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Some 3,5-acetal derivatives of D-glucitol *

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ABSTRACT

Ethylidenation of 1,6-di-*O*-benzoyl-2,4-*O*-benzylidene-D-glucitol gave the 3,5-*O*-ethylidene derivative in poor yield, whereas reaction with 2,2-dimethoxypropane gave the 3,5-*O*-isopropylidene derivative in good yield. Removal of the benzoyl and benzylidene groups, with further derivatisation, gave a variety of compounds containing the relatively unstable 3,5-acetal ring. Attempted tosylation of 3,5-*O*-isopropylidene-D-glucitol gave a derivative of 1,4-anhydro-D-glucitol. Reduction of various ditosylates revealed selective reaction of axial tosyloxymethyl groups.

INTRODUCTION

In another connection, some 2,4-monoacetals of arabinitol were required. The direct synthesis of such thermodynamically unstable *β-threo* acetals is not feasible because the more stable 2,3-acetals are formed preferentially [2,3]. A possible synthesis of compounds in this class involves degradation of 3,5-acetals of glucitol, but these compounds are also not easily accessible. However, the 3,5-acetal occurs commonly in bi- or tri-cyclic acetals with the *gluco* configuration [2,3]. Furthermore, 3,5-*O*-benzylidene-D-glucitol was obtained, in unspecified yield, by partial hydrogenolysis of 2,4:3,5-di-*O*-benzylidene-D-glucitol and then converted into 1,3,5-tri-*O*-acetyl-2,4-*O*-benzylidene-D-arabinitol [4]. We now report the synthesis of two new 3,5-acetals of D-glucitol, and some derivatives thereof, by this general strategy from mixed 2,4:3,5-diacetals.

DISCUSSION

In the partial hydrogenolysis of 2,4:3,5-di-*O*-benzylidene-D-glucitol, both acetal rings are susceptible, so that two mono-acetals are obtained [4], and, furthermore,

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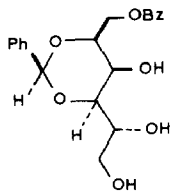

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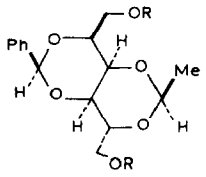

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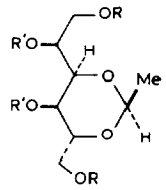
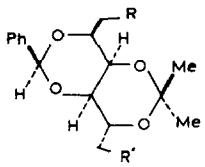
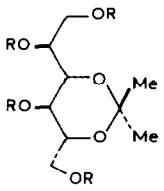
3 R = H



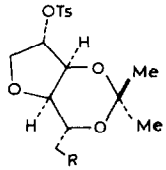
4 R = Bz, R' = H
5 R = R' = H
6 R = R' = Bz



7 R = R' = OBz
8 R = R' = OH
9 R = R' = OTs
17 R = OH, R' = H
18 R = OTs, R' = H



10 R = H
11 R = Bz



13 R = OTs
19 R = H

the desired 3,5-acetal is inherently the less stable [3]. An improvement in this strategy could involve hydrogenolysis of a mixed diacetal in which the 2,4-*O*-benzylidene group is the more susceptible to hydrogenolysis.

Acid-catalysed reaction between acetaldehyde, acetylene, or 1,1-diethoxyethane and 1,6-di-*O*-benzoyl-2,4-*O*-benzylidene-D-glucitol [5] (**1**) gave crystalline 1,6-di-*O*-benzoyl-2,4-*O*-benzylidene-3,5-*O*-ethylidene-D-glucitol (**2**), a mixed diacetal of the required type, in low yield. Several variations in the reaction conditions were explored without significant improvement in the yield. TLC of the mother liquor revealed a complex mixture of products, thus accounting for the low yield. The complex mixture was due, at least in part, to formation of diastereoisomers of the 3,5-acetal and also, in those reactions involving more forcing conditions, to acetal exchange giving both di-*O*-ethylidene and di-*O*-benzylidene derivatives [6]. Nevertheless, because no chromatography was required and the acetal **1** is readily available, the synthesis was convenient and yielded reasonable amounts of the mixed diacetal. The benzoate and benzylidene groups were easily removed from **2**,

with sodium methoxide and catalytic hydrogenolysis respectively, in either order, to give **3–5**.

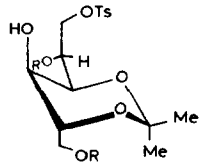
In order to avoid the formation of diastereoisomeric products, Mills [3] recommended the use of acetals from symmetrical ketones. Reaction of **1** with acetone gave 1,6-di-*O*-benzoyl-2,4-*O*-benzylidene-3,5-*O*-isopropylidene-D-glucitol (**7**) in low yield, but the same mixed diacetal was obtained in good yield when 2,2-dimethoxypropane was used. The benzoate groups were removed from **7** with sodium methoxide to give the parent diacetal **8**, from which the syrupy 1,6-ditosylate **9** was obtained. Unlike the above ethylidene acetals, **7–9** were not susceptible to complete hydrogenolysis under conventional conditions. Progressive diminution in the rates of hydrogenolysis of benzyl compounds has been attributed to inhibition by products of the reduction, such as toluene [7]. By adding **8** in portions and by replacing the hydrogen at intervals, the benzylidene group was removed to give 3,5-*O*-isopropylidene-D-glucitol (**10**) as an unstable syrup. The tetrabenzoate (**11**) of **10** was a syrup, and acetylation of **10** gave hexa-*O*-acetyl-D-glucitol (**12**).

In a further attempt to make a crystalline derivative, **10** was treated with an excess of tosyl chloride in pyridine, but the product was 1,4-anhydro-3,5-*O*-isopropylidene-2,6-di-*O*-toluene-*p*-sulphonyl-D-glucitol (**13**). Removal of the isopropylidene group from **13** by acid hydrolysis and tosylation of the syrupy product gave 1,4-anhydro-2,3,5,6-tetra-*O*-toluene-*p*-sulphonyl-D-glucitol (**14**), identical with the product obtained by tosylation of 1,4-anhydro-D-glucitol.

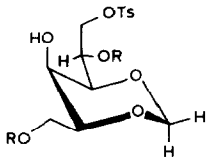
The facile formation of a 1,4-anhydro derivative during attempted monotosylation of 2,3,5-tri-*O*-benzyl-D-arabinitol has been reported [8], which contrasts with the selective tosylation of 2,4-*O*-methylene-D-glucitol to give a 1,6-disulphonate that was sufficiently stable to be isolated [9].

If, as seems likely, the 1,4-anhydro ring in **13** arises by sulphonylation at O-1 followed by intramolecular attack of O-4, then there is a marked difference in reactivity compared to the possible intramolecular attack of O-3 on C-6 in the 2,4-*O*-methylene derivative. The difference in the rates of these two processes can be rationalised by consideration of relative stabilities of conformations suitable for the formation of five-membered rings. Possible conformations are **15a** and **16a** with the corresponding Newman projections along the C-3–C-2 bond of the 3,5-acetal **15b** and the C-4–C-5 bond of the 2,4-acetal **16b**. In the compound that undergoes intramolecular cyclisation, the two oxygen atoms which are not involved in the cyclisation are antiperiplanar (**15b**) and therefore in a more stable orientation. In contrast, in the compound that does not undergo cyclisation, the corresponding two oxygen atoms are in the less stable synclinal orientation (**16b**). As charge separation develops in the transition state, the dipolar forces in **15** should be more favourable [10] than those in **16**.

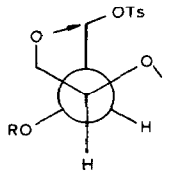
Marked differences in reactivity towards nucleophiles of the two sulphonyloxymethyl groups in derivatives of 2,4:3,5-diacetals of glucitol have been observed [9], with displacement at the axial sulphonyloxymethyl group occurring more readily. In a similar way, different reactivity was observed for the tosylate groups in



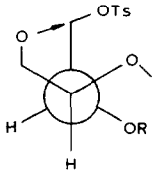
15a



16a



15b



16 b

the mixed diacetal **9**. Reduction of **9** with a suspension of lithium aluminium hydride in tetrahydrofuran–ether gave 2,4-*O*-benzylidene-6-deoxy-3,5-*O*-isopropylidene-D-glucitol (**17**) by C–O bond cleavage of the 6-sulphonate and S–O bond cleavage of the 1-sulphonate. In contrast, on treatment of a solution of **9** in tetrahydrofuran with a clear solution of the hydride in ether, the 6-sulphonate was reduced but the 1-sulphonate was unaffected during 5 h to give **18**.

The C–O bond cleavage of tosylates in nucleophilic reactions is generally preferred over S–O bond cleavage because the tosyloxy ion is the better leaving group, but steric and stereoelectronic retardation effects will be more marked at carbon than at the more remote sulphur. Furthermore, the sulphur atom in a sulphonate is a hard Lewis acid, whereas the carbon borders on hard and soft [11]. The hydride ion is a soft nucleophile and prefers to attack carbon in the absence of other unfavourable effects. In contrast, hydroxide is a hard nucleophile with a greater tendency to attack the harder sulphur atom. Thus, it is likely that insoluble lithium hydroxide is the reagent that causes S–O bond cleavage in **9**, to give the free hydroxyl group, but that this happens only when attack at carbon is hindered.

Reduction of the 2,6-ditosylate **13** gave 1,4-anhydro-6-deoxy-3,5-*O*-isopropylidene-2-*O*-toluene-*p*-sulphonyl-D-glucitol (**19**), i.e., only the axial tosyloxymethyl group was reduced. Thus, it is clear that, in **9** and **13**, the axial tosyloxymethyl group is readily reduced, whereas the equatorial tosyloxymethyl group in **9** and the secondary tosyl group in **13** are not, in line with earlier observations on related compounds [9].

EXPERIMENTAL

Light petroleum refers to the fraction having bp 40–60°. Pyridine was dried by distillation from P_2O_5 and stored over KOH pellets. Column chromatography was carried out with silica gel (Merck 7734).

1,6-Di-O-benzoyl-2,4-O-benzylidene-3,5-O-ethylidene-D-glucitol (**2**).—(*a*) A suspension of 1,6-di-*O*-benzoyl-2,4-*O*-benzylidene-D-glucitol [5] (**1**, 60 g) in 1,1-dimethoxyethane (300 mL) containing toluene-*p*-sulphonic acid (15 g) was shaken overnight. Chloroform was added to give a clear solution which was neutralised by stirring with anhyd K_2CO_3. The mixture was filtered, and the solvent was evaporated to leave a syrup which crystallised from EtOH to yield **2** (1.5 g, 2.4%), mp 150–152°, $[\alpha]_D^{20}$ −5.8° (*c* 1, $CHCl_3$). ^{1}H-NMR data: δ 8.9–7.3 (m, 15 H, 3 Ph), 5.65 (s, 1 H, PhC*H*), 5.15 (q, 1 H, *J* 5 Hz, MeC*H*), 1.39 (d, 3 H, *J* 5 Hz, *Me*CH).

Anal. Calcd for $C_{29}H_{28}O_8$: C, 69.0; H, 5.5. Found: C, 68.8; H, 5.3.

TLC (19:1 benzene–ether) of the mother liquor revealed three components with R_F 0.71, 0.64, and 0.34, in addition to **2** (R_F 0.50).

(*b*) Acetaldehyde, produced by heating paraldehyde with concd H_2SO_4, was bubbled for 30 min into a solution of **1** (2 g) and toluene-*p*-sulphonic acid (0.2 g) in $CHCl_3$ (10 mL). The mixture was then neutralised with anhyd K_2CO_3 and filtered, and the solvent was evaporated to leave a syrup (2.2 g) which crystallised from EtOH to give **2** (0.1 g, 4.7%), mp 150°.

(*c*) To a cold solution of **1** (5 g) in dry benzene (20 mL) was added a mixture of mercuric acetate (0.6 g) in concd H_2SO_4 (0.1 mL), and then acetylene was bubbled into the mixture. After 1 h, the mixture was neutralised by stirring with anhyd K_2CO_3, then filtered, and the solvent was evaporated to leave a syrup. Crystallisation from EtOH gave **2** (0.2 g, 3.9%), mp 150°. TLC of the residue showed the same four components as in (*a*).

2,4-O-Benzylidene-3,5-O-ethylidene-D-glucitol (**3**).—Sodium (0.16 g) was reacted with dry MeOH (10 mL) and the resulting solution added to a solution of **2** (0.2 g) in dry MeOH (20 mL). After storage overnight at room temperature, the mixture was neutralised with CO_2, then filtered, and the solvent was evaporated. The residue was recrystallised from EtOAc–light petroleum to give **3** (50 mg, 53%), mp 195–197°, $[\alpha]_D^{20}$ + 1° [*c* 1, $(CH_3)_2SO$]. ^{1}H-NMR data [$(CD_3)_2SO$]: δ 7.1–7.6 (m, 5 H, Ph), 6.67 (s, 1 H, PhC*H*), 5.02 (q, 1 H, *J* 5 Hz, MeC*H*), 1.17 (d, 3 H, *J* 5 Hz, *Me*CH).

Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.8; H, 6.8. Found: C, 60.3; H, 6.7.

1,6-Di-O-benzoyl-3,5-O-ethylidene-D-glucitol (**4**).—A solution of **2** (1 g) in MeOH (500 mL) was shaken overnight under H_2 with 10% Pd–C (0.75 g), then filtered, and the solvent was evaporated. The syrupy residue was crystallised from $CHCl_3$–light petroleum to give **4** (0.4 g, 49%), mp 76°, $[\alpha]_D^{20}$ +22° (*c* 1, $CHCl_3$). ^{1}H-NMR data: δ 7.3–8.2 (m, 10 H, 2 Ph), 5.26 (q, 1 H, *J* 5 Hz, MeC*H*), 1.38 (d, 3 H, *J* 5 Hz, *Me*CH).

Anal. Calcd for $C_{22}H_{24}O_8$: C, 63.4; H, 5.8. Found: C, 63.3; H, 5.5.

1,2,4,6-Tetra-O-benzoyl-3,5-O-ethylidene-D-glucitol (**6**).—Conventional treatment of **4** (0.1 g) with benzoyl chloride (1 mL) and dry pyridine (10 mL), with column chromatography (19:1 benzene–ether) of the product, gave **6**, isolated as a glass (0.1 g, 66%), $[\alpha]_D^{20}$ −7.4° (*c* 1, $CHCl_3$). ^{1}H-NMR data: δ 7.2–8.2 (m, 20 H, 4 Ph), 5.41 (q, 1 H, *J* 5 Hz, MeC*H*), 1.40 (d, 3 H, *J* 5 Hz, *Me*CH).

Anal. Calcd for $C_{36}H_{32}O_{10}$: C, 69.2; H, 5.1. Found: C, 69.5; H, 5.3.

3,5-O-Ethylidene-D-glucitol (**5**).—Treatment of **4** (2.5 g) with NaOMe, as described for **3**, gave **5** (1 g, 83%), mp 60–62°, $[\alpha]_D^{20}$ +22° (*c* 1, H_2O). ^{1}H-NMR data: δ 5.25 (q, 1 H, *J* 5 Hz, MeC*H*), 1.37 (d, 3 H, *J* 5 Hz, *Me*CH).

Anal. Calcd for $C_8H_{18}O_6$: C, 46.15; H, 7.75. Found: C, 45.8; H, 7.7.

1,6-Di-O-benzoyl-2,4-O-benzylidene-3,5-O-isopropylidene-D-glucitol (**7**).—(*a*) A suspension of **1** (5 g) and toluene-*p*-sulphonic acid (0.1 g) in acetone (150 mL) was shaken overnight, then neutralised with anhyd K_2CO_3, and filtered, and the solvent was evaporated. The residue was recrystallised from EtOH to give **1** (3 g, 60%). Concentration of the mother liquor and column chromatography (19:1 benzene–ether) of the syrupy residue gave **7** (0.3 g, 6%), mp 90° (from EtOH), $[\alpha]_D^{20}$ −2° (*c* 1, $CHCl_3$). ^{1}H-NMR data: δ 7.3–8.3 (m, 15 H, 3 Ph), 5.54 (s, 1 H, PhC*H*), 1.35 and 1.49 (2 s, each 3 H, Me_2C).

Anal. Calcd for $C_{30}H_{30}O_8$: C, 69.5; H, 5.8. Found: C, 69.75; H, 5.8.

(*b*) A mixture of **1** (1 g), toluene-*p*-sulphonic acid (0.1 g), 2,2-dimethoxypropane (15 mL), and dry *N*,*N*-dimethylformamide (15 mL) was stirred for 2 h, then stored at room temperature overnight. The resulting solution was stirred with anhyd K_2CO_3 until neutral, filtered, and concentrated. Trituration of the syrupy residue with water gave a solid which was recrystallised from EtOH to give **7** (0.9 g, 90%), mp 90°.

2,4-O-Benzylidene-3,5-O-isopropylidene-D-glucitol (**8**).—Treatment of **7** (1 g) with NaOMe, as described for **3**, gave **8** (0.5 g, 84%), mp 65° (from benzene), $[\alpha]_D^{20}$ +6.1° (*c* 1, MeOH). ^{1}H-NMR data: δ 7.2–7.8 (m, 5 H, Ph), 5.41 (s, 1 H, PhC*H*), 1.35 and 1.44 (2 s, each 3 H, Me_2C).

Anal. Calcd for $C_{16}H_{20}O_6$: C, 61.9; H, 7.2. Found: C, 61.7; H, 7.3.

2,4-O-Benzylidene-3,5-O-isopropylidene-1,6-di-O-toluene-p-sulphonyl-D-glucitol (**9**).—A solution of toluene-*p*-sulphonyl chloride (4 g) in dry pyridine (10 mL) was added dropwise during 30 min to a stirred solution of **8** (1.6 g) in dry pyridine (10 mL) at 0°. The mixture was stored at room temperature overnight, a few drops of water were then added, and, after 10 min, the mixture was poured into ice–water. Column chromatography (9:1 benzene–ether) of the resulting syrup gave **9**, isolated as a glass (2.3 g, 74%), $[\alpha]_D^{20}$ +5° (*c* 1, $CHCl_3$). ^{1}H-NMR data: δ 7.2–7.8 (m, 13 H, aromatic), 5.36 (s, 1 H, PhC*H*), 2.46 (s, 6 H, 2 Ph*Me*), 1.2 and 1.3 (2 s, each 3 H, Me_2C).

Anal. Calcd for $C_{30}H_{34}O_{10}S_2$: C, 58.25; H, 5.5, S, 10.6. Found: C, 58.3; H, 5.5; S, 10.6.

3,5-O-Isopropylidene-D-glucitol (**10**).—A solution of **8** (0.5 g) in EtOH (20 mL) was added dropwise to a stirred suspension of 10% Pd–C (0.1 g) in EtOH (50 mL)

under an atmosphere of H_2. The stirring was continued and the H_2 replaced by fresh H_2 at intervals. After 18 h, when TLC indicated that the reaction was complete, the mixture was filtered through Celite and concentrated *in vacuo* to leave a syrup (0.3 g, 83%), $[\alpha]_D^{20}$ −1.3° (*c* 1, MeOH), which hydrolysed on storage.

*Characterisation of 3,5-*O*-isopropylidene-*D*-glucitol.*—(*a*) *Benzoylation.* To a stirred solution of freshly prepared **10** (0.3 g) in dry pyridine (10 mL) at ~0° was added benzoyl chloride (2 g). The mixture was stirred at room temperature overnight, a few drops of water were added and, after 30 min, the mixture was poured into ice–water. Column chromatography (benzene) of the resulting syrup gave 1,2,4,6-tetra-*O*-benzoyl-3,5-*O*-isopropylidene-D-glucitol (**11**; 0.5 g, 56%), $[\alpha]_D^{20}$ +12.5° (*c* 1, $CHCl_3$). ^{1}H-NMR data: δ 7.4–8.0 (m, 20 H, 4 Ph), 1.4 and 1.5 (2 s, each 3 H, Me_2C).

Anal. Calcd for $C_{37}H_{34}O_{10}$: C, 69.5; H, 5.3. Found: C, 69.4; H, 5.2.

(*b*) *Acetylation.* Acetic anhydride (4 mL) was added dropwise to a solution of freshly prepared **10** (1.5 g) in dry pyridine (20 mL) at 0°. The mixture was stirred overnight, then poured into ice–water, and the resulting precipitate was recrystallised from EtOH to give 1,2,3,4,5,6-hexa-*O*-acetyl-D-glucitol (0.6 g, 17%), mp 98–100°, identical with an authentic sample. No other crystalline product was obtained.

(*c*) *Toluene-*p*-sulphonylation.* A solution of toluene-*p*-sulphonyl chloride (9 g) in dry pyridine (10 mL) was added dropwise to a solution of freshly prepared **10** (0.4 g) in dry pyridine (20 mL) at 0°. The mixture was stored at room temperature overnight and then processed conventionally to give 1,4-anhydro-3,5-*O*-isopropylidene-2,6-di-*O*-toluene-*p*-sulphonyl-D-glucitol (**13**; 0.62 g, 67%), mp 132–134° (from EtOH), $[\alpha]_D^{20}$ +14° (*c* 1, $CHCl_3$). ^{1}H-NMR data: δ 7.2–7.8 (m, 8 H, aromatic), 2.34 (s, 6 H, 2 Ph*Me*), 1.14 and 1.20 (2 s, each 3 H, Me_2C).

Anal. Calcd for $C_{23}H_{28}O_9S_2$: C, 53.8; H, 5.5; S, 12.5. Found: C, 53.6; H, 5.4; S, 12.2.

*1,4-Anhydro-2,3,5,6-tetra-*O*-toluene-*p*-sulphonyl-D-glucitol* (**14**).—(*a*) Toluene-*p*-sulphonic acid (0.2 g) was added to a solution of **13** (0.15 g) in $CHCl_3$ (5 mL) and aq 95% EtOH (2 mL), and the mixture was stored at room temperature for 48 h. TLC (1:1 benzene–ether) then showed absence of **13**. Anhydrous K_2CO_3 (2 g) was added, the mixture was filtered, the residue was washed with $CHCl_3$, and the combined filtrate and washings were concentrated. Column chromatography (1:1 benzene–ether) of the residue gave a syrup (0.1 g, 76%), $[\alpha]_D^{20}$ +1.0° (*c* 1, $CHCl_3$), to a solution of which in dry pyridine (2 mL) at ~0° was added dropwise a solution of toluene-*p*-sulphonyl chloride (0.4 g) in dry pyridine (3 mL). The mixture was stored overnight, water (2 drops) was added, and, after 30 min, the mixture was poured into ice–water. The product was extracted with $CHCl_3$, the extract was washed successively with ice-cold 2 M HCl, aq $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. Column chromatography (1:1 benzene–ether) of the resulting syrup and recrystallisation from EtOH gave **14** (0.09 g, 50%), mp 113–114°, $[\alpha]_D^{20}$ +12° (*c* 1, $CHCl_3$). ^{1}H-NMR data: δ 7.3–7.76 (m, 16 H, aromatic), 2.4 (s, 12 H, 4 Ph*Me*).

(*b*) A solution of 1,4-anhydro-D-glucitol [12] (0.33 g) in dry pyridine (5 mL) was treated with a solution of toluene-*p*-sulphonyl chloride (1.52 g) in dry pyridine (5 mL). The next day, the mixture was processed as in (*a*) to give **14** (0.6 g, 60%), mp 113–114°, $[\alpha]_D^{20}$ +13° (*c* 1, $CHCl_3$).

Anal. Calcd for $C_{34}H_{36}O_{13}S_4$: C, 52.3; H, 4.6; S, 16.4. Found: C, 52.0; H, 4.8; S, 16.0.

2,4-O-Benzylidene-6-deoxy-3,5-O-isopropylidene-D-glucitol (**17**).—A solution of **9** (0.2 g) in dry tetrahydrofuran (20 mL) was added dropwise to a suspension of $LiAlH_4$ (0.5 g) in tetrahydrofuran (10 mL), which was boiled gently under reflux until (16 h) all **9** had disappeared (TLC). Ethyl acetate and satd aq NH_4Cl were added, and the organic layer was separated, dried ($MgSO_4$), and concentrated. Column chromatography (1:1 benzene–ether) of the resulting syrup gave **17** (20 mg, 22%), $[\alpha]_D^{20}$ +3.4° (*c* 1, $CHCl_3$). ^{1}H-NMR data: δ 7.2–7.6 (m, 5 H, Ph), 5.4 (s, 1 H PhC*H*), 1.26–1.42 (m, 9 H, Me and Me_2C).

*2,4-O-Benzylidene-6-deoxy-3,5-O-isopropylidene-1-O-toluene-*p*-sulphonyl-D-glucitol* (**18**).—A suspension of $LiAlH_4$ (3 g) in dry ether (250 mL) was heated under reflux and then allowed to settle. The clear supernatant solution (100 mL) was added dropwise to a solution of **9** (1 g) in dry tetrahydrofuran (50 mL). The solution was boiled under reflux for 5 h, EtOAc (10 mL) and water (20 mL) were added, the mixture was concentrated, satd aq NH_4Cl (200 mL) was added to the residue, and the mixture was extracted with EtOAc (3 × 100 mL). The combined extracts were dried ($MgSO_4$) and concentrated, and the residue was crystallised from EtOH to give **18** (0.6 g, 76%), mp 95°, $[\alpha]_D^{20}$ +4.6° (*c* 1, $CHCl_3$). ^{1}H-NMR data: δ 7.20–7.82 (m, 9 H, aromatic), 5.40 (s, 1 H, PhC*H*), 2.36 (s, 3 H, Ph*Me*), 1.28–1.38 (m, 9 H, Me and Me_2C).

Anal. Calcd for $C_{23}H_{28}O_7S$: C, 61.6; H, 6.3; S, 7.1. Found: C, 61.6; H, 6.4; S, 7.1.

*1,4-Anhydro-6-deoxy-3,5-O-isopropylidene-2-O-toluene-*p*-sulphonyl-D-glucitol* (**19**).—A solution of **13** (4 g) in dry tetrahydrofuran (40 mL) was added to a suspension of $LiAlH_4$ (0.8 g) in dry tetrahydrofuran (10 mL). The mixture was boiled under reflux for 22 h, when all **13** had been consumed (TLC; 9:1 benzene–ether). Ethyl acetate (1 mL) was added, the mixture was poured into water and extracted with ether (3 × 100 mL), the combined extracts were dried ($MgSO_4$), and the solvent was evaporated. Column chromatography (9:1 benzene–ether) of the syrupy residue gave **19** (1 g, 38%), $[\alpha]_D^{20}$ +3.3° (*c* 1, $CHCl_3$). ^{1}H-NMR data: δ 7.2–7.8 (m, 4 H, aromatic), 2.45 (s, 3 H, Ph*Me*), 1.20–1.27 (m, 9 H, Me and Me_2C).

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