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REACTION OF METHANESULPHONYL CHLORIDE–*N*,*N*-DIMETHYLFORMAMIDE WITH PARTIALLY ESTERIFIED DERIVATIVES OF SUCROSE*

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ABSTRACT

Treatment of sucrose 2,3,3′,4′,6-penta-acetate (**1**) with methanesulphonyl chloride–*N*,*N*-dimethylformamide (reagent *A*) gave the 1′,4,6′-trichloride **2**, the 1′-*O*-formyl-4,6′-dichloride **3**, the 4,6′-dichloride **4**, and the 1′,4-di-*O*-formyl-6′-chloride **5**. De-esterification of **3** afforded the unsubstituted 4,6′-dichloride **6** which, on acetylation, gave the corresponding hexa-acetate **7**, also prepared by acetylation of **4**. In compounds **2**, **3**, and **4**, substitution at C-4 by chloride ion occurred with inversion of configuration. The structure of **5** was confirmed by conversion into the known 6′-chloro-6′-deoxysucrose hepta-acetate by de-esterification followed by acetylation. Treatment of sucrose 1′,2,3,3′,4′,6′-hexa-acetate (**10**) with the reagent gave the 4,6-dichloride **11** and 4-*O*-formyl-6-chloride **12**. The formyl group in **12** was selectively removed by using an anion-exchange resin to give **16**. De-esterification of **12** with methanolic sodium methoxide gave 6-chloro-6-deoxysucrose (**13**) which, on acetylation and benzoylation, afforded the hepta-acetate **14** and the hepta-benzoate **15**, respectively. Alternatively, **15** was prepared by the reaction of 1′,2,3,3′,4,4′,6′-hepta-*O*-benzoylsucrose with reagent *A*. Treatment of **14** with sodium methoxide in methanol followed by acetylation gave 3,6-anhydrosucrose hexa-acetate (**24**). Reaction of sucrose 2,3,3′,4,4′-pentabenzoate (**17**) with reagent *A* gave the known 1′,6,6′-trichloro-1′,6,6′-trideoxysucrose pentabenzoate (**18**) and 1′-*O*-formyl-6,6′-dichloride **19**. Treatment of **19** with anion-exchange resins selectively removed the formyl group to give **20**. The structure of **20** was confirmed by conversion into the 1′-chlorosulphate-6,6′-dichloride (**21**). Treatment of sucrose 1′,2,3,3′,4,4′-hexabenzoate (**22**) with reagent *A* gave the expected 6,6′-dichloride (**23**).

INTRODUCTION

The reaction of hexopyranosides with methanesulphonyl chloride–*N*,*N*-dimethylformamide resulted in the selective replacement of primary hydroxyl groups by chloride[2]. In our previous investigation, this reaction with sucrose gave the

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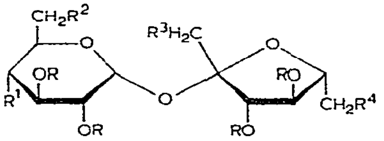
*Sucrochemistry: Part XV. For Part XIV, see Ref. 1.

expected 6,6′-dichloro-6,6′-dideoxysucrose in 85% yield[3]. Hough and his co-workers[4] have reinvestigated the reaction with methyl α- and β-D-glucopyranosides, extended its application to methyl β-maltoside, and shown that substitution also occurs at secondary positions. The replacement of the hydroxyl group attached to a chiral centre has been demonstrated to proceed *via* an S_N2 process[4].

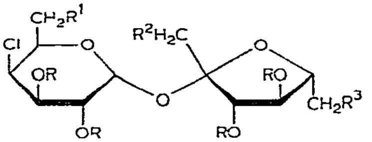
We now report an extension of this reaction to various partially esterified derivatives of sucrose to give chlorodeoxy and chlorodeoxy-formate derivatives. The formation of formic esters during the reaction of sugars with methanesulphonyl chloride–*N*,*N*-dimethylformamide *via* hydrolysis of the $[Me_2N{=}CHOR]^+\ Cl^-$ complex has been recognised by Evans *et al.*[2]. However, the isolation of such intermediates has not hitherto been reported.

RESULTS AND DISCUSSION

Treatment of sucrose 2,3,3′,4′,6-penta-acetate[5] (**1**) with methanesulphonyl chloride in *N*,*N*-dimethylformamide at 85° gave a mixture of products which, on fractionation by chromatography on silica gel, gave the 1′,4,6′-trichloride **2**, the 1′-*O*-formyl-4,6′-dichloride **3**, the 4,6′-dichloride **4**, and the 1′,4-di-*O*-formyl-6′-chloride **5**. The structures of these compounds were established on the basis of p.m.r. and mass-spectral data, and by chemical transformations.



1 $R = Ac, R^1 = R^3 = R^4 = OH, R^2 = OAc$
5 $R = Ac, R^1 = R^3 = OCHO, R^2 = OAc, R^4 = Cl$
8 $R = H, R^1 = R^2 = R^3 = OH, R^4 = Cl$
9 $R = Ac, R^1 = R^2 = R^3 = OAc, R^4 = Cl$
10 $R = Ac, R^1 = R^2 = OH, R^3 = R^4 = OAc$
12 $R = Ac, R^1 = OCHO, R^2 = Cl, R^3 = R^4 = OAc$
13 $R = H, R^1 = R^3 = R^4 = OH, R^2 = Cl$
14 $R = Ac, R^1 = R^3 = R^4 = OAc, R^2 = Cl$
15 $R = Bz, R^1 = R^3 = R^4 = OBz, R^2 = Cl$
16 $R = Ac, R^1 = OH, R^2 = Cl, R^3 = R^4 = OAc$



2 $R = Ac, R^1 = OAc, R^2 = R^3 = Cl$
3 $R = Ac, R^1 = OAc, R^2 = OCHO, R^3 = Cl$
4 $R = Ac, R^1 = OAc, R^2 = OH, R^3 = Cl$
6 $R = H, R^1 = R^2 = OH, R^3 = Cl$
7 $R = Ac, R^1 = R^2 = OAc, R^3 = Cl$
11 $R = Ac, R^1 = Cl, R^2 = R^3 = OAc$

In the p.m.r. spectrum of **2** in deuteriobenzene, only resonances due to H-1, H-2, H-3′, and H-4′ were interpretable on a first-order basis. The signals due to H-3 and H-4 appeared in the region τ 4.36–4.53. The mass spectrum of **2** contained fragment ions at *m/e* 307 (3:1 doublet, 1 Cl) and 283 (9:6:1 triplet, 2 Cl) corresponding to hexopyranosyl and ketofuranosyl cations, respectively. The structure of **3** was supported by its p.m.r. spectrum; the signals assigned to H-1, H-2, H-3, H-3′, H-4, H-4′ and the *O*-formyl protons were confirmed by spin-decoupling experiments.

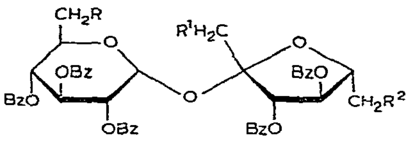
The derived first-order coupling constants ($J_{1,2}$ 3.0, $J_{2,3}$ 6.75, $J_{3,4} = J_{4,5} = 1.5$, $J_{3',4'} = J_{4',5'} = 6.5$ Hz) confirmed the $^4C_1$ conformation for the expected D-galactose moiety in **3**. The mass spectrum of **3** showed peaks (3:1 doublets) at *m/e* 307 and 293 due to hexopyranosyl and ketofuranosyl cations, respectively. De-esterification of **3** with sodium methoxide in methanol afforded 6′-chloro-6′-deoxy-β-D-fructofuranosyl 4-chloro-4-deoxy-α-D-galactopyranoside (**6**). Conventional treatment of **6** with acetic anhydride in pyridine gave the corresponding crystalline hexa-acetate **7**. In the p.m.r. spectrum of **7**, the resonances due to H-1, H-2, H-3, H-3′, H-4, and H-4′ were recognisable, and the derived first-order coupling constants supported the expected *galacto* configuration for the hexopyranosyl moiety. The mass-spectral data of **7** showed an intense peak at *m/e* 307 (3:1 doublet) due to oxycarbonium ions.

In the p.m.r. spectrum of **4**, although only the signals for H-1 and H-4 were interpretable, the overall pattern suggested the hexopyranosyl ring to have the *galacto* configuration. On addition of trichloroacetyl isocyanate to a solution of **4** in deuteriochloroform, a singlet at τ 1.07 appeared due to the imino proton, thereby confirming the presence of a hydroxyl group in **4**. The mass spectrum of **4** contained fragment ions corresponding to the two oxycarbonium ions at *m/e* 307 and 265. Treatment of **4** with acetic anhydride in pyridine afforded 6′-chloro-6′-deoxy-β-D-fructofuranosyl 4-chloro-4-deoxy-α-D-galactopyranoside hexa-acetate (**7**).

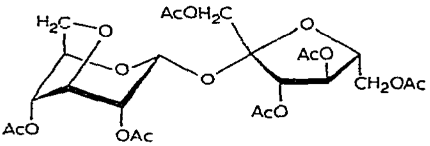
The structure of **5** was supported by its p.m.r. spectrum; the derived first-order coupling constants ($J_{1,2}$ 3.5, $J_{2,3}$ 10.0, $J_{3,4} = J_{4,5} = 9.5$ Hz) indicated the pyranoid moiety to have the *gluco* configuration. The mass-spectral data of **5** showed ions at *m/e* 317 and 293 due to hexopyranosyl and ketofuranosyl cations, respectively. The structural assignment was confirmed by de-esterification with methanolic sodium methoxide followed by acetylation using acetic anhydride and pyridine to give the known[6] 6′-chloro-6′-deoxysucrose hepta-acetate (**9**).

Reaction of sucrose 1′,2,3,3′,4′,6′-hexa-acetate[7] (**10**) with methanesulphonyl chloride and *N*,*N*-dimethylformamide at 85° gave two products, which were separated on silica gel and subsequently characterised as β-D-fructofuranosyl 4,6-dichloro-4,6-dideoxy-α-D-galactopyranoside hexa-acetate (**11**) and 6-chloro-6-deoxy-4-*O*-formylsucrose hexa-acetate (**12**). The structure of **11** was supported by its p.m.r. spectrum; the first-order coupling constants ($J_{1,2}$ 3.5, $J_{2,3}$ 10.5, $J_{3,4} = J_{4,5} = 3.0$, $J_{3',4'} = J_{4',5'} = 5.0$ Hz) indicated the hexopyranosyl ring to have the *galacto* configuration. The mass spectrum of **11** showed the expected ions at *m/e* 283 and 331 due to hexopyranosyl and ketofuranosyl cations, respectively. Compound **12** was identified from its p.m.r. spectrum, in which the parameters $J_{1,2}$ 3.5, $J_{2,3}$ 10.0, and $J_{3,4} = J_{4,5} = 9.5$ Hz clearly showed that the hexopyranosyl ring had the *gluco* configuration. The formyl group in **12** was selectively removed by treatment with IRA-94S (HO^-) resin in methanol to give 6-chloro-6-deoxysucrose hexa-acetate (**16**). The p.m.r. spectrum of **16** indicated HO-4 to be unsubstituted since there were no signals for H-4 in the region τ 4.5–5.4, where it usually occurs in acetylated derivatives of sucrose. On addition of trichloroacetyl isocyanate to a solution of **16** in deuteriochloroform, a singlet appeared at τ 1.28, thus confirming the presence of a hydroxyl group. De-esterification of **12** with methanolic sodium methoxide gave 6-chloro-6-deoxysucrose (**13**) which, with acetic anhydride–pyridine, afforded the corresponding hepta-acetate **14**. When **13** was treated with benzoyl chloride in pyridine, it gave the expected 6-chloro-6-deoxysucrose heptabenzoate (**15**). The structural assignment for **15** was confirmed by the reaction of sucrose heptabenzoate[8] with methanesulphonyl chloride and *N*,*N*-dimethylformamide which also gave **15**. Treatment of **12** with M sodium methoxide in methanol gave a single product which was characterised as 3,6-anhydrosucrose hexa-acetate (**24**) on the basis of p.m.r. and mass-spectral data.

Treatment of sucrose 2,3,3′,4,4′-pentabenzoate[9] (**17**) with methanesulphonyl chloride and *N*,*N*-dimethylformamide afforded, after chromatography on silica gel, the 1′,6,6′-trichloride[10] **18** and 1′-*O*-formyl-6,6′-dichloride **19** in yields of 26 and 68%, respectively. The p.m.r. spectrum and physical constants of **18** were identical with those of the known[10] 1′,6,6′-trichloro-1′,6,6′-trideoxysucrose pentabenzoate. The structure of **19** was supported by its p.m.r. spectrum. Deformylation of **19** with either IR-45 or IRA-94S (HO^-) resins in methanol gave 6,6′-dichloro-6,6′-dideoxysucrose hexabenzoate (**20**). Compound **20** was obtained for the first time in crystalline form, and its structure was confirmed by conversion into the known[10] 6,6′-dichloro-6,6′-dideoxysucrose 1′-chlorosulphate pentabenzoate (**21**).



17 R = R^1 = R^2 = OH
18 R = R^1 = R^2 = Cl
19 R = R^2 = Cl, R^1 = OCHO
20 R = R^2 = Cl, R^1 = OH
21 R = R^2 = Cl, R^1 = OSO_2Cl
22 R = R^2 = OH, R^1 = OBz
23 R = R^2 = Cl, R^1 = OBz



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Treatment of sucrose hexabenzoate[11] (**22**) with methanesulphonyl chloride–*N*,*N*-dimethylformamide gave the expected 6,6′-dichloride **23** in 91% yield. The p.m.r. spectrum and the physical constants of **23** were identical with those of the known[10,12] 6,6′-dichloro-6,6′-dideoxysucrose hexabenzoate[12].

EXPERIMENTAL

For details of the general procedures, see Part VI[13].

Reaction of **1** *with mesyl chloride*–N,N-*dimethylformamide.* — A solution of sucrose 2,3,3′,4′,6-penta-acetate (**1**, 5 g) in *N*,*N*-dimethylformamide (50 ml) was treated with methanesulphonyl chloride (5 ml), initially at −5° for 2 h and then at 98° for 24 h. The reaction mixture was then poured into ice–water, and the precipitate was collected, washed well with water, and dissolved in ether. The dried (Na_2SO_4) solution was concentrated and the residue was eluted from a column of silica gel (100 g) with ether–light petroleum (1:1) to afford the following products.

(*a*) 1′,6′-Dichloro-1′,6′-dideoxy-β-D-fructofuranosyl 4-chloro-4-deoxy-α-D-galactopyranoside penta-acetate (**2**; 400 mg, 6.2%), $[\alpha]_D$ +69° (*c* 0.6, chloroform). N.m.r. data ($CDCl_3$): τ 4.3 (*d*, 1 proton, $J_{1,2}$ 3.0 Hz, H-1), 4.32 (*d*, 1 proton, $J_{3',4'}$ 6.0 Hz, H-3′), 4.6 (*t*, 1 proton, $J_{4',5'}$ 6.0 Hz, H-4′), 4.5–4.77 (*m*, 3 protons, H-2,3,4), 7.84–7.95 (15 protons, 5 Ac); in deuteriobenzene: τ 4.4 (*d*, 1 proton, $J_{1,2}$ 3.0 Hz, H-1), 4.45 (*q*, 1 proton, $J_{2,3}$ 7.5 Hz, H-2), 4.1 (*d*, 1 proton, $J_{3',4'}$ 6.5 Hz, H-3′), 4.43 (*t*, 1 proton, $J_{4',5'}$ 6.5 Hz, H-4′), 4.36–4.54 (2 protons, H-3,4), 8.15–8.43 (15 protons, 5 Ac). Mass-spectral data [(a) indicates a 3:1 doublet and (b) a 9:6:1 triplet due to the ^{35}Cl and ^{37}Cl isotopes in hexopyranosyl and ketofuranosyl cations containing 1 and 2 chlorine substituents, respectively]: *m/e* 307a, 283b, 247a, 223b, 205a, 163b, 181b, 145a,b.

Anal. Calc. for $C_{22}H_{19}Cl_3O_8$: C, 43.6; H, 4.8; Cl, 17.3. Found: C, 43.9; H, 5.1; Cl, 17.6.

(*b*) 6′-Chloro-6′-deoxy-1′-*O*-formyl-β-D-fructofuranosyl 4-chloro-4-deoxy-α-D-galactopyranoside penta-acetate (**3**; 1.2 g, 19.8%), $[\alpha]_D$ +67° (*c* 1, chloroform). N.m.r. data: τ 4.33 (*d*, 1 proton, $J_{1,2}$ 3.0 Hz, H-1), 4.67 (*q*, 1 proton, $J_{2,3}$ 6.75 Hz, H-2), 4.55 (*q*, $J_{3,4}$ 1.5 Hz, H-3), 5.7 (*t*, 1 proton, $J_{4,5}$ 1.5 Hz, H-4), 4.5 (*d*, 1 proton, $J_{3',4'}$ 6.5 Hz, H-3′), 4.49 (*t*, 1 proton, $J_{4',5'}$ 6.5 Hz, H-4′), 2.01 (*s*, 1 proton, HCO), 7.8–7.9 (15 protons, 5 Ac). Mass-spectral data [(a) and (b) indicate 3:1 doublets (1 Cl) due to hexopyranosyl and ketofuranosyl cations, respectively]: *m/e* 307a, 293b, 247a, 233b, 205b, 145a.

Anal. Calc. for $C_{23}H_{30}Cl_2O_{16}$: C, 43.6; H, 4.7; Cl, 11.0. Found: C, 44.0; H, 5.0; Cl, 11.2.

(*c*) 6′-Chloro-6′-deoxy-β-D-fructofuranosyl 4-chloro-4-deoxy-α-D-galactopyranoside penta-acetate penta-acetate (**4**) as a syrup (0.5 g, 19%), $[\alpha]_D$ +53.5° (*c* 1.1, chloroform). N.m.r. data: τ 4.35 (*d*, 1 proton, $J_{1,2}$ 3.0 Hz, H-1), 4.68 (*t*, 1 proton, $J_{4,5}$ 1.5 Hz, H-4), 4.54–4.74 (*m*, 4 protons, H-2,3,3′,4′), 7.74–7.93 (15 protons, 5 Ac). Mass-spectral data [(a) and (b) indicate ions as 3:1 doublets (1 Cl) corresponding to hexopyranosyl and ketofuranosyl cations, respectively]: *m/e* 307a, 265b, 247a, 205b, 145a.

Anal. Calc. for $C_{26}H_{40}Cl_2O_{15} \cdot C_4H_{10}O$: C, 47.1; H, 6.0; Cl, 10.6. Found: C, 47.5; H, 6.0; Cl, 10.6.

(*d*) 6′-Chloro-6′-deoxy-1′,4-di-*O*-formylsucrose penta-acetate (**5**) as a syrup (1.2 g, 19.7%), $[\alpha]_D$ +38° (*c* 0.6, chloroform). N.m.r. data: τ 4.34 (*d*, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 5.07 (*q*, 1 proton, $J_{2,3}$ 10.0 Hz, H-2), 4.47 (*q*, 1 proton, $J_{3,4}$ 9.5 Hz, H-3), 4.8 (*t*, 1 proton, $J_{4,5}$ 9.5 Hz, H-4), 4.5 (*d*, 1 proton, $J_{3',4'}$ 6.0 Hz, H-3′), 4.59 (*t*, 1 proton, $J_{4',5'}$ 6.0 Hz, H-4′), 1.94,1.98 (*s*, 2 protons, HCO), 7.72–7.98 (15 protons, 5 Ac). Mass-spectral data [(a) indicates ions due to hexopyranosyl cation and (b) a 3:1 doublet (1 Cl) due to ketofuranosyl cation]: *m/e* 317a, 293b, 233b, 211a, 205b, 169a, 145a, 109b.

Anal. Calc. for $C_{32}H_{51}ClO_{21} \cdot 2C_4H_{10}O$: C, 47.6; H, 6.3; Cl, 5.3. Found: C, 48.1; H, 5.8; Cl, 5.3.

6′-Chloro-6′-deoxy-β-D-fructofuranosyl 4-chloro-4-deoxy-α-D-galactopyranoside

(6). — (*a*) A solution of **3** (500 mg) in dry methanol (50 ml) was treated with sodium methoxide to pH 10 and then stored at room temperature for 5 h. T.l.c. (chloroform–methanol, 3:1) showed a slow-moving product. The solution was deionised with Amberlyst 15 (H^+) resin and concentrated to give a solid residue (300 mg, 98.3%), $[\alpha]_D$ +71° (*c* 1, ethanol).

Anal. Calc. for $C_{13}H_{24}Cl_2O_{10}\cdot CH_4O$: C, 39.5; H, 6.1; Cl, 18.0. Found: C, 39.5; H, 6.1; Cl, 17.4.

(*b*) Similar treatment of **4** with sodium methoxide in methanol also afforded **6** (98%).

*6'-Chloro-6'-deoxy-β-*D*-fructofuranosyl 4-chloro-4-deoxy-α-*D*-galactopyranoside hexa-acetate* (**7**). — Conventional treatment of **6** (200 mg) with acetic anhydride (1 ml) in pyridine (10 ml) at room temperature for 24 h gave **7** (235 mg, 70%), m.p. 103–104° (from ether–light petroleum), $[\alpha]_D$ +77° (*c* 1, chloroform). N.m.r. data: τ 4.32 (*d*, 1 proton, $J_{1,2}$ 3.0 Hz, H-1), 4.8 (*q*, 1 proton, $J_{2,3}$ 10.5 Hz, H-2), 4.65 (*q*, 1 proton, $J_{3,4}$ 3.0 Hz, H-3), 4.71 (*t*, 1 proton, $J_{4,5}$ 3.0 Hz, H-4), 4.62 (*d*, 1 proton, $J_{3',4'}$ 6.0 Hz, H-3'), 4.56 (*t*, 1 proton, $J_{4',5'}$ 6.0 Hz, H-4'), 7.75–8.0 (18 protons, 6 Ac). Mass-spectral data [(a) indicates 3:1 doublets (1 Cl) due to oxycarbonium ions]: *m/e* 307a, 247a, 205a, 145a.

Anal. Calc. for $C_{27}H_{32}Cl_2O_5$: C, 45.6; H, 5.1; Cl, 11.1. Found: C, 45.7; H, 5.1; Cl, 10.6.

6'-Chloro-6'-deoxysucrose (**8**). — A solution of **5** (200 mg) in methanol was treated with sodium methoxide to pH 10 at room temperature for 5 h. The reaction mixture was worked up as described previously to give **8** (87 mg, 80%) as an amorphous powder, $[\alpha]_D$ +64° (*c* 1, water).

Anal. Calc. for $C_{12}H_{24}ClO_{10}\cdot H_2O$: C, 38.0; H, 6.3; Cl, 9.2. Found: C, 38.3; H, 6.3; Cl, 8.6.

Conventional acetylation of **8** (100 mg) with acetic anhydride in pyridine at room temperature afforded the hepta-acetate[6] **9** (161.6 mg, 89%), m.p. 114–117° (from ether–light petroleum), $[\alpha]_D$ +50° (*c* 1, chloroform); lit.[6] m.p. 116–117°, $[\alpha]_D$ +56.3° (*c* 0.4). N.m.r. data: τ 4.55 (*q*, 1 proton, $J_{3',4'}$ 5.0 Hz, H-3'), 5.65 (*t*, 1 proton, $J_{4',5'}$ 5.0 Hz, H-4'); signals for H-1, H-2, and H-4 were identical with those reported[6]. Mass-spectral data [(a) indicates ions due to hexopyranosyl cations and (b) 3:1 doublets (1 Cl) due to ketofuranosyl cations]: *m/e* 331a, 307b, 271a, 247b, 229a, 211a, 205b, 187b, 169a, 145b, 109a.

Reaction of **10** *with methanesulphonyl chloride*–N,N-*dimethylformamide*. — A solution of sucrose 1',2,3,3',4',6'-hexa-acetate[7] (**10**, 5 g) in *N*,*N*-dimethylformamide (50 ml) was treated with methanesulphonyl chloride (5 ml), initially at −5° and then at 98° for 24 h. The reaction mixture was worked up as described previously. The dichloromethane solution of the residue was dried (Na_2SO_4) and concentrated, and the residue was eluted from a column of silica gel (100 g) with ether–light petroleum (1:1). The following products were obtained.

(*a*) β-D-Fructofuranosyl 4,6-dichloro-4,6-dideoxy-α-D-galactopyranoside hexa-acetate (**11**; 2.65 g, 50%), m.p. 78–80° (from ether–light petroleum), $[\alpha]_D$ +103°

(*c* 1, chloroform). N.m.r. data: τ 4.16 (*d*, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 4.77 (*q*, 1 proton, $J_{2,3}$ 10.5 Hz, H-2), 4.6 (*q*, 1 proton, $J_{3,4}$ 3.0 Hz, H-3), 4.67 (*t*, 1 proton, $J_{4,5}$ 3.0 Hz, H-4), 4.55 (*d*, 1 proton, $J_{3',4'}$ 5.0 Hz, H-3'), 4.54 (*t*, 1 proton, $J_{4',5'}$ 5.0 Hz, H-4'), 7.82–7.93 (18 protons, 6 Ac). Mass-spectral data [(a) indicates 9:6:1 triplets (2 Cl) corresponding to hexopyranosyl cations and (b) indicates ketofuranosyl cations]: *m/e* 331b, 283a, 211b, 181a, 169b, 145a, 109b.

Anal. Calc. for $C_{24}H_{32}Cl_2O_{15}$: C, 45.6; H, 5.1; Cl, 11.5. Found: C, 45.6; H, 5.5; Cl, 11.0.

(*b*) 6-Chloro-6-deoxy-4-*O*-formylsucrose hexa-acetate (**12**; 1.32 g, 24%), m.p. 54–56° (from ether–light petroleum), $[\alpha]_D$ +69° (*c* 1.2, chloroform). N.m.r. data: τ 4.24 (*d*, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 5.11 (*q*, 1 proton, $J_{2,3}$ 10.0 Hz, H-2), 4.47 (*t*, 1 proton, $J_{3,4}$ 9.5 Hz, H-3), 4.74 (*t*, 1 proton, $J_{4,5}$ 9.5 Hz, H-4), 4.55 (*d*, 1 proton, $J_{3',4'}$ 5.75 Hz, H-3'), 4.6 (*t*, 1 proton, $J_{4',5'}$ 5.75 Hz, H-4'), 1.98 (1 proton, HCO), 7.8–7.98 (18 protons, 6Ac). Mass-spectral data [(a) indicates hexopyranosyl cations as 3:1 doublets (1 Cl) and (b) ketofuranosyl cations]: *m/e* 331b, 293a, 233a, 211b, 205a, 169b, 145a, 109b.

Anal. Calc. for $C_{29}H_{43}ClO_{19}\cdot C_4H_{10}O$: C, 47.8; H, 5.6; Cl, 4.8. Found: C, 48.1; H, 5.8; Cl, 4.7.

6-Chloro-6-deoxysucrose (**13**). — Treatment of **12** (500 mg) with sodium methoxide in methanol (50 ml) to pH 10 at room temperature for 4 h gave (t.l.c., chloroform–methanol, 4:1) a slow-moving product. The solution was deionised using Amberlyst 15 (H^+) resin and concentrated to give **13** (225 mg, 82%), m.p. 96–99° (trituration from acetone), $[\alpha]_D$ +46° (*c* 1, water).

Anal. Calc. for $C_{12}H_{24}ClO_{11}$: C, 38.0; H, 6.3; Cl, 9.2. Found: C, 38.3; H, 6.3; Cl, 8.6.

Conventional acetylation of **13** (200 mg) with acetic anhydride (2 ml) in pyridine (50 ml) at room temperature afforded 6-chloro-6-deoxysucrose hepta-acetate (**14**; 330 mg, 91%), m.p. 112–114° (from ether–light petroleum), $[\alpha]_D$ +69° (*c* 1, chloroform). N.m.r. data: τ 4.26 (*d*, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 5.15 (*q*, 1 proton, $J_{2,3}$ 10.0 Hz, H-2), 4.55 (*q*, 1 proton, $J_{3,4}$ 9.5 Hz, H-3), 4.87 (*t*, 1 proton, $J_{4,5}$ 9.5 Hz, H-4), 4.57 (*d*, 1 proton, $J_{3',4'}$ 6.0 Hz, H-3'), 4.79 (*t*, 1 proton, $J_{4',5'}$ 6.0 Hz, H-4'), 7.8–8.0 (21 protons, 7 Ac). Mass-spectral data [(a) ions indicate hexopyranosyl cations as 3:1 doublets (1 Cl) and (b) ketofuranosyl cations]: *m/e* 331b, 307a, 247a, 211b, 205a, 169b, 145a, 109b.

Anal. Calc. for $C_{26}H_{37}ClO_{17}$: C, 47.7; H, 5.35; Cl, 5.35. Found: C, 48.0; H, 5.5; Cl, 5.2.

Conventional benzoylation of **13** (100 mg) with benzoyl chloride (1 ml) in pyridine, initially at 0° and then at room temperature for 24 h, gave 6-chloro-6-deoxysucrose heptabenzoate (**15**; 272 mg, 90%), m.p. 93–95° (from ether), $[\alpha]_D$ +16° (*c* 1, chloroform). N.m.r. data: τ 3.82 (*d*, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 4.62 (*q*, 1 proton, $J_{2,3}$ 10.0 Hz, H-2), 3.82 (*t*, 1 proton, $J_{3,4}$ 10.0 Hz, H-3), 4.34 (*t*, 1 proton, $J_{4,5}$ 10.0 Hz, H-4), 3.98 (*d*, 1 proton, $J_{3',4'}$ 5.3 Hz, H-3'), 3.96 (*t*, 1 proton, $J_{4',5'}$ 5.3 Hz, H-4), 1.78–3.0 (*m*, 35 protons, 7 Bz).

Anal. Calc. for $C_{61}H_{49}Cl_4O_{11}$: C, 67.3; H, 4.5; Cl, 3.2. Found: C, 66.8; H, 4.7; Cl, 3.2.

6-Chloro-6-deoxysucrose hexa-acetate (**16**). — A solution of **12** (500 mg) in dry methanol (50 ml) was treated with IRA-94S (HO^-) resin (3 g) at room temperature for 20 h. T.l.c. (ether–light petroleum 6:1) showed a slow-moving, major product. The filtered mixture was concentrated to a syrup which, on elution from a column of silica gel (50 g) using ether–light petroleum, afforded **16** (354 mg, 76%), as a syrup, $[\alpha]_D$ +45° (*c* 1.1, chloroform). N.m.r. data: τ 4.3 (*d*, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 5.2 (*q*, 1 proton, $J_{2,3}$ 10.3 Hz, H-2), 4.63 (*q*, 1 proton, $J_{3,4}$ 9.5 Hz, H-3), 4.6 (*d*, 1 proton, $J_{3',4'}$ 5.0 Hz, H-3'), 4.64 (*t*, 1 proton, $J_{4',5'}$ 5.0 Hz, H-4'), 7.02 (*m*, 1 proton, HO), 7.8–7.91 (18 protons, 6 Ac). Mass-spectral data [(a) indicates a 3:1 doublet (1 Cl) due to hexopyranosyl cation, and (b) indicates ketofuranosyl cations]: *m/e* 331b, 265a, 211b, 205a, 169b, 109b.

Anal. Calc. for $C_{28}H_{43}ClO_{17}\cdot C_4H_{10}O$: C, 48.9; H, 6.3; Cl, 5.2. Found: C, 49.2; H, 6.2; Cl, 5.8.

3,6-Anhydrosucrose hexa-acetate (**24**). — A solution of **12** (1.5 g) in methanolic sodium methoxide (M, 70 ml) was refluxed for 2 h. Sodium chloride was filtered off and the solution was concentrated to dryness. The residue was then treated with acetic anhydride (5 ml) and pyridine (100 ml) at room temperature for 24 h. The solution was concentrated and the residue was dissolved in dichloromethane. The organic layer was washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and concentrated. Crystallisation from ether–light petroleum gave **24** (1.05 g, 83%), m.p. 158–160°, $[\alpha]_D$ +24° (*c* 1, chloroform). N.m.r. data: τ 4.5 (*d*, 1 proton, $J_{1,2}$ 3.3 Hz, H-1), 4.94 (*m*, 1 proton, H-2), 4.55 (*d*, 1 proton, $J_{3',4'}$ 5.0 Hz, H-3'), 7.78–7.93 (18 protons, 6 Ac). Mass-spectral data [(a) and (b) indicate ions due to hexopyranosyl and ketofuranosyl cations, respectively]: 331b, 271b, 229a, 211b, 169a or b, 127a, 109b.

Anal. Calc. for $C_{22}H_{32}O_{16}$: C, 50.0; H, 5.5. Found: C, 50.5; H, 5.7.

Reaction of **17** *with methanesulphonyl chloride and* N,N-*dimethylformamide*. — A solution of sucrose 2,3,3',4,4'-pentabenzoate[9] (**17**, 5 g) in *N*,*N*-dimethylformamide (50 ml) was treated with methanesulphonyl chloride (5 ml), initially at −5° for 2 h and then at 89° for 24 h. The reaction mixture was worked up as described above. The dichloromethane solution of the solid residue was dried (Na_2SO_4) and concentrated, and the syrupy residue was eluted from a column of silica gel (100 g) with ether–light petroleum (1:1). The following fractions were obtained.

(*a*) 1',6,6'-Trichloro-1',6,6'-trideoxysucrose pentabenzoate[10] (**17**; 1.22 g, 26%), m.p. and mixed m.p. 90–92°. The n.m.r. spectrum was identical with that for a standard sample[10]. (*b*) 6,6'-Dichloro-6,6'-dideoxy-1'-*O*-formylsucrose pentabenzoate (**18**; 3.47 g, 68%), m.p. 85–87° (from methanol), $[\alpha]_D$ +1° (*c* 1, chloroform). N.m.r. data: τ 3.95 (*d*, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 4.58 (*q*, 1 proton, $J_{2,3}$ 10.0 Hz, H-2), 4.94 (*t*, 1 proton, $J_{3,4}$ 10.0 Hz, H-3), 4.4 (*q*, 1 proton, $J_{4,5}$ 9.5 Hz, H-4), 4.05 (*d*, 1 proton, $J_{3',4'}$ 6.0 Hz, H-3'), 4.08 (*t*, 1 proton, $J_{4',5'}$ 6.0 Hz, H-4'), 1.74–2.75 (26 protons, 5 Bz and HCO).

Anal. Calc. for $C_{48}H_{40}Cl_2O_{16}$: C, 61.1; H, 4.2; Cl, 7.4. Found: C, 61.3; H, 4.4; Cl, 7.7.

6,6'-Dichloro-6,6'-dideoxysucrose pentabenzoate (**20**). — (*a*) A solution of **19** (200 mg) in methanol (50 ml) was stirred with Amberlite IR-45 (HO^-) resin (1.5 g) at room temperature for 20 h. T.l.c. (ether–light petroleum, 5:1) showed a slow-moving product. The filtered mixture was concentrated to a syrup which was crystallised from methanol to give **20** (196 mg, 92%), m.p. 140–142°, $[\alpha]_D$ −11° (*c* 1, chloroform). N.m.r. data: τ 3.99 (*d*, 1 proton, $J_{1,2}$ 3.5 Hz, H-1), 4.57 (*q*, 1 proton, $J_{2,3}$ 10.0 Hz, H-2), 3.9 (*t*, 1 proton, $J_{3,4}$ 10.0 Hz, H-3), 4.4 (*t*, 1 proton, $J_{4,5}$ 10.0 Hz, H-4), 7.4 (*t*, 1 proton, *J* 7.0 Hz, OH), 1.77–2.83 (*m*, 25 protons, 5 Bz).

Anal. Calc. for $C_{47}H_{40}Cl_2O_{14}$: C, 62.8; H, 4.45; Cl, 7.8. Found: C, 62.5; H, 4.75; Cl, 7.5.

(*b*) A similar treatment of **19** (500 mg) in methanol (100 ml) with Amberlite IRA-94S (HO^-) resin (3 g) for 6 h afforded **20** (192 mg, 90%).

Treatment of **20** (100 mg) with sulphuryl chloride (0.2 ml) in a mixture of chloroform (3 ml) and pyridine (1 ml) at −40° for 0.5 h gave 2,3,3',4,4'-penta-*O*-benzoyl-6,6'-dichloro-6,6'-dideoxysucrose 1'-chlorosulphate[10] (**21**), m.p. and mixed m.p. 136–138°; the n.m.r. spectrum was identical with that of a standard sample.

Reaction of **22** *with mesyl chloride and* N,N-*dimethylformamide*. — A solution of sucrose 1',2,3,3',4,4'-hexabenzoate[11] (**22**, 2 g) in *N*,*N*-dimethylformamide (25 ml) was treated with methanesulphonyl chloride (2.5 ml), initially at −5° for 2 h and then at 85° for 24 h. The reaction was worked up as described above. The dichloromethane solution of the solid residue was decolorised, dried (Na_2SO_4), and concentrated. Crystallisation of the residue from methanol afforded 6,6'-dichloro-6,6'-dideoxysucrose hexabenzoate[10] (**23**; 1.88 g, 91%), m.p. and mixed m.p. 165–167°. The n.m.r. and i.r. spectra were identical with those of a standard sample[10,12].

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