ 4.95 and 5.03, respectively. Thus, two of the four hydroxyl groups in **2** were located at C-2 and C-4. Reacetalation of **2** using reagent *A* gave the diacetal **1** in 80% yield, which confirmed that no acetyl migration occurred during the deacetalation of **1** to give **2**.

The positions of the remaining two hydroxyl groups in **2** were established by the following sequence of reactions. Treatment of **2** with trityl chloride and pyridine at 88° for 4 h afforded the ditrityl ether **3** as the minor, and the monotrityl ether **4** as the major, product. The position of the trityl group at C-6 in **4** was established by converting **4** into the known[8,9] 6-*O*-tritylsucrose hepta-acetate, using acetic anhydride and pyridine. When the tritylation of **2** was carried out at 90° for 24 h, it gave the ditrityl ether **3** in 85% yield. The slow tritylation reaction to give **3** indicated that the second primary-hydroxyl group was located at C-1′. This was confirmed by treatment of **2** with methanesulphonyl chloride and pyridine to give the tetrasulphonate **5**, which, with a refluxing solution of sodium iodide in butanone, afforded the 6-deoxy-6-iodo



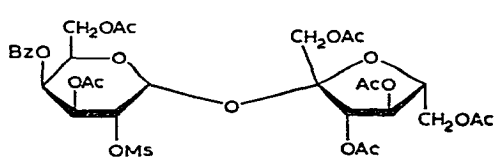
1



2 R = R^1 = R^2 = R^3 = H
3 R = R^3 = H R^1 = R^2 = Tr
4 R = R^2 = R^3 = H R^1 = Tr
5 R = R^1 = R^2 = R^3 = Ms
6 R = R^2 = R^3 = Ms OR^1 = I
7 R = R^3 = Ms R^1 = R^2 = Tr
8 R = R^3 = Ms R^1 = R^2 = H
9 R = R^3 = Ms R^1 = R^2 = Ac

derivative **6** in 95% yield. The structure of **6** was indicated by its p.m.r. spectrum. The majority of the ring protons were assigned and confirmed by spin-decoupling experiments. The mass spectrum of **6** showed ions at *m/e* 439 and 367 due to hexopyranosyl and ketofuranosyl cations, respectively.

The involvement of C-4 in **1** in cyclic acetal formation was also established by the following chemical modifications of **3**. Treatment of **3** with methanesulphonyl chloride in pyridine gave the corresponding 2,4-disulphonate **7**. Detritylation of **7**, using hydrogen bromide in acetic acid in a mixture of chloroform and acetic acid at 0°, gave the expected 1′,6-dihydroxy compound **8**. The structure of **8** was confirmed from its p.m.r. spectrum. Addition of trichloroacetyl isocyanate to a solution of **8** in deuteriochloroform generated two singlets at τ 0.72 and 1.02 in the p.m.r. spectrum, due to the imino protons of the resulting carbamate groups, thereby confirming the presence of two hydroxyl groups in **8**. The mass spectrum of **8** showed ions due to hexopyranosyl and ketofuranosyl cations at *m/e* 361 and 289, respectively. Conventional acetylation of **8** gave the corresponding hexa-acetate **9**. In comparison with the p.m.r. data for sucrose octa-acetate, the signals for H-2 and H-4 in **9** appeared at slightly higher field, *i.e.*, at τ 5.35 and 5.2, respectively, thereby providing further evidence that the two sulphonates in **9** were located at C-2 and C-4. The mass spectrum of **9** indicated the expected ions at *m/e* 403 and 331 due to hexopyranosyl and ketofuranosyl cations, respectively. Replacement of the 4-sulphonate group in **9**, using sodium benzoate in hexamethylphosphoric triamide, gave product **10** with inversion of configuration at C-4. The derived first-order coupling constants ($J_{1,2}$ 3.75, $J_{2,3}$ 10.5, $J_{3,4}$ 3.5, $J_{4,5}$ 1.4, $J_{3',4'}$ 6.0, and $J_{4',5'}$ 6.0 Hz) for **10** confirmed the α-D-*galacto*



10

configuration and the $^4C_1$ conformation for the hexopyranosyl moiety. The mass spectrum of **10** contained fragment ions corresponding to hexopyranosyl (*m/e* 429) and ketofuranosyl (*m/e*/ 331) cations.

EXPERIMENTAL

For details of general procedure, see Part VI[8].

1'2:4,6-Di-O-isopropylidenesucrose tetra-acetate (**1**). — A solution of sucrose (5 g) in *N,N*-dimethylformamide (250 ml) was treated with 2,2-dimethoxypropane (25 ml) in the presence of toluene-*p*-sulphonic acid (500 mg) at room temperature for 80 min. The solution was then neutralised with IR-45(HO^-) resin, filtered, and concentrated. The syrupy residue was treated with acetic anhydride (30 ml) and pyridine (80 ml). T.l.c. (ether–light petroleum, 4:1) showed three major components. The reaction mixture was concentrated by codistillation with toluene to give a syrupy product, which on elution from a column of silica gel (200 g), using ether–light petroleum (1:1), afforded the fast-moving compound **1** (1.43 g, 15%), m.p. 85–87°, $[\alpha]_D$ +12.8° (*c* 1.01, chloroform). N.m.r. data (C_6D_6): τ 3.66 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 6.58 (q, 1 H, $J_{2,3}$ 9.0 Hz, H-2), 4.39 (t, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 4.76 (d, 1 H, $J_{3',4'}$ 5.5 Hz, H-3'), 4.53 (q, 1 H, $J_{4',5'}$ 4.0 Hz, H-4'), 6.48–6.78 (1 H, H-4), 8.15, 8.25, 8.33, 8.4 (s, 12 H, 4Ac), 8.65, 8.71, 8.82, 8.9 (s, 12 H, 4Me).

Anal. Calc. for $C_{26}H_{38}O_{15}$: C, 52.71; H, 6.44. Found: C, 52.6; H, 6.44.

3,3',4',6'-Tetra-O-acetylsucrose (**2**). — The diacetal **1** (1 g) was heated with 60% aqueous acetic acid (20 ml) at 50° for 25 min. T.l.c. (ether–acetone, 5:1) showed a slow-moving product. The solution was concentrated by codistillation with toluene to give **2** (0.77 g, 90%), m.p. 121–123° (from acetone–ether), $[\alpha]_D$ +58.6° (*c* 1.45, chloroform). N.m.r. data (C_5D_5N): τ 4.0 (d, 1 H, $J_{1,2}$ 3.5 Hz H-1), 3.98 (t, 1 H, $J_{2,3}$ 10.0 Hz, H-3), 3.8 (d, 1 H, $J_{3',4'}$ 6.5 Hz, H-3'), 4.11 (t, 1 H, $J_{4',5'}$ 6.5 Hz, H-4'), 2.65–3.02, 2.24–2.46 (2 m, 4 H, 4OH), 7.93, 8.03, 8.1 (12 H, 4Ac).

Anal. Calc. for $C_{20}H_{30}O_{15}$: C, 47.05; H, 5.8. Found: C, 47.3; H, 5.9.

Compound **2** (120 mg) was treated with 2,2-dimethoxypropane (1.2 ml) and toluene-*p*-sulphonic acid (20 mg) in *N,N*-dimethylformamide (7 ml) at room temperature for 2 h. The reaction mixture was diluted with dichloromethane (100 ml), washed with aqueous sodium hydrogen carbonate and water, dried, and concentrated. T.l.c. (ether–light petroleum, 6:1) showed a major product, which was coincident with **1**. The syrup, on elution from a column of silica gel (20 g) with ether–light petroleum (1:1), gave **1** (100 mg, 80%), m.p. and mixture m.p. 85–87°, The n.m.r. spectrum was identical with that of the previously prepared sample.

Tritylation of **2**. — (*a*) A solution of **2** (4.5 g) in pyridine was treated with trityl chloride (4 g) at 88° for 4 h. T.l.c. (ether) showed a minor fast-moving and a major slow-moving product. The reaction mixture was diluted with dichloromethane, washed with aqueous sodium hydrogen carbonate and water, and dried (Na_2SO_4). The solution was concentrated and triphenylmethanol was removed by crystallisation from methanol. The filtrate was then concentrated, and the syrupy residue was

eluted from a column of silica gel (100 g) with ether to give the following two fractions. (*i*) 3,3′,4′,6′-Tetra-*O*-acetyl-1′,6-di-*O*-tritylsucrose (**3**) (1.3 g, 14.8%), $[\alpha]_D$ +48.2° (*c* 0.83, chloroform). N.m.r. data: τ 4.75 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.95 (t, 1 H, $J_{2,3}$ 9.5 Hz, H-3), 4.24 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3′), 4.65 (t, 1 H, $J_{4',5'}$ 6.0 Hz, H-4′), 2.43–2.85 (m, 30 H, 2Tr), 7.83, 7.86, 7.93, 7.98 (s, 12 H, 4Ac).

Anal. Calc. for $C_{62}H_{62}O_{17}$: C, 69.01; H, 5.75. Found: C, 68.8; H, 5.7.

(*ii*) 3,3′,4′,6′-Tetra-*O*-acetyl-6-*O*-tritylsucrose (**4**) (4.5 g, 67.72%), $[\alpha]_D$ +44.5° (*c* 1, chloroform).

Anal. Calc. for $C_{45}H_{50}O_{18}$: C, 61.5; H, 5.69. Found: C, 62.1; H, 5.8.

Conventional treatment of **4** (200 mg) with acetic anhydride (1 ml) in pyridine (15 ml) at room temperature for 24 h gave 6-*O*-tritylsucrose hepta-acetate as an amorphous powder (210 mg, 95%). The n.m.r. spectrum was identical with that of the standard sample[8,9].

(*b*) When **2** (2 g) was treated with trityl chloride (2 g) in pyridine at 90° for 24 h, it afforded, after working-up as described previously and chromatography of the product, mainly **3** (3 g, 76.5%).

3,3′,4′,6′-Tetra-O-*acetyl-1′,2,4,6-tetra*-O-*methanesulphonylsucrose* (**5**). — A solution of **2** (2 g) in pyridine (50 ml) was treated with methanesulphonyl chloride (2 ml) at 0° for 1 h and then kept at room temperature for 24 h. To the cooled reaction mixture, water (1 ml) was added, and the solution was left at room temperature for 30 min. The reaction mixture was poured into ice–water, and the resulting precipitate was collected, washed well with water, and dried *in vacuo* overnight. Crystallisation from ethanol gave **5** (2.41 g, 75%), m.p. 85–86°, $[\alpha]_D$ +39.9° (*c* 2.34, chloroform). N.m.r. data: τ 4.19 (d, 1 H, $J_{1,2}$ 3.75 Hz, H-1), 5.2 (q, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.49 (q, 1 H, $J_{3,4}$ 9.25 Hz, H-3), 5.16 (t, 1 H, $J_{4,5}$ 9.25 Hz, H-4), 4.49 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3′), 4.58 (t, 1 H, $J_{4',5'}$ 6.0 Hz, H-4′), 6.85–6.91 (12 H, 4Ms), 7.8, 7.85, 7.89 (12 H, 4Ac). Mass-spectral data [(a) indicates hexopyranosyl and (b) ketofuranosyl cations]: *m/e* 439a, 379a, 367b, 283a, 247b, 211b, 205a, 169b, 151b, and 109.

Anal. Calc. for $C_{24}H_{38}O_{23}S_4$: C, 35.03; H, 4.62; S, 15.57. Found: C, 35.00; H, 4.8; S, 15.3.

3,3′,4′,6′-Tetra-O-*acetyl-6-deoxy-6-iodo-1′,2,4-tri*-O-*methanesulphonylsucrose* (**6**). — A solution of **5** (500 mg) in butanone (50 ml) was refluxed with sodium iodide (1 g) for 24 h. T.l.c. (ether–acetone, 9:1) showed a fast-moving product. The filtered reaction mixture was concentrated, and a solution of the residue in dichloromethane was washed with aqueous sodium thiosulphate and with water, and dried (Na_2SO_4). The solution was concentrated, and the residue was crystallised from ethanol to give **6** (490 mg, 95%), m.p. 81–82°, $[\alpha]_D$ +52.42° (*c* 1.13, chloroform). N.m.r. data: τ 4.15 (d, 1 H, $J_{1,2}$ 3.75 Hz, H-1), 5.31 (q, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.44 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 5.36 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.51 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3′), 4.5 (t, 1 H, $J_{4',5'}$ 6.0 Hz, H-4′), 6.1 (m, 1 H, H-5), 6.84, 6.85 (9 H, 3Ms), 7.77, 7.85, 7.87 (12 H, 4Ac). Mass-spectral data [(a) and (b) indicate ions due to hexopyranosyl and ketofuranosyl cations, respectively]: *m/e* 471a, 411a, 367b, 315a, 247b, 237a, 211b, 169b, and 109.

Anal. Calc. for $C_{23}H_{35}IO_{20}S_3$: C, 32.3; H, 4.1; I, 14.9; S, 11.2. Found: C, 32.5; H, 4.1; I, 14.0; S, 11.1.

*3,3',4',6'-Tetra-*O*-acetyl-2,4-di-*O*-mesyl-1',6-di-*O*-tritylsucrose* (7). — A solution of **3** (2.5 g) in pyridine (50 ml) was treated with mesyl chloride (2.5 ml) at 0° and then kept at room temperature for 24 h. To the cooled reaction mixture, water (1 ml) was added, the solution was left at room temperature for 30 min and then poured into ice–water, the precipitate was collected, washed with water, and taken up in dichloromethane, and the solution was dried (Na_2SO_4). Concentration gave **7** (2.6 g, 89.9%) as a crystalline powder, m.p. 189–190°, $[\alpha]_D$ +50.7° (*c* 0.74, chloroform). N.m.r. data: τ 4.42 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.35 (q, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.5 (q, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5.0 (q, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.03 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3'), 4.59 (t, 1 H, $J_{4',5'}$ 6.0 Hz, H-4'), 2.45–2.85 (30 H, 2Tr), 7.15, 7.53 (2 s, 6 H, 2Ms), 7.84, 7.93, 7.94, 7.96 (4 s, 12 H, 4Ac).

Anal. Calc. for $C_{60}H_{62}O_{19}S_2$: C, 62.17; H, 5.39; S, 5.56. Found: C, 62.1; H, 5.4; S, 5.7.

*3,3',4',6'-Tetra-*O*-acetyl-2,4-di-*O*-mesylsucrose* (**8**). — A solution of **7** (2.5 g) in a mixture of chloroform (4 ml) and glacial acetic acid (7 ml) was treated with hydrogen bromide in acetic acid (45%, 2 ml) at 0° for 5–10 min. The reaction mixture was diluted with dichloromethane and washed successively with aqueous sodium acetate, water, aqueous sodium hydrogen carbonate, and water. The solution was dried (Na_2SO_4) and concentrated to give a crystalline residue. Triphenylmethanol was removed by crystallisation from methanol at 0°, and the resulting solution was concentrated to give a syrup, which was purified by elution from a small column of silica gel, using ether, to give **8** (1.2 g, 71.8%), $[\alpha]_D$ +39.9° (*c* 2.34, chloroform). N.m.r. data: τ 4.24 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.23 (q, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.46 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 5.2 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.5 (d, 1 H, $J_{3',4'}$ 6.5 Hz, H-3'), 4.54 (t, 1 H, $J_{4',5'}$ 6.5 Hz, H-4'), 6.9 (s, 6 H, 2Ms), 7.8, 7.85, 7.89 (12 H, 4Ac). Mass-spectral data [(a) and (b) indicate ions due to hexopyranosyl and ketofuranosyl cations, respectively]: *m/e* 361a, 289b, 265a, 229b, 205a, 187b, and 127b.

Anal. Calc. for $C_{22}H_{34}O_{19}S_2$: C, 39.63; H, 5.1; S, 9.6. Found: C, 40.02; H, 4.8; S, 9.4.

Conventional treatment of **8** (1.2 g) with acetic anhydride (2 ml) and pyridine (20 ml) at room temperature gave 2,4-di-*O*-mesylsucrose hexa-acetate (**9**) (1.3 g, 96%) as a syrup, $[\alpha]_D$ +44.5° (*c* 1, chloroform). N.m.r. data: τ 4.29 (d, 1 H, $J_{1,2}$ 3.75 Hz, H-1), 5.35 (q, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.49 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5.2 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.51 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3'), 4.64 (t, 1 H, $J_{4',5'}$ 6.0 Hz, H-4'), 6.9, 6.95 (2 s, 6 H, 2Ms), 7.8–7.94 (12 H, 4Ac). Mass-spectral data [(a) and (b) indicate ions due to hexopyranosyl and ketofuranosyl cations, respectively]: *m/e* 403a, 343a, 331b, 283a, 271b, 211b, 187a, 169b, and 109b.

Anal. Calc. for $C_{26}H_{38}O_{21}S_2$: C, 41.6; H, 5.06; S, 8.5. Found: C, 42.3; H, 5.2; S, 8.1.

*1',3',4',6'-Tetra-*O*-acetyl-β-*D*-fructofuranosyl 3,6-di-*O*-acetyl-4-*O*-benzoyl-2-*O*-mesyl-α-*D*-galactopyranoside* (**10**). — A solution of **9** (500 mg) in hexamethyl-

phosphoric triamide (7 ml) was heated with sodium benzoate (1 g) at 90° for 24 h. The reaction mixture was poured into ice–water, and the precipitate was collected, washed well with water, and taken up in dichloromethane. The dried (Na_2SO_4) solution was concentrated to a syrup, which was purified on a small column of silica gel, using ether–light petroleum (1:1), to give **10** (487 mg, 90%) as a syrup, $[\alpha]_D$ +15.5° (*c* 1.84, chloroform). N.m.r. data: τ 4.13 (d, 1 H, $J_{1,2}$ 3.75 Hz, H-1), 4.98 (q, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 4.54 (q, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 4.22 (q, 1 H, $J_{4,5}$ 1.4 Hz, H-4), 4.51 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3'), 4.45 (t, 1 H, $J_{4',5'}$ 6.0 Hz, H-4'), 6.94 (s, 3 H, Ms), 1.9–2.14 (m, 5 H, Bz), 7.81, 7.85, 7.9, 7.99, 8.03 (18 H, 6Ac). Mass-spectral data [(a) and (b) represent ions due to hexopyranosyl and ketofuranosyl cations, respectively]: *m/e* 429a, 369a, 331b, 291a, 271b, 231a, 211a, 169, and 109.

Anal. Calc. for $C_{32}H_{40}O_{20}S \cdot 2C_4H_{10}O$: C, 51.8; H, 6.4; S, 3.46. Found: C, 51.6; H, 5.9; S, 4.1.

ACKNOWLEDGMENTS

We thank Professor A. J. Vlitos, Chief Executive of the Tate & Lyle Research Centre, for his interest and support, and Dr. K. J. Parker for helpful discussions.

REFERENCES

1 P. H. Fairclough, L. Hough, and A. C. Richardson, *Carbohyd. Res.*, 40 (1975) 285–298.
2 M. E. Evans and F. W. Parrish, *Tetrahedron Lett.*, (1966) 3805–3807.
3 M. E. Evans, F. W. Parrish, and L. Long, Jr., *Carbohyd. Res.*, 3 (1967) 453–462.
4 A. Hasegawa and H. G. Fletcher, Jr., *Carbohyd. Res.*, 29 (1973) 209–222, 223–237.
5 A. Hasegawa, *Carbohyd. Res.*, 29 (1973) 239–245.
6 K. S. Mufti and R. Khan, *British Patent Application* (1973).
7 J. F. Stoddart and W. A. Szarek, *J. Chem. Soc.*, (1971) 437–442.
8 T. Otake, *Bull. Chem. Soc. Jap.*, 43 (1970) 3199–3205.
9 R. Khan and M. R. Jenner, unpublished results.
10 L. Hough and K. S. Mufti, *Carbohyd. Res.*, 25 (1972) 497–503.