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THE PREPARATION OF 4,6-DICHLORO-4,6-DIDEOXY-α-D-GALACTOPYRANOSYL 6-CHLORO-6-DEOXY-β-D-FRUCTOFURANOSIDE AND THE CONVERSION OF CHLORINATED DERIVATIVES INTO ANHYDRIDES*

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ABSTRACT

Under carefully controlled conditions, sucrose is converted by selective reaction with sulphuryl chloride into either 6-chloro-6-deoxy-α-D-glucopyranosyl 6-chloro-6-deoxy-β-D-fructofuranoside or 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 6-chloro-6-deoxy-β-D-fructofuranoside, which could be isolated without recourse to chromatography. Treatment of the dichloride with sodium methoxide gave 3,6-anhydro-α-D-glucopyranosyl 3,6-anhydro-β-D-fructofuranoside in high yield. In contrast, 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 6-chloro-6-deoxy-β-D-fructofuranoside gave, in two distinct stages, 3,6-anhydro-4-chloro-4-deoxy-α-D-galactopyranosyl 6-chloro-6-deoxy-β-D-fructofuranoside and 3,6-anhydro-4-chloro-4-deoxy-α-D-galactopyranosyl 3,6-anhydro-β-D-fructofuranoside. The structures of these products were ascertained by ^{1}H-n.m.r. and mass spectrometry.

INTRODUCTION

Reagents which effect the stereoselective replacement of hydroxyl groups by chlorine[2,3] are of great synthetic value, since the chlorodeoxy function, once introduced, may be readily modified by nucleophilic replacement or be reductively removed by hydrogenation. In the carbohydrate field, such reagents offer a convenient synthesis of a wide variety of novel amino and deoxy sugars, etc. Sulphuryl chloride is one such reagent[2], and we report on its use for the introduction of either two or three chlorine substituents into sucrose, and the conversion of the resulting chlorodeoxysucrose analogues, by the action of base, into anhydrides.

*Sucrochemistry: Part XIX. For Part XVIII, see Ref. 1.

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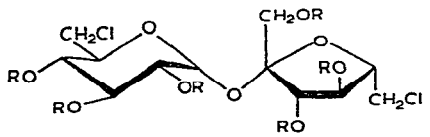
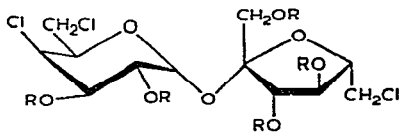
RESULTS AND DISCUSSION

Selective substitution of hydroxyl groups in sucrose can be achieved by tritylation[4], esterification[5], de-esterification[6], cyclic acetal formation[7], or chlorination using the mesyl chloride–*N*,*N*-dimethylformamide reagent[8]. However, the preparation of substituted derivatives directly from sucrose, without the need for laborious chromatographic separation, is not usually possible.

We have reported[9] on the reaction of sucrose with sulphuryl chloride at (*a*) −78°, (*b*) room temperature, and (*c*) 50°, and the results showed that selective chlorination of sucrose was possible when the reaction was carried out at low temperatures. We have therefore reinvestigated this reaction in order to find optimal conditions for the direct preparation of di- and tri-chlorinated derivatives. The reaction of sucrose with sulphuryl chloride in chloroform–pyridine initially at −78° and then at −30° to −35° (with careful monitoring by t.l.c.) gave, after 4 days, one major product. The reaction mixture on dechlorosulphation and acetylation gave crystalline, known 6,6′-dichloro-6,6′-dideoxysucrose hexa-acetate (**2**).

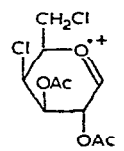


1 R = H
2 R = Ac

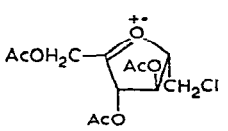


3 R = SO_2Cl
4 R = H
5 R = Ac
6 R = Bz
7 R = Ms
8 R = *p*-Nitrobenzoyl

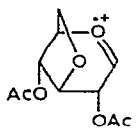
When a similar reaction mixture was kept at −5° to −10° for 16 h, one major product (*X*, different from the dichloro derivative **1**) was formed, and isolated crystalline in 30% yield. At least two other products were formed, but they were not further investigated. Elemental analysis of *X* showed it to be a "trichloro-sucrose", and it gave a crystalline pentamethanesulphonate and penta-*p*-nitrobenzoate. The mass spectrum of the syrupy penta-acetate of *X* showed two major ions at high mass (*m*/*e* 283 and 307), corresponding to ions *A* and *B* formed by the usual cleavage of the interglycosidic bonds[9].



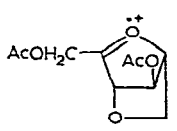
A (*m*/*e* 283)



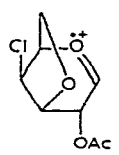
B (*m*/*e* 307)



C (*m*/*e* 229)



D (*m*/*e* 229)



E (*m*/*e* 205)

Ion *A* was associated with two other ions at *m/e* 285 and 287, in the ratio 9:6:1, indicative of the presence of two chlorine substituents, and the ion at *m/e* 307 has associated with it one at *m/e* 309 (ratio 3:1), showing the presence of 1 chlorine substituent. Ion *A* further fragmented to give ions at *m/e* 223, 181, 163, 145, and 117, as expected[3]. Ion *B* fragmented *via* sequential loss of either acetic acid, ketene, and acetic acid, or ketene, acetic acid, and acetic acid, giving rise to ions *m/e* 265, 247, 205, and 145.

The ^{1}H-n.m.r. spectrum of the penta-acetate of *X* showed (Table I) some similarity to that of 6,6′-dichloro-6,6′-dideoxysucrose hexa-acetate[9], but one major difference was the appearance of the signal for H-4 as a narrow quartet at higher field (τ 5.29) with coupling constants of 3.0 and 1.5 Hz. The chemical shift indicates chlorine substitution at C-4, and the values of the coupling constants are indicative of the *galacto* configuration[3]. Thus, *X* is 4,6-dichloro-4,6-dideoxy-α-D-galacto-pyranosyl 6-chloro-6-deoxy-β-D-fructofuranoside (**4**)*.

TABLE I

^{1}H-N.M.R. PARAMETERS[a]

Compound	**5**	**14**	**12**		**5**	**14**	**12**
H-1	4.50 (d)	[d]	4.52 (d)	$J_{1,2}$	3.0	3.0	2.5
H-2	[b]	4.86 (q)	4.77 (q)	$J_{2,3}$	—	5.5	5.5
H-3	[b]	[e]	[f]	$J_{3,4}$	3.0	0	0
H-4	5.29 (q)	5.36 (d)	5.31 (d)	$J_{4,5}$	1.5	1.5	1.5
H-5	5.49 (sx)	[e]	6.06 (q)	$J_{5,6a}$	6.5	—	9.0 (*exo*)
H-6a	[c]	[e]	[f]	$J_{5,6b}$	6.5	—	0 (*endo*)
H-6b	[c]	[e]	[f]	$J_{3',4'}$	—	—	}
H-1′a	[c]	[e]	[f]	$J_{4',5'}$	—	—	} 2.5 and 0
H-1′b	[c]	[e]	[f]				
H-3′	[b]	[d]	[f]				
H-4′	[b]	[d]	4.90 (d)				
H-5′	[c]	[e]	[f]				
H-6′a	[c]	[e]	[f]				
H-6′b	[c]	[e]	[f]				

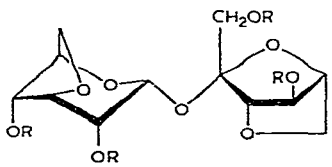
[a]First-order chemical shifts (τ values) and coupling constants at 100 MHz in deuteriochloroform; key: d, doublet; q, quartet; sx, sextet; cm, complex multiplet. [b]4.5–4.9 (m). [c]5.7–6.5 (cm). [d]4.5–4.7 (cm). [e]5.5–6.4 (cm). [f]5.4–5.9 (cm).

Further confirmation of the structure of **4** was obtained from the derived pentamethanesulphonate (**7**), the physical constants of which were identical with those reported for the product obtained[11] from sucrose octamethanesulphonate by nucleophilic substitution with lithium chloride in hexamethylphosphoric triamide.

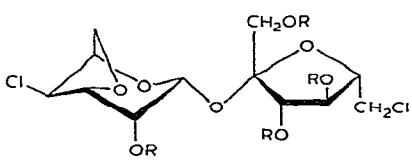
*A trichlorosucrose, isolated as the crystalline penta(chlorosulphate) (**3**) has been prepared independently by treating sucrose octa(chlorosulphate) with pyridine hydrochloride in chloroform[10]. This product, on dechlorosulphation, was identical on t.l.c. with that prepared by us.

The order of reactivity of sulphonic esters of sucrose is known[12] to be $6 \approx 6' \gg 4 > 1'$. It is therefore not surprising that the sulphuryl chloride reagent, which chlorinates by chlorosulphation of hydroxyl groups followed by nucleophilic replacement of the chlorosulphate groups, should show a similar reactivity, and thus the expected product of trisubstitution is the 4,6,6′-isomer (**4**).

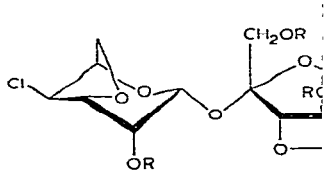
Anhydro derivatives of sucrose have been prepared in this laboratory[5] and elsewhere[13], from a variety of sulphonic esters of sucrose. Since the above chlorodeoxy derivatives are now readily available from sucrose, we have studied their base-catalysed conversion into anhydrides. As expected, by analogy with 6,6′-di-*O*-tosylsucrose[5], 6,6′-dichloro-6,6′-dideoxysucrose (**1**) gave 3,6-anhydro-α-D-glucopyranosyl 3,6-anhydro-β-D-fructofuranoside (**9**) in high yield, which was further characterised as its tetra-acetate (**10**). The mass spectrum of **10** gave a major ion at *m/e* 229, corresponding to the oxycarbonium ions *C* and *D*. In this case and in other anhydrides discussed, the fragmentation of oxycarbonium ion containing anhydro rings was relatively simple. Thus, the only other ions of note in the mass spectrum of **10** were observed at *m/e* 245, 169, 139, 127, 109, and 97, corresponding, respectively, to the oxycarbonium ion(s) +16 (O), −60 (CH_3CO_2H), −90 ($-CH_3CO_2H-CH_2O$), −102 ($-CH_3CO_2H-CH_2CO$), −120 ($-CH_3CO_2H-CH_3CO_2H$) and −132 ($-CH_3CO_2H$, $-CH_2O-CH_2CO$).



9 R = H
10 R = Ac



13 R = H
14 R = Ac



11 R = H
12 R = Ac

When 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 6-chloro-6-deoxy-β-D-fructofuranoside (**4**) was treated with excess of boiling, methanolic sodium methoxide, 3,6-anhydro-4-chloro-4-deoxy-α-D-galactopyranosyl 3,6-anhydro-β-D-fructofuranoside (**11**) was obtained, and characterised as its triacetate (**12**). Milder conditions gave, exclusively, a monoanhydride formulated as 3,6-anhydro-4-chloro-4-deoxy-α-D-galactopyranosyl 6-chloro-6-deoxy-β-D-fructofuranoside (**13**) on the basis of n.m.r. and mass-spectral data obtained from its derived tetra-acetate (**14**). Thus, the n.m.r. spectra for the two acetylated anhydrides **12** and **14** (Table I) both showed very similar chemical shifts and coupling constants for the protons in the galactopyranosyl ring, and these were different from those of the trichloro-penta-acetate **5** from which they were derived, indicating that anhydride formation had taken place in the galactopyranosyl ring in both cases. Furthermore, the value (5.5 Hz) of $J_{2,3}$ indicated the $^1C_4$ conformation for this ring, and the values of $J_{5,6exo}$ (9.0 Hz) and $J_{5,6endo}$ (0 Hz) are, as expected, similar to those reported for acylated 3,6:3′,6′-dianhydro-α,α-trehalose[14].

Further evidence for these structures was obtained from mass spectrometry. The dianhydro-monochloro-triacetate **12** gave ions of high mass at *m/e* 205 (1 Cl) and 229 corresponding to the oxycarbonium ions *E* and *D*. Also present were minor ions derived from *D* at *m/e* 245, 169, 139, 127, 109, and 97, which had been observed in the mass spectrum of **10**, and fragmentation of *E* gave ions at *m/e* 163 (1 Cl) and 145 (1 Cl), corresponding to $E-42$ ($-CH_2CO$) and $E-60$ ($-CH_3CO_2H$), which were also observed in the spectrum of the monoanhydride-dichloro-tetra-acetate **14**. For **14**, the two oxycarbonium ions were observed at *m/e* 307 (1 Cl) and 205 (1 Cl), corresponding to *B* and *E*, both of which fragmented in a manner already described.

From these results, it is clear that anhydride formation for 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 6-chloro-6-deoxy-β-D-fructofuranoside (**4**) is much more favourable in the galactopyranosyl ring than in the fructofuranosyl ring. No selectivity in anhydride formation has been observed in related systems, under similar conditions, in which the pyranosyl ring has the D-*gluco* configuration. Thus, 6-chloro-6-deoxy-α-D-glucopyranosyl 6-chloro-6-deoxy-β-D-fructofuranoside (**1**) gives only the dianhydride **9**, and 6-chloro-6-deoxy-α-D-glucopyranosyl 1,6-dichloro-1,6-dideoxy-β-D-fructofuranoside gives only 3,6-anhydro-α-D-glucopyranosyl 1,4:3,6-dianhydro-β-D-fructofuranoside on treatment with boiling, methanolic sodium methoxide[15]. The change in conformation ($^4C_1 \rightarrow {}^1C_4$) brought about by 3,6-anhydro formation in galactopyranosyl rings will alleviate steric interaction from the group at C-4, as this is axially disposed in the $^4C_1$ conformation but equatorially disposed in the $^1C_4$ conformation, and this would be expected to facilitate 3,6-anhydride formation, thus accounting for the observed selectivity.

EXPERIMENTAL

General. — Pyridine was dried over calcium hydride, and chloroform was dried over magnesium sulphate. Chlorination reactions were monitored by t.l.c. [(Silica Gel 60 F.254, Merck) (chloroform–methanol–acetone–water, 57:20:20:3)] by withdrawing aliquots of the reaction mixture, and dechlorosulphating by adding them to a suspension of sodium carbonate in methanol containing a catalytic amount of sodium iodide. Detection was effected by spraying with 5% ethanolic sulphuric acid followed by heating at 120–130°. Dry-column chromatography was performed on Silica Gel 7734 (Merck). Evaporations were carried out at 40–50° under reduced pressure. Melting points are uncorrected. Optical rotations were measured on a Perkin–Elmer 141 polarimeter in 1-dm tubes. N.m.r. spectra were measured at 100 MHz (Varian HA-100) with Me_4Si as internal reference. Mass spectra were determined with A.E.I. MS-9 and MS-30 spectrometers at 70 eV.

*2,3,4-Tri-*O*-acetyl-6-chloro-6-deoxy-*α*-D-glucopyranosyl 1,3,4-tri-*O*-acetyl-6-chloro-6-deoxy-*β*-D-fructofuranoside* (**2**). — To a stirred suspension of sucrose (4 g) in chloroform (60 ml) and pyridine (20 ml) at −70°, sulphuryl chloride (8 ml) was added dropwise during 0.5 h. Stirring was continued for 3 h, during which period the temperature was allowed to rise to −30°. The reaction mixture was maintained at this temperature for 4 days, and t.l.c. then showed the presence of one major product.

The reaction mixture was poured into ice-cold, 10% sulphuric acid (250 ml), and the chloroform layer was separated, washed with saturated, aqueous sodium hydrogen carbonate and water, and dried ($MgSO_4$). Evaporation of the chloroform solution afforded a syrupy mass, which was dissolved in methanol and dechlorosulphated with a catalytic amount of sodium iodide in the presence of excess of sodium carbonate. The filtered solution was concentrated to dryness. The residue was dissolved in pyridine (25 ml), acetic anhydride (8 ml) was added, and the mixture was kept at room temperature for 24 h and then poured into ice–water. The crystalline precipitate was filtered off, dried, and recrystallised from propan-2-ol to give **2** (1.1 g, 15%). identical on t.l.c. with the authentic sample, m.p. and mixture m.p. 119–120°; lit[9], m.p. 117–119°.

2,4-Di-O-acetyl-3,6-anhydro-α-D-glucopyranosyl 1,4-di-O-acetyl-3,6-anhydro-β-D-fructofuranoside (**10**). — The hexa-acetate **2** (1.0 g) was *O*-deacetylated by treatment with methanol containing a catalytic amount of sodium methoxide. Evaporation of the solution gave a syrupy residue, which was dissolved in M methanolic sodium methoxide (15 ml) and the solution heated under reflux. After 4.5 h, t.l.c. indicated the presence of a single product that moved slightly faster than the starting material. No other products were detected (t.l.c.) during the reaction The reaction mixture was cooled, brought to pH 7 with Amberlite IR-120(H^+) resin, filtered, and evaporated to dryness. The resulting syrup was dissolved in pyridine (15 ml), and acetic anhydride (3 ml) added. After 24 h, at room temperature, t.l.c. (chloroform–acetone, 8:1) indicated the formation of a single product. The reaction mixture was poured into ice–water and extracted with chloroform, and the organic layer was washed successively with 2M HCl, aqueous $NaHCO_3$, and water, and dried ($MgSO_4$). Evaporation of the chloroform solution afforded **10** as an amorphous solid (0.45 g, 60%) identical (t.l.c.) with an authentic sample[5], m.p. 65–70°.

4,6-Dichloro-4,6-dideoxy-α-D-galactopyranosyl 6-chloro-6-deoxy-β-D-fructofuranoside (**4**). — To a cooled (*ca.* −50°) suspension of sucrose (8 g) in chloroform (120 ml) and pyridine (40 ml), sulphuryl chloride (16 ml) was added dropwise with stirring during 1.5 h. The mixture was maintained at *ca.* −30° for 1 h, allowed to attain −5°, and then stored in the refrigerator (−5 to 0°) for 15 h. T.l.c. indicated one major and at least two minor products. Work-up of the reaction mixture could be performed as described above for **2**. Alternatively, the reaction mixture was filtered into a stirred suspension of sodium carbonate (20 g) in methanol (200 ml) containing a catalytic amount of sodium iodide, stirred for 0.5 h, and filtered. The filtrate was concentrated to dryness, and the residue was extracted with a small volume of chloroform–methanol (8:1), which was then applied to the top of a small column of silica gel. Elution with the same solvent mixture gave, in the first 100 ml, traces of minor products*, and then the major product, which was isolated as a solid that

*These could not be separated due to their very close R_F values; the sodium-fusion test showed the presence of both sulphur and chlorine, suggesting them to be cyclic sulphates, which are known to be formed under these reaction conditions.

crystallised from dichloromethane–acetone to give **4** (2.7 g, 29%), m.p. 115–116°, $[\alpha]_D$ +88° (*c* 1.0, methanol) (Found: C, 36.09; H, 4.91; Cl, 25.57. $C_{12}H_{13}Cl_3O_8$ calc.: C, 36.23; H, 4.71; Cl, 26.8%).

Acetylation (pyridine–acetic anhydride) of **4** gave the penta-acetate **5** (95%) as an amorphous solid, m.p. 57–60°, $[\alpha]_D$ +90.3° (*c* 1.0, methanol) (Found: C, 43.80; H, 4.74; Cl, 17.93. $C_{22}H_{29}Cl_3O_{13}$ calc.: C, 43.45; H, 4.77; Cl, 17.53%).

Benzoylation (pyridine–benzoyl chloride) of **4** gave the pentabenzoate **6** (90%) as an amorphous solid*, m.p. 70–73° $[\alpha]_D$ +59.2° (*c* 1.0, acetone).

p-Nitrobenzoylation (pyridine–*p*-nitrobenzoyl chloride) gave the penta-*p*-nitrobenzoate **8** (86%), m.p. 136–139° (from ethanol), $[\alpha]_D$ +69.9° (*c* 1.0, acetone) (Found: C, 49.73; H, 3.36; Cl, 9.38; N, 6.24. $C_{47}H_{39}Cl_3N_5O_{23}$ calc.: C, 49.18; H, 3.40; Cl, 9.29; N, 6.10%).

Mesylation (pyridine–mesyl chloride) of **4** gave the pentamethanesulphonate **7** (85%), m.p. 162–163° (from dichloromethane–ethanol), $[\alpha]_D$ +63.6° (*c* 1.0, acetone); lit.[11] m.p. 163–165°, $[\alpha]_D$ +53.2° (*c* 0.8, acetone) (Found: C, 26.52; H, 4.02; Cl, 14.04; S, 20.29. $C_{17}H_{29}Cl_3S_5O_{18}$ calc.: C, 25.90; H, 3.68; Cl, 13.52; S, 20.32%).

*3,6-Anhydro-4-chloro-4-deoxy-α-*D*-galactopyranosyl 6-chloro-6-deoxy-β-*D*-fructofuranoside* (**13**). — A solution of **4** (3 g) in 0.25M methanolic sodium methoxide (50 ml) was heated at 45° for 4 h. T.l.c. then showed the presence of a single product that moved faster than the starting material. The reaction mixture was cooled, brought to pH 7 with Amberlite IR-120(H^+) resin, filtered, and concentrated to dryness. A solution of the residue in a small volume of chloroform–methanol (1:1) was added to a small column of silica gel and eluted with chloroform–methanol (1:1). Evaporation gave a solid which crystallised from dichloromethane–acetone to give **13** (2.2 g, 80%), m.p. 105–106°, $[\alpha]_D$ +1.7° (*c* 1.0, methanol) (Found: C, 39.80; H, 5.40; Cl, 20.88. $C_{12}H_{18}Cl_2O_8$ calc.: C, 39.89; H, 4.99; Cl, 19.67%).

Acetylation in the usual manner (pyridine–acetic anhydride) gave the tetra-acetate **14** (95%) as an amorphous solid, m.p. 53–56°, $[\alpha]_D$ −55.5° (*c* 1.0, acetone) (Found: C, 45.19; H, 5.04; Cl, 13.20. $C_{20}H_{26}Cl_2O_{12}$ calc.: C, 45.36; H, 4.92; Cl, 13.42%).

*3,6-Anhydro-4-chloro-4-deoxy-α-*D*-galactopyranosyl 3,6-anhydro-β-*D*-fructofuranoside* (**11**). — A solution of **13** (2 g) in M methanolic sodium methoxide (40 ml) was heated under reflux for 4 h. T.l.c. then showed the presence of a single product that moved faster than the starting material. The solution was brought to pH 7 with Amberlite IR-120(H^+) resin, filtered, and concentrated to dryness. The residue was extracted with a small volume of dichloromethane–methanol (1:1), the extract was passed through a small column of silica gel, and the column was washed with the same solvent. Evaporation, and crystallisation of the residue from dichloromethane–acetone afforded **11** (1.5 g, 83%), m.p. 113–115° (dec.), $[\alpha]_D$ +30.7° (*c* 1.0, methanol) (Found: C, 43.82; H, 5.23; Cl, 11.36. $C_{12}H_{17}ClO_8$ calc.: C, 44.38; H, 5.24; Cl, 10.94%).

**Note added in proof.* Subsequently obtained crystalline m.p. 91–92° (from ethanol).

Acetylation in the usual manner (pyridine–acetic anhydride) of **11** gave the triacetate **12** (95%) as an amorphous solid that melted over a wide range (60–70°), $[\alpha]_D$ +31.2° (*c* 1.0, acetone) (Found: C, 48.11; H, 5.33; Cl, 7.93. $C_{18}H_{23}ClO_{11}$ calc.: C, 47.95; H, 5.11; Cl, 7.88%).

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