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SYNTHESIS AND REACTIONS OF CYCLIC ACETAL DERIVATIVES OF 6,6′-DICHLORO-6,6′-DIDEOXYSUCROSE*†

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ABSTRACT

Treatment of 6,6′-dichloro-6,6′-dideoxysucrose with a combination of 2,2-dimethoxypropane, *N*,*N*-dimethylformamide, and toluene-*p*-sulphonic acid (reagent *A*), followed by acetylation, gave the 1′,2:3,4-diacetal **1** (39%) and the 1′,2-acetal **2** (37%). A similar reaction of methyl 6-chloro-6-deoxy-α-D-glucopyranoside with reagent *A* yielded the corresponding 2,3- and 3,4-acetal derivatives in yields of 29% and 9%, respectively. The structures of **1** and **2** have been confirmed by ^{1}H-n.m.r. spectroscopy and by chemical transformations.

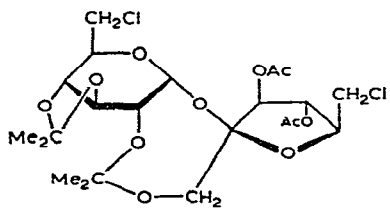
INTRODUCTION

In our previous study of the acetalation of sucrose with 2,2-dimethoxypropane–*N*,*N*-dimethylformamide–toluene-*p*-sulphonic acid (reagent *A*), 4,6-*O*-isopropylidene and 1′,2:4,6-di-*O*-isopropylidene derivatives were isolated in yields of 55% and 15%, respectively[2,3]. This suggested a preference for reaction at positions 4 and 6 of sucrose. In order to investigate further the distribution of acetals at other locations in the sucrose molecule, the action of reagent *A* on 6,6′-dichloro-6,6′-dideoxysucrose[4] has been studied. We also now describe the acetalation of a model compound, methyl 6-chloro-6-deoxy-α-D-glucopyranoside[5] using reagent *A*.

RESULTS AND DISCUSSION

Treatment of 6,6′-dichloro-6,6′-dideoxysucrose[4] with reagent *A* gave, after conventional acetylation with acetic anhydride and pyridine, the crystalline 1′,2:3,4-diacetal **1** in 33% yield. The residual syrup was then chromatographed on silica gel to afford, in addition to **1** (6.5%), the 1′,2-acetal **2** in 37% yield. The structures of **1** and **2** were determined by ^{1}H-n.m.r. spectroscopy and by chemical transformations.

*Dedicated to the memory of Professor Edward J. Bourne.
†Sucrochemistry: Part XXIII. For Part XXII, see Ref. 1.



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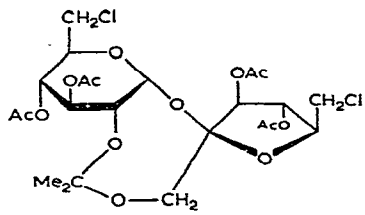

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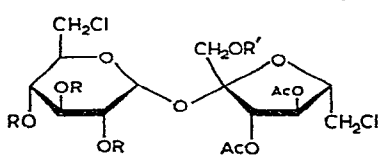
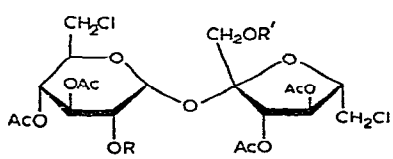
In the ^{1}H-n.m.r. spectrum of the 1′,2:3,4-diacetal **1**, the resonances due to H-2, H-3, and H-4 were detected at τ 5.95, 6.22, and 6.79, respectively. The shift of these signals to high field relative to the position of the corresponding resonances in sucrose octa-acetate revealed the involvement of C-2, C-3, and C-4 in cyclic acetal linkages. The four methyl resonances of the two isopropylidene rings in **1** appeared at τ 8.46–8.62. Further proof of the structure of **1** was obtained by deacetalation, using 60% aqueous acetic acid, to give the tetrahydroxy derivative **3** in 99% yield. The location of the free hydroxyl groups at C-2, C-3, and C-4 in **3** was confirmed by the ^{1}H-n.m.r. spectrum. Although the resonances were not individually allocated to H-2, H-3, and H-4 of **3**, they were shown by spin-decoupling experiments to be in the region τ 5.43–6.12. The shifting of these signals to higher field revealed that C-2, C-3, and C-4 carried hydroxyl, instead of acetoxyl, groups. Addition of trichloroacetyl isocyanate to a solution of **3** in deuteriochloroform caused the appearance of four singlets (at τ 0.79, 1.10, 1.13, and 1.75) due to imino protons, and shifted the signals due to H-2, H-3, and H-4 (τ 4.80, 4.42, and 4.70, respectively). These results confirmed the presence of four hydroxyl groups in **3**. The position of the fourth hydroxyl group in **3** was ascertained when treatment with trityl chloride and pyridine at 60° for 16 h gave the 1′-trityl ether **4**. The presence of a trityl group at C-1′ in **4** was confirmed[6] by the ^{1}H-n.m.r. data: H-3′ resonated at lower field (τ 4.25) than H-1. Conventional acetylation of **4** with acetic anhydride and pyridine gave the penta-acetate **5**. The structure of **5** was supported by ^{1}H-n.m.r. and mass-spectral data. Conventional mesylation of **4** with mesyl chloride and pyridine gave the trimesylate **6**. The structural assignment of **6** was supported by its ^{1}H-n.m.r. spectrum. In comparison with the ^{1}H-n.m.r. spectrum of sucrose octa-acetate, the resonances due to H-2, H-3, and H-4 in **6** appeared at slightly higher field (τ 5.46, 4.94, and 5.15, respectively), thereby



3 R = R′ = H
4 R = H, R′ = Tr
5 R = Ac, R′ = Tr
6 R = Ms, R′ = Tr

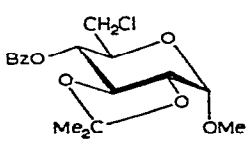


7 R = R′ = H
8 R = H, R′ = Tr
9 R = Ms, R′ = Tr

confirming that the three sulphonate groups were located at C-2, C-3, and C-4. As observed with **4** and **5**, the signals due to H-3′ occurred at lower field (τ 4.10) than for H-1.

In the ^{1}H-n.m.r. spectrum of the 1′,2-acetal **2**, the resonances due to H-2 appeared at relatively high field (τ 6.15). The signals for H-2 in acetylated derivatives of sucrose usually appear in the region τ 5.00–5.30, and the shift to higher field therefore indicated the involvement of C-2 in the acetal linkage. When **2** was treated with 60% aqueous acetic acid it gave the dihydroxy derivative **7** in 85% yield. In the ^{1}H-n.m.r. spectrum of **7**, the resonances due to H-2 were shown by spin-decoupling experiments to be in the region τ 6.15–6.40, thereby confirming the location of one of the hydroxyl groups at position 2. On addition of trichloroacetyl isocyanate to a solution of **7** in deuteriochloroform, singlets appeared at τ 0.93 and 1.13 in the ^{1}H-n.m.r. spectrum, due to imino protons of the resulting carbamate groups. This confirmed the presence of two hydroxyl groups in **7**. The location of the second hydroxyl group in **7** was ascertained when treatment with trityl chloride and pyridine at 60° for 24 h afforded the trityl ether **8**. The structure of **8** was supported by its ^{1}H-n.m.r. spectrum; the characteristic low-field doublet due to H-3′ at τ 4.23 indicated[6] the location of the trityl group at C-1′. The signals due to H-2 appeared, as expected, in the region τ 6.40–6.60. Conventional acetylation of **8** with acetic anhydride and pyridine gave the penta-acetate **6**, whose optical rotation and ^{1}H-n.m.r. and mass-spectral data were identical with those of the sample prepared from the diacetal **1**. Treatment of **8** with mesyl chloride and pyridine afforded the corresponding mesylate **9**. The structural assignment was supported by the ^{1}H-n.m.r. spectrum.

In order to obtain further information about the order of preference for isopropylidene acetals in 6,6′-dichloro-6,6′-dideoxysucrose[4], a model compound, methyl 6-chloro-6-deoxy-α-D-glucopyranoside was treated with reagent *A* at room temperature for 1.5 h. Chromatography of the product mixture on silica gel gave two homogeneous, syrupy fractions which were immediately benzoylated with benzoyl chloride and pyridine. The fast-moving fraction afforded the syrupy 2,3-acetal **10** (28%), and the slow-moving fraction gave the crystalline 3,4-acetal **11** (9%). The structures of **10** and **11** were ascertained by ^{1}H-n.m.r. spectroscopy. In the spectrum of **10**, the signals due to H-2 and H-3 appeared at τ 6.31 and 5.75, respectively, thereby indicating the presence of a cyclic acetal at C-2 and C-3. The methyl protons of the isopropylidene group in **10** appeared as a singlet at τ 8.55. The low-field triplet at τ 4.64 was assigned to H-4 by spin-decoupling experiments, and this confirmed that the benzoyloxy group was located at C-4. The structural assignment of **11** was confirmed by its ^{1}H-n.m.r. spectrum; the signals due to H-3 and H-4 appeared at



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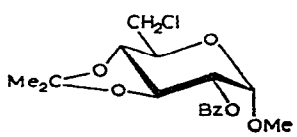

11

τ 5.86 and 6.29, respectively, thereby confirming the presence of a cyclic acetal at C-3 and C-4. The presence of the benzoyloxy group at C-2 in **11** was indicated by the fact that the resonances due to H-2 appeared at τ 4.90. The methyl protons of the isopropylidene group in **11** gave rise to a singlet at τ 8.55.

On the basis of these results, it is apparent that there is a marked preference for the formation of the 1′,2-acetal in 6,6′-dichloro-6,6′-dideoxysucrose, and that the order of preference is 1′,2>2,3>3,4. However, the formation of a 2,3-isopropylidene acetal in 6,6′-dichloro-6,6′-dideoxysucrose is precluded by the formation of the more-favoured 1′,2-acetal.

EXPERIMENTAL

For details of general procedure, see Part VI[7].

Reaction of 6,6′-dichloro-6,6′-dideoxysucrose[4] *with reagent* A. — A solution of 6,6′-dichloro-6,6′-dideoxysucrose (13 g) in *N*,*N*-dimethylformamide (150 ml) was stirred with 2,2-dimethoxypropane (50 ml) in the presence of toluene-*p*-sulphonic acid (1 g) at room temperature for 4 h. The solution was then neutralised with Amberlite IR-45 (HO^-) resin and concentrated by codistillation with toluene. The syrupy residue was treated with acetic anhydride (20 ml) and pyridine (100 ml) at room temperature for 16 h. T.l.c. (ether–light petroleum, 4:1) revealed two fast-moving, major products. The solution was concentrated by codistillation with toluene to give 3′,4′-di-*O*-acetyl-6,6′-dichloro-6,6′-dideoxy-1′,2:3,4-di-*O*-isopropylidenesucrose (**1**; 6.16 g, 33%), m.p. 191–193° (from methanol), $[\alpha]_D$ −19.5° (*c* 1.02, chloroform). N.m.r. data: τ 3.80 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1); 4.89 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3′); 4.57 (q, 1 H, $J_{4',5'}$ 4.5 Hz, H-4′); 7.85, 7.93 (2 s, 6 H, 2 Ac); 8.46, 8.54, 8.62 (3 s, 12 H, 4 Me).

Anal. Calc. for $C_{22}H_{32}Cl_2O_{11}$: C, 48.6; H, 5.9; Cl, 13.1. Found: C, 48.9; H, 5.9; Cl, 13.1.

The product from the mother liquors was chromatographed on a column of silica gel, using ether–light petroleum (1:1), to give, in addition to **1** (1.2 g, 6.5%), 3,4:3′,4′-tetra-*O*-acetyl-6,6′-dichloro-6,6′-dideoxy-1′,2-*O*-isopropylidenesucrose (**2**; 7.5 g, 37%), m.p. 154° (from ether), $[\alpha]_D$ +9.5° (*c* 1, chloroform). N.m.r. data: τ 3.83 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1); 6.18 (q, 1 H, $J_{2,3}$ 9.5 Hz, H-2); 4.69 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3); 5.09 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4); 4.86 (d, 1 H, $J_{3',4'}$ 6.5 Hz, H-3′); 4.55 (q, 1 H, $J_{4',5'}$ 5.0 Hz, H-4′); 8.78, 8.83, 8.85, 9.01 (4 s, 12 H, 4 Ac); 9.54, 9.75 (2 s, 6 H, 2 Me).

Anal. Calc. for $C_{23}H_{32}Cl_2O_{13}$: C, 47.0; H, 5.49; Cl, 12.1. Found: C, 47.0; H, 5.42; Cl, 12.2.

3′,4′-Di-O-acetyl-6,6′-dichloro-6,6′-dideoxysucrose (**3**). — Treatment of the 1′,2:3,4-diacetal **1** (4 g) with 60% aqueous acetic acid at 85° for 15 min gave, after concentration, a syrupy product. T.l.c. (dichloromethane–methanol, 4:1) revealed a slow-moving, major product. Elution of the syrup from a column of silica gel, using ether–acetone (10:1), gave **3** (3.4 g, 99%), $[\alpha]_D$ +6.3° (*c* 1, chloroform). N.m.r. data:

τ 4.58 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1); 4.61 (d, 1 H, $J_{3',4'}$ 5.0 Hz, H-3'); 4.65 (t, 1 H, $J_{4',5'}$ 5.0 Hz, H-4'); 7.83, 7.89 (2 s, 6 H, 2 Ac). Mass-spectral data [(a) indicates 3:1 doublets (1 Cl) due to fructofuranosyl cations]: *m/e* 265a, 205a, and 145a.

Anal. Calc. for $C_{16}H_{24}Cl_2O_{11}$: C, 41.5; H, 5.2; Cl, 15.3. Found: C, 41.6; H, 5.3; Cl, 15.2.

3',4'-Di-O-acetyl-6,6'-dichloro-6,6'-dideoxy-1'-O-tritylsucrose (**4**). — A solution of **3** (1 g) was treated with trityl chloride (2 g) in pyridine (20 ml) at 60° for 16 h. The reaction mixture was then poured into ice–water, and the precipitate was collected and taken up in dichloromethane. The solution was dried (Na_2SO_4) and concentrated, and the residue was eluted from a column of silica gel with ether–light petroleum (1:1) to give **4** (800 mg, 53%) as a syrup, $[\alpha]_D$ +67.9° (*c* 1.06, chloroform). N.m.r. data: τ 4.82 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1); 4.30 (d, 1 H, $J_{3',4'}$ 5.5 Hz, H-3'); 4.60 (t, 1 H, $J_{4',5'}$ 5.5 Hz, H-4'); 2.52–2.85 (m, 15 H, Tr); 7.93, 7.99 (2 s, 6 H, 2 Ac).

Anal. Calc. for $C_{35}H_{38}Cl_2O_{11}$: C, 59.6; H, 5.4; Cl, 10.0. Found: C, 59.3; H, 5.4; Cl, 10.1.

Conventional acetylation of **4** (200 mg), with acetic anhydride (1 ml) and pyridine (5 ml) at room temperature, afforded, after concentration by codistillation with toluene, 6,6'-dichloro-6,6'-dideoxy-1'-*O*-tritylsucrose penta-acetate (**5**; 220 mg, 93%), $[\alpha]_D$ +64.5° (*c* 1.03, chloroform). N.m.r. data: τ 4.65 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1); 5.26 (q, 1 H, $J_{2,3}$ 10.0 Hz, H-2); 4.63 (q, 1 H, $J_{3,4}$ 10.0 Hz, H-3); 4.99 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4); 4.15 (d, 1 H, $J_{3',4'}$ 5.75 Hz, H-3'); 4.64 (t, 1 H, $J_{4',5'}$ 5.75 Hz, H-4'); 2.50–2.82 (m, 15 H, Tr); 7.91, 7.97, 8.00, 8.04, 8.13 (5 s, 15 H, 5 Ac). Mass-spectral data [(a) indicates 3:1 doublet (1 Cl) due to hexopyranosyl cations]: *m/e* 307a, 247a, 205a, and 145a.

Anal. Calc. for $C_{41}H_{44}Cl_2O_{14}$: C, 59.2; H, 5.3; Cl, 8.5. Found: C, 59.4; H, 5.8; Cl, 8.3.

Conventional mesylation of **4** (330 mg), using mesyl chloride (2 ml) and pyridine (10 ml), initially at 0° and then at room temperature for 16 h, gave 3',4'-di-*O*-acetyl-6,6'-dichloro-6,6'-dideoxy-2,3,4-tri-*O*-mesyl-1'-*O*-tritylsucrose (**6**) (240 mg, 55%), m.p. 102–105° (from methanol), $[\alpha]_D$ +51° (*c* 0.69, chloroform). N.m.r. data: τ 4.50 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1); 5.50 (q, 1 H, $J_{2,3}$ 9.5 Hz, H-2); 4.99 (q, 1 H, $J_{3,4}$ 9.0 Hz, H-3); 5.20 (t, 1 H, $J_{4,5}$ 9.0 Hz, H-4); 4.16 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3'); 4.63 (t, 1 H, $J_{4',5'}$ 6.0 Hz, H-4'); 2.50–2.81 (m, 15 H, Tr); 6.81 6.85, 7.12 (3 s, 9 H, 3 Ms); 7.89, 7.93 (2 s, 6 H, 2 Ac). Mass-spectral data [(a) and (b) indicate 3:1 doublets (1 Cl) due to hexopyranosyl and ketofuranosyl cations, respectively]: *m/e* 415a, 319b, 265a, 223b, 205a, and 145a,b.

Anal. Calc. for $C_{38}H_{44}Cl_2O_{17}S_3$: C, 48.6; H, 4.72; Cl, 7.54; S, 10.23. Found: C, 48.5; H, 4.67; Cl, 7.75; S, 10.02.

3,3',4,4'-Tetra-O-acetyl-6,6'-dichloro-6,6'-dideoxysucrose (**7**). — Treatment of the 1',2-acetal **2** (3.8 g) with 60% aqueous acetic acid (120 ml) at 100° for 8 min gave, after concentration, **7** (3 g, 85%), m.p. 150–152°, $[\alpha]_D$ +40.2° (*c* 1.04, chloroform). N.m.r. data: τ 4.51 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1); 6.16–6.40 (H-2); 4.80 (q, 1 H, $J_{2,3}$ 9.0 Hz, H-3); 5.04 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-4); 4.66 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3');

4.53 (t, 1 H, $J_{4',5'}$ 6.0 Hz, H-4'); 7.79, 7.92, 7.95 (3 s, 12 H, 4 Ac). Mass-spectral data [(a) indicates 3:1 doublets (1 Cl) due to oxycarbonum ions]: *m/e* 265a, 205a, and 145a.

Anal. Calc. for $C_{20}H_{28}Cl_2O_{13}$: C, 43.9; H, 5.2; Cl, 13.0. Found: C, 44.0; H, 5.0; Cl, 13.1.

3,3',4,4'-Tetra-O-acetyl-6,6'-dichloro-6,6'-dideoxy-1'-O-tritylsucrose (**8**). — A solution of **7** (4.23 g) in pyridine (100 ml) was treated with trityl chloride (9 g) at 60° for 24 h. The reaction was worked up as described previously to afford **8** (3.2 g, 52%) as a syrup, $[\alpha]_D$ +67.9° (*c* 1.06, chloroform). N.m.r. data: τ 4.84 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1); 6.40–6.60 (H-2); 4.83 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3); 5.05 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4); 4.25 (d, 1 H, $J_{3',4'}$ 5.0 Hz, H-3'); 4.62 (t, 1 H, $J_{4',5'}$ 5.0 Hz, H-4'); 5.64–5.90 (m, 2 H, H-5,5'); 2.46–2.82 (m, 15 H, Tr); 7.79, 7.97 (12 H, 4 Ac). Mass-spectral data [(a) represents 3:1 doublets (1 Cl) due to hexopyranosyl cations]: *m/e* 265a, 205a, and 145a.

Anal. Calc. for $C_{39}H_{42}Cl_2O_{13}$: C, 59.3; H, 5.4; Cl, 9.0. Found: C, 59.5; H, 5.4; Cl, 9.1.

Conventional acetylation of **8** (1 g), with acetic anhydride (2 ml) and pyridine (15 ml) at room temperature for 16 h, gave 6,6'-dichloro-6,6'-dideoxy-1'-*O*-tritylsucrose penta-acetate (**5**; 1.04 g, 99%). The optical rotation and the ^{1}H-n.m.r. and mass-spectral data were identical with those of the sample prepared previously.

Conventional mesylation of **8** (1.2 g), using mesyl chloride (2 ml) and pyridine (50 ml), gave 3,3',4,4'-tetra-*O*-acetyl-6,6'-dichloro-6,6'-dideoxy-2-*O*-mesyl-1'-*O*-tritylsucrose (**9**; 1.27 g, 94%) as a syrup, $[\alpha]_D$ +65° (*c* 0.98, chloroform). N.m.r. data: τ 4.65 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1); 5.50 (q, 1 H, $J_{2,3}$ 9.75 Hz, H-2); 4.66 (q, 1 H, $J_{3,4}$ 9.5 Hz, H-3); 4.96 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4); 4.14 (d, 1 H, $J_{3',4'}$ 5.75 Hz, H-3'); 4.63 (t, 1 H, $J_{4',5'}$ 5.75 Hz, H-4'); 7.23 (s, 3 H, Ms); 2.48–2.78 (m, 15 H, Tr); 7.90, 7.95, 8.00 (3 s, 12 H, 4 Ac). Mass-spectral data [(a) and (b) indicate 3:1 doublets (1 Cl) due to hexopyranosyl and ketofuranosyl cations, respectively]: *m/e* 343a, 283a, 265b, 223a, 205b, and 145a,b.

Anal. Calc. for $C_{40}H_{44}Cl_2O_{15}S$: C, 55.4; H, 5.11; Cl, 8.17; S, 3.70. Found: C, 55.8; H, 5.34; Cl, 8.45; S, 3.66.

Reaction of methyl 6-chloro-6-deoxy-α-D-glucopyranoside[5] *with reagent* A. — A solution of methyl 6-chloro-6-deoxy-α-D-glucopyranoside (1.3 g) in *N,N*-dimethylformamide (60 ml) was stirred with 2,2-dimethoxypropane (10 ml) in the presence of toluene-*p*-sulphonic acid (100 mg) at room temperature for 1.5 h. The solution was concentrated to small volume and partitioned between dichloromethane and water. The organic layer was dried (Na_2SO_4) and concentrated to give a syrup which consisted (t.l.c.; ethyl acetate–light petroleum, 1:1) of two major products. Elution of the mixture from a column of silica gel, using ethyl acetate–light petroleum (1:2), gave two fractions. The fast-moving major fraction (432 mg, 28%) afforded, on conventional benzoylation with benzoyl chloride (0.5 ml) and pyridine (3 ml), methyl 4-*O*-benzoyl-6-chloro-6-deoxy-2,3-*O*-isopropylidene-α-D-glucopyranoside (**10**; 540 mg, 89%), $[\alpha]_D$ +106° (*c* 1, chloroform). N.m.r. data: τ 4.89 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1)

6.31 (q, 1 H, $J_{2,3}$ 9.0 Hz, H-2); 5.76 (t, 1 H, $J_{3,4}$ 9.0 Hz, H-3); 4.64 (t, 1 H, $J_{4,5}$ 9.0 Hz, H-4); 1.91–2.66 (m, 5 H, Bz); 8.55 (s, 6 H, 2 Me). Mass-spectral data [oxycarbonium ions indicate 3:1 doublets (1 Cl)]: *m/e* 356, 341, and 281.

Anal. Calc. for $C_{17}H_{21}ClO_6$: C, 57.2; H, 5.9. Found: C, 57.4; H, 6.1.

The slow-moving fraction (140 mg, 9%) gave, after conventional benzoylation with benzoyl chloride (0.3 ml) and pyridine (5 ml), crystalline methyl 2-*O*-benzoyl-6-chloro-6-deoxy-3,4-*O*-isopropylidene-α-D-glucopyranoside (**11**; 180 mg, 91%), $[\alpha]_D$ +129° (*c* 0.5, chloroform). N.m.r. data: τ 4.78 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1); 4.89 (q, 1 H, $J_{2,3}$ 9.0 Hz, H-2); 5.86 (t, 1 H, $J_{3,4}$ 9.0 Hz, H-3); 6.29 (t, 1 H, $J_{4,5}$ 9.0 Hz, H-4); 1.39–2.82 (m, 5 H, Bz); 8.54 (s, 6 H, 2 Me). Mass-spectral data [oxycarbonium ions reveal 3:1 doublets (1 Cl)]: *m/e* 356 and 341.

Anal. Calc. for $C_{17}H_{21}ClO_6$: C, 57.2; H, 5.9. Found: C, 57.2; H, 6.1.

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