Sucrochemistry. Part XII.[1] Reaction of Sucrose with Sulphuryl Chloride

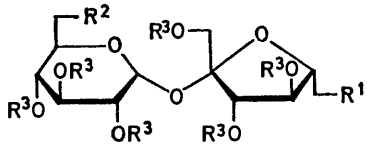
By **John M. Ballard, Leslie Hough, Anthony C. Richardson,*** and (in part) **Peter H. Fairclough,** Department of Chemistry, Queen Elizabeth College, London W8 7AH

Reaction of sucrose with sulphuryl chloride at −78° afforded, after dechlorosulphation, a mixture of 6′-chloro-6′-deoxysucrose and 6,6′-dichloro-6,6′-dideoxysucrose, which were obtained, after chromatographic fractionation, in a combined yield of 72%. At room temperature, a complex mixture of products was formed from which 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 3′,4′-anhydro-1′,6′-dichloro-1′,6′-dideoxy-β-D-*ribo*-hexulofuranoside 2,3-sulphate was isolated in 17% yield. At 50°, a mixture of greater complexity arose and in addition to the foregoing anhydro-derivative a 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 1′,4′,6′-trichloro-1′,4′,6′-trideoxy-β-D-hexulofuranoside 2,3-sulphate and 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 1′,4′,6′-trichloro-1′,3′,4′,6′-tetradeoxy-β-D-*glycero*-hex-3′-enulofuranoside 2,3-sulphate were isolated, all in rather low yields. The structures of these products were assigned on the basis of n.m.r. and mass spectrometry.

THE reaction of carbohydrates with sulphuryl chloride, a study originated by Helferich *et al.*,[2] and extended by J. K. N. Jones *et al.*[3] usually results in the replacement of suitably placed hydroxy-groups by chlorine; when the hydroxy-group is attached to a chiral centre, inversion of configuration occurs. The initial product is a chlorosulphate ester which undergoes nucleophilic substitution with the same steric and polar constraints as sulphonic esters.[4] For example, Jones and his colleagues[3] have established that secondary hydroxy-groups adjacent to the anomeric centre do not undergo replacement and that the presence of a vicinal axial or β-*trans*-axial group[4] inhibits the reaction. However, the 'assumed' S_N2 character of the displacement reaction has been questioned by Khan,[5] who has shown that reaction of primary chlorosulphates with azide anion affords not the azide, but the chloro-derivative, suggesting that the reaction is intramolecular, similar to the S_Ni reaction but with inversion of configuration.

The reaction of sucrose with sulphuryl chloride at −78° has been studied by Jones *et al.*,[6,7] who obtained an impure product thought to be a mixture of tri- and dichloro-derivatives. They showed that the D-glucopyranosyl ring of sucrose had been converted largely into the 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 2,3-sulphate system, as would have been predicted from their results on methyl α-D-glucopyranoside.[7] In view of our interest in functionally modified derivatives of sucrose we have reinvestigated this sulphuryl chloride reaction under various conditions in an attempt to optimise product yields.[8]

Reaction of sucrose with sulphuryl chloride in a mixture of chloroform and pyridine at −78°, conditions which can lead to poly(chlorosulphate) esters,[9] afforded a crude syrupy product which on dechlorosulphation with sodium iodide gave a mixture of at least two products, both distinguishable from sucrose. Chromatographic separation of the mixture afforded the two syrupy components in 43 and 29% yield which were identified as 6′-chloro-6′-deoxy-sucrose (2) and 6,6′-dichloro-6,6′-dideoxy-sucrose (1), respectively, and characterised as their crystalline acetate esters, (4) and (3), respectively. The dichloro-derivative (1) was recognised by comparison of its hexa-acetate (3) with an authentic specimen;[10] the monochloro-sucrose was assumed to be the 6′-chloro-derivative on the basis of its mass spectrum. The spectrum showed the two oxycarbonium ions resulting from the cleavage of the two glycosidic linkages at *m/e* 331 and 307 in a ratio of 1 : 2. The peak at 307 was

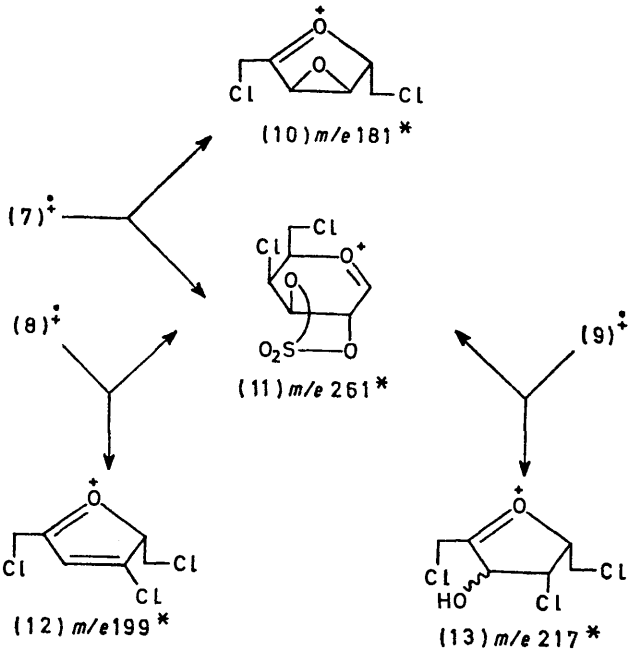


(1) $R^1 = R^2 = Cl, R^3 = H$
(2) $R^1 = Cl, R^2 = OH, R^3 = H$
(3) $R^1 = R^2 = Cl, R^3 = Ac$
(4) $R^1 = Cl, R^2 = OAc, R^3 = Ac$
(5) $R^1 = Cl, R^2 = OMs, R^3 = Ms$
(6) $R^1 = OH, R^2 = OAc, R^3 = Ac$

associated with an isotope peak at 309 (ratio 3 : 1) indicating one chlorine substituent. Our previous experience with the mass spectrometry of sucrose derivatives has indicated that the cleavage of the fructosyl glycosidic bond is the most favoured initial fragmentation, since the carbonium ion produced is tertiary; hence the more intense fragment at *m/e* 307 suggested that the chlorine was attached to the fructose ring. Since the most reactive hydroxy-group on fructofuranoid rings is that at C-6, the chloro-group was assigned to this position. The 1′-substituent, being adjacent to the anomeric group, is far less reactive[4] than that at C-6′. The structure of the 6′-chloro-derivative (2) was confirmed by its independent synthesis from 1′,2,3,3′,4,4′,6-hepta-*O*-acetylsucrose (6)[11] by reaction with the mesyl

[1] Part XI, R. Khan, K. S. Mufti, and M. R. Jenner. *Carbohydrate Res.*, in the press.
[2] B. Helferich, G. Sproek, and E. Besler, *Ber.*, 1925. **58**, 886.
[3] S. S. Ali, T. J. Mepham, I. M. E. Thiel, E. Buncel, and J. K. N. Jones, *Carbohydrate Res.*, 1967, **5**, 118 and earlier papers; E. Buncel, *Chem. Rev.*, 1970. **70**, 323.
[4] A. C. Richardson, *Carbohydrate Res.*, 1969. **10**. 395.
[5] R. Khan, *Carbohydrate Res.*, 1972. **25**. 504.
[6] V. Kollonitsch, 'Sucrose Chemicals,' published by C. H. Kline and Co., for the International Sugar Research Foundation, Washington, D.C., 1970. p. 85.
[7] P. D. Bragg, J. K. N. Jones, and J. C. Turner, *Canad. J. Chem.*, 1959, **37**, 1412.
[8] Preliminary communication, J. M. Ballard, L. Hough, and A. C. Richardson, *J.C.S. Chem. Comm.*, 1972, 1097.
[9] H. J. Jennings and J. K. N. Jones, *Canad. J. Chem.*, 1965. **43**, 2372.
[10] L. Hough and K. S. Mufti, *Carbohydrate Res.*, 1972, **25**. 497.
[11] J. M. Ballard, L. Hough, and A. C. Richardson, *Carbohydrate Res.*, 1972, **24**. 152.

chloride–*NN*-dimethylformamide reagent,[12] which afforded 6′-chloro-6′-deoxysucrose hepta-acetate (4) (74%), identical with that produced by acetylation of (2). The selectivity of the sulphuryl chloride reaction for the 6′-position of sucrose is in contrast to the nucleophilic substitution reaction of sucrose 6,6′-ditosylate with chloride anion, which favoured the 6-position.[10]

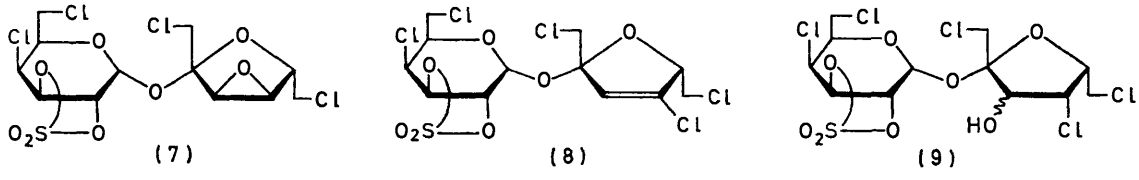


The sulphuryl chloride reaction was repeated at −78° but the reaction mixture was then allowed to warm to room temperature and maintained at that temperature for 2 h, to give a complex mixture, as indicated by t.l.c. Fortunately, the major product (*A*) was readily isolated by silica gel chromatography, crystalline and in 17% yield. When the reaction was conducted at 50° a mixture of even greater complexity was obtained. Extensive fractionation of the mixture by chromatography afforded product (*A*) in reduced yield (2%) together with two other crystalline components, (*B*) and (*C*), in 3 and 0·2% yields, respectively.

The structures of products (*A*)—(*C*) were all assigned on the basis of their n.m.r. and mass spectral data. The mass spectra contained a common fragment at *m/e* 261 which was in each case the highest mass fragment of significant intensity. Accurate mass determination indicated the molecular formula $C_6H_7Cl_2O_5S$, which corresponded to the oxycarbonium ion derived from a 4,6-dichloro-4,6-dideoxy-α-D-galactopyranoside 2,3-sulphate. Consequently it was certain that the glucopyranosyl portion of sucrose had reacted in an analogous manner to that of methyl α-D-glucopyranoside,[7] and that the three compounds differed only in the fate of the fructofuranoid ring. In the spectrum of product (*A*) the base peak occurred at *m/e* 181. Accurate mass measurement indicated the composition $C_6H_7Cl_2O_2$ and the ion was accordingly assigned the anhydro-dichloro-dideoxy-hexulofuranosyl structure (10).

In the ^{1}H n.m.r. spectrum of (*A*) the resonances due to H-1, H-2, H-3, H-4, and H-5 were clearly recognisable (Table), consistent with the hexopyranosyl ring having the expected *galacto*-configuration. The resonances due to other ring protons occurred as a triplet (H-5′, confirmed by irradiation at the H-6′ frequency) and an 'AB-like' quartet due to H-3′ and H-4′ in which the higher field doublet (H-4′) was weakly coupled (*ca.* 1 Hz) to H-5′. The pattern of the H-3′ and H-4′ resonances and their chemical shifts (τ 6) were typical of protons attached to an oxiran ring which was fused to a larger ring (*cf.* refs. 13 and 14). The small coupling between H-4′ and H-5′ suggested that these protons were *trans*, since it has been noted in the case of 2,3-anhydrohexopyranosides that $J_{1.2}$ and $J_{3.4}$ are significant only when the protons concerned are *trans* to the oxiran ring.[13] Related data for 2,3-anhydrofuranosides are sparse but $J_{1.2}$ and $J_{3.4}$ have been observed to be *ca.* 0 for methyl 2,3-anhydro-5-*O*-benzyl-α-D-ribopyranoside,[14] suggesting that the 3′,4′-anhydro-ring in (*A*) is *cis* to H-5′. The structure (7) is therefore proposed for (*A*).

Product (*B*) gave rise to a fragment at *m/e* 199 in its mass spectrum. Accurate mass measurement indicated that the fragment ($C_6H_6Cl_3O$) was the oxycarbonium ion (12) which originated from a trichloro-trideoxy-hexenulofuranoside. In the ^{1}H n.m.r. spectrum of (*B*) the resonances attributable to the galactopyranosyl ring were readily assigned and were in similar positions to those observed in the ^{1}H n.m.r. spectrum of (7) (Table). In addition a doublet at τ 3·78 was assigned to an olefinic proton which was coupled (2·2 Hz) to a quartet at τ 5·06; the latter collapsed to a triplet upon irradiation at the frequency of the olefinic doublet. The quartet was therefore assigned to H-5′ of the furanosyl ring; consequently



[12] M. E. Evans, L. Long, and F. W. Parrish. *J. Org. Chem.*, 1968. **33**. 1074.

[13] D. H. Buss, L. Hough, L. D. Hall, and J. F. Manville, *Tetrahedron*, 1965, **21**, 69; L. Hough. P. A. Munroe, and A. C. Richardson, *J. Chem. Soc.* (*C*), 1971, 1090.

[14] J. A. Wright. N. F. Taylor, and J. J. Fox. *J. Org. Chem.*, 1969, **34**. 2632.

the double bond must be between C-3 and C-4 and two of the chlorine substituents at C-1′ and C-6′. The third chlorine atom must be situated at either C-3′ or C-4′ and the two structures cannot be distinguished on the basis of the spectroscopic evidence available. However the introduction of chlorine at C-3′ would be unfavourable since it is adjacent to the anomeric centre. Consequently (*B*) is assigned the structure (8).

The mass spectrum of product (*C*) contained fragment ions corresponding to the two oxycarbonium ions at *m/e* 261 and 217. Accurate mass measurement of the latter indicated a formula $C_6H_8Cl_3O_2$ suggesting that the hexulofuranosyl ring had been converted into a trichlorotrideoxy-hexulofuranosyl system. The ^1H n.m.r. spectrum of (*C*) showed resonances due to H-1, H-2, and H-3 of the D-galactopyranosyl system but the remaining resonances were overlapped (Table). However the addition of trichloroacetyl isocyanate to the solution resulted in the appearance of a singlet at τ 1·35 (1H) due to the NH of the carbamate ($Cl_3C{\cdot}CO{\cdot}NH{\cdot}CO_2R$) formed from the reaction of a single hydroxy-group with the reagent. In addition the overlapped portion of the spectrum was rendered amenable to first-order analysis by the deshielding of a doublet resonance by about 1 p.p.m. to τ 4·28 (*J ca.* 6 Hz). The only methine proton in the hexulofuranosyl unit of sucrose derivatives to appear as such a doublet is H-3′, which is normally observed with a coupling of *ca.* 6—8 Hz. Consequently (*C*) has a 3′-hydroxy-group and the chloro-groups attached to the hexulofuranosyl system must be located at positions 1′, 4′, and 6′. The deshielding of H-3′ in this way uncovered both the H-4′ resonance at τ 5·00 as a double doublet (*J ca.* 4 and 6 Hz) and the resonances due to H-5′, H-5, and H-4 (see Table). The observed coupling constants do not permit the determination of the chiralities of C-3′ and C-4′ but the 4′-chloro-group most probably originated with inversion of configuration, consequently the structure (9) is assigned to compound (*C*) in which the chirality of C-3′ remains an open question.

The Scheme shows the way in which the three products (*A*)—(*C*) might arise. In all three cases the glucopyranosyl unit reacts in the same way as methyl α-D-glucopyranoside [7] to give the 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl group independently and simultaneously with events taking place on the hexulofuranosyl portion of the molecule. The latter are initiated by the formation of the tetra-chlorosulphated fructofuranosyl unit, which then undergoes displacement at the primary positions, less readily at C-1′ than at C-6′. The resulting 1′,6′-dichloro-3′,4′-bis(chlorosulphate) could then either undergo displacement of the 4′-chlorosulphate group to give the 1′,4′,6′-trichloro-3′-chlorosulphate or undergo epoxide formation. The formation of epoxides from a vicinal *trans*-bis(chlorosulphate) has been observed previously in the case of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside bis(chlorosulphate),[15] and appears to be analogous to the formation of the same epoxide from the corresponding dimesylate [16] and ditosylate.[17] Product (*C*)(9), depending on the chirality of C-3′, could arise either from the 3′,4′-epoxide (7) by ring opening by chloride, or by dechlorosulphation of the 1′,4′,6′-trichloro-3′-*O*-chlorosulphate. The yield of the epoxide appeared to decrease as the reaction was prolonged but in view of the very low recovery of the products of reaction it would be tendentious to assume that (*C*) arose from the epoxide (7). Product (*B*) was probably formed from the 1′,4′,6′-trichloro-3′-*O*-chlorosulphate by an *E*2 elimination of the chlorosulphate group (Scheme).

In the ^1H n.m.r. spectra of compounds (7)—(9) the

^1H N.m.r. spectral parameters: first-order chemical shifts (τ) and coupling constants (Hz) at 100 MHz

Compound	(4) [a]	(5) [b]	(7) [a]	(8) [a]	(9) [a]	(9) [c]
H-1	4·36(d)	3·93(d)	4·14(d)	3·85(d)	4·22(d)	4·25(d)
H-2	5·14(dd)		4·93(dd)	4·91(dd)	4·89(dd)	4·90(dd)
H-3			4·67(dd)	4·66(dd)	4·67(dd)	4·44(dd)
H-4	4·95(t)		5·24(m)	5·25(m)	*ca.* 5·2(m)	5·2(m)
H-5			5·46(t)	5·52(t)	*ca.* 5·5(m)	5·35(t)
H-6			*ca.* 6·35(m)	*ca.* 6·3(m)	*ca.* 6·2(m)	*ca.* 6·3
H-1′			6·40	*ca.* 6·15(q)	6·38(t)	*ca.* 6·3
H-3′	4·5—4·7(m)	4·46(d)	5·93(d)	3·78(d)	*ca.* 5·2(m)	4·28(d)
H-4′		4·66(t)	6·03(dd)		*ca.* 5·2(m)	5·00(dd)
H-5′			5·77(t)	5·06(q)	*ca.* 5·5(m)	5·40(t)
H-6′	6·24(d)		*ca.* 6·35(m)	6·11(m)	*ca.* 6·2(m)	*ca.* 6·3
$J_{1,2}$	3·5	*ca.* 3	3·3	3·3	3·0	*ca.* 3
$J_{1,4}$	0		*ca.* 1	*ca.* 1	*ca.* 1	
$J_{2,3}$	10·0		10·2	10·3	10·2	*ca.* 10
$J_{3,4}$	9·5		3·2	3·1	3·0	*ca.* 3
$J_{4,5}$	9·5		1·6	1·8		
$J_{5,6a}$			*ca.* 6	*ca.* 6·5		*ca.* 6
$J_{5,6b}$			*ca.* 6	*ca.* 6·5		*ca.* 6
$J_{2',4'}$		0·5	2·8			*ca.* 6
$J_{3',5'}$		0	0	2·2	0	0
$J_{4',5'}$		7·5	1·0			*ca.* 4
$J_{5',6'a}$			*ca.* 7	2·8		*ca.* 6
$J_{5',6'b}$			*ca.* 7	2·8		*ca.* 6

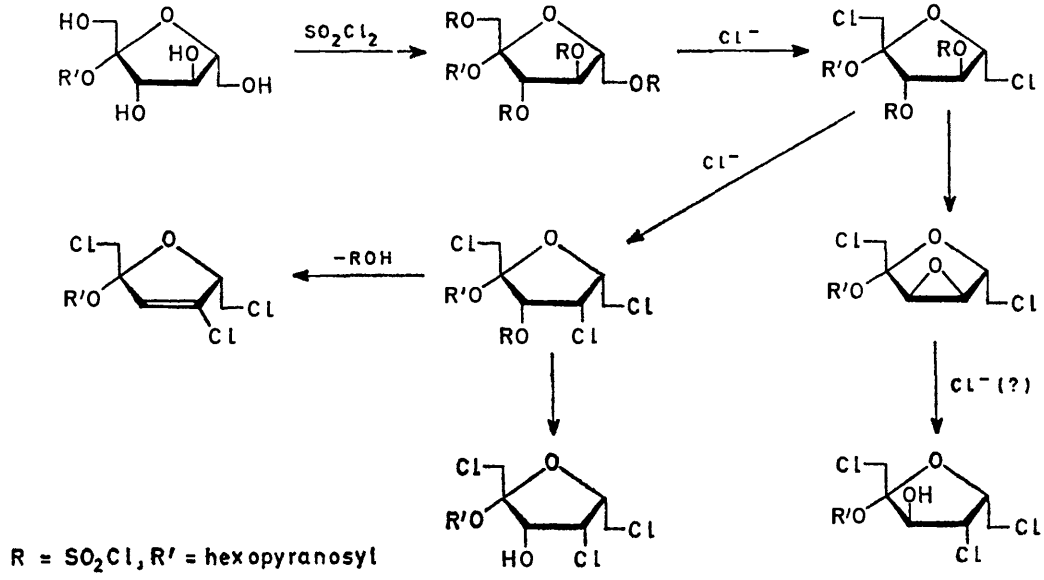
[a] In $CDCl_3$. [b] In $(CD_3)_2CO$. [c] In $CDCl_3$ after addition of trichloroacetyl isocyanate.

[15] H. J. Jennings and J. K. N. Jones, *Canad. J. Chem.*, 1963. **41**, 1151.

[16] Y. Ali and A. C. Richardson, *Carbohydrate Res.*, 1967, **5**. 441.

[17] N. K. Richtmyer and C. S. Hudson, *J. Amer. Chem. Soc.*, 1941, **63**, 1727.

H-4 resonance was broad, ill-resolved, and devoid of fine structure. However in the case of compound (8) extensive decoupling experiments showed that irradiation at the H-1 frequency resulted in the appearance of the H-4 signal as a well resolved double doublet (J 3·1 and 1·8 Hz) which had the expected structure of the H-4 resonance of a galactopyranoside. Furthermore irradiation at the H-4 frequency removed a very small coupling from the H-1 doublet. These results showed that there was a small long-range coupling between H-1 and H-4 which has not been previously observed in a α-galactopyranosides, although long-range coupling between an equatorial 4-fluorine atom and an equatorial 1-proton has been observed in derivatives of 4-deoxy-4-fluoro-α-D-glucopyranose.[18]



SCHEME

EXPERIMENTAL

Optical rotations were determined for solutions in chloroform unless otherwise stated. Dry column chromatography was performed on Kieselgel 7734 (Merck) according to the method of ref. 19, with solvent systems (A) ethyl acetate–ethanol–water (10 : 3 : 2), (B) ethyl acetate–light petroleum (1 : 5), or (C) chloroform–ethanol (60 : 1). Mass spectra were determined with A.E.I. MS-9 and MS-30 spectrometers at 70 eV (ion source at 150—200°).

Reaction of Sucrose with Sulphuryl Chloride.—(a) *At* −78°. Sulphuryl chloride (42 g, 0·31 mol) was added dropwise over 0·5 h to a stirred solution of sucrose (5 g, 0·0146 mol) in a mixture of pyridine (150 ml) and chloroform (150 ml) maintained at about −78° by cooling in an acetone–solid CO_2 bath. After a further 5 h at this temperature the mixture was then poured into ice-cold 10% sulphuric acid (600 ml). A white precipitate was filtered off, washed well with chloroform, and not further investigated. The chloroform layer and the washings were combined and washed well with aqueous sodium hydrogen carbonate and then with water and dried (Na_2SO_4). Concentration to dryness gave a syrup (12·7 g), which gave a positive reaction for chlorosulphate groups.[20] A portion of the syrup (5 g) in methanol (50 ml) was dechlorosulphated by the addition of barium carbonate (20 g) followed by a catalytic amount of sodium iodide. The mixture was stirred for 1 h, then filtered and evaporated to dryness. The residue was extracted with methanol and the extract concentrated to dryness to give a syrupy product which contained two components as indicated by t.l.c. These were separated by dry column chromatography [19] [solvent (B)] to give syrupy 6,6′-dichlorosucrose (1) as the first component eluted (0·63 g, 29%). Acetylation afforded (42%) the hexa-acetate (3), m.p. 117—119° (aqueous ethanol), $[\alpha]_D$ +55·7° (*c* 0·3) (Found: C, 45·4; H, 5·3; Cl, 10·8. Calc. for $C_{24}H_{32}Cl_2O_{15}$: C, 45·6; H, 5·1; Cl, 11·1%) (lit.,[10] m.p. 117—118°, $[\alpha]_D$ +55°).

Further elution of the column gave 6′-chloro-6′-deoxysucrose (2) (0·88 g, 43%) as a syrup. Acetylation afforded the *hepta-acetate* (4), m.p. 117—118°, $[\alpha]_D$ +54° (*c* 0·4) (Found: C, 47·8; H, 5·55; Cl, 5·35. $C_{26}H_{35}ClO_{17}$ requires C, 47·7; H, 5·35; Cl, 5·35%).

Mesylation of (2) afforded the crystalline *heptamesylate* (5), m.p. 214—218° (acetone–methanol), $[\alpha]_D$ +47·3° (*c* 0·5 in Me_2CO) (Found: C, 25·8; H, 3·9; Cl, 3·4. $C_{19}H_{35}ClO_{24}S_7$ requires C, 25·1; H, 3·9; Cl, 3·9%).

(b) *At room temperature.* Redistilled sulphuryl chloride (8·5 ml, 12 mol) was added dropwise over 10 min to a stirred solution of sucrose (3 g) in a mixture of pyridine (60 ml) and ethanol-free chloroform (30 ml) at about −78°. The mixture was maintained at this temperature for 2 h and then allowed to warm to room temperature. After 2 h at room temperature the mixture was poured into 500 ml of ice-cold 10% sulphuric acid. The chloroform layer was separated and washed well with aqueous sodium hydrogen carbonate,

[18] A. B. Foster, R. Hems, and J. H. Westwood. *Carbohydrate Res.*, 1970, **15**, 41; L. Phillips and V. Wray. *J. Chem. Soc.* (*B*), 1971, 1618.

[19] L. Hough, A. K. Palmer, and A. C. Richardson, *J.C.S. Perkin I*, 1972, 2513.

[20] H. J. Jennings and J. K. N. Jones. *Canad. J. Chem.*, 1962, **40**, 1408.

then water, and dried (Na_2SO_4). T.l.c. (chloroform–ethanol, 30 : 1) indicated the presence of a major fast-moving component and a multitude of minor products which were much less mobile on the chromatogram. The chloroform solution was then concentrated to dryness and the fast-moving component was isolated by dry column chromatography on silica gel (200 g) [solvent (C)]. The appropriate fraction was concentrated to dryness to give needles of product (*A*) [4,6-*dichloro*-4,6-*dideoxy*-α-D-*galactopyranosyl* 3′,4′-*anhydro*-1′,6′-*dichloro*-1′,6′-*dideoxy*-β-D-ribo-*hexulofuranoside* 2,3-*sulphate* (7)], m.p. 146—148° (propan-2-ol), $[\alpha]_D$ +68·5° (*c* 0·5) (Found: C, 32·4; H, 3·5; Cl, 29·5; S, 7·0. $C_{12}H_{14}Cl_4O_8S,1/3C_3H_8O$ requires C, 32·5; H, 3·5; Cl, 29·6; S, 6·7%), τ 8·84 (2H, d, solvent of crystallisation), *m/e* [' a ' indicates 3 : 1 doublet (1 Cl) and ' b ' 9 : 6 : 1 triplet (2 Cl)] 261 b (15), 181 b (100), 149 a (24), 135 b (10), 123 b (8), 111 (20), 109 (18), 107 (8), 103 b (10), 97 b (28), 83 b (70), 77 a (50), 75 (35), 71 (15), 69 (25), 55 a (18), and 49 a (13) (Found: *m/e* 180·9836. Calc. for $C_6H_7Cl_2O_2$: 180·9823).

(c) *At* 50°. Sulphuryl chloride (65 g, 8 mol) was added to a solution of sucrose (20 g) in pyridine (180 ml) maintained at 50°. After 48 h t.l.c. [solvent (A)] indicated that a mixture of products had been formed, containing product (*A*) and two slightly faster moving components [near the solvent front in solvent (A)]. The mixture was then cooled and was decanted from some tarry matter directly onto a dry column of silica gel (*ca.* 2 kg) which was then eluted with solvent (A). The fractions containing (*A*) and the other two components were combined (none contained a pure component) and concentrated to an orange coloured syrup (1·9 g). The mixture was fractionated on a dry column of silica gel [19] [solvent (B); 5 ml fractions].

The first eluted component was compound (*B*) (8), which crystallised with ease and was recrystallised from ethanol (0·73 g, 3%) to give 4,6-*dichloro*-4,6-*dideoxy*-α-D-*galacto-pyranosyl* 1′,4′,6′-*trichloro*-1′,3′,4′,6′-*tetradeoxy*-β-D-glycero-*hex*-3′-*enulofuranoside* 2,3-*sulphate*, m.p. 111—112°, $[\alpha]_D$ +79° (*c* 0·4) (Found: C, 30·4; H, 2·8; Cl, 36·9; S, 7·9. $C_{12}H_{13}Cl_5O_7S$ requires C, 30·1; H, 2·7; Cl, 37·1; S, 6·7%), *m/e* [' a ' indicates 3 : 1 doublet (1 Cl), ' b ' indicates 9 : 6 : 1 triplet (2 Cl), and ' c ' indicates 27 : 27 : 9 : 1 quartet (3 Cl)] 261 b (2), 213 a (3), 199 c (14), 167 c (8), 163 b (10), 144 a (20), 109 (60), 81 (13), 75 b (10), 64 (100), 53 (27), and 48 (41) (Found: *m/e* 260·9388. Calc. for $C_6H_7Cl_2O_5S$: 260·9393. Found: *m/e* 198·9481. Calc. for $C_6H_6Cl_3O$: 198·9485).

The fractions containing the second component [compound (C)] crystallised upon evaporation and were recrystallised from ethyl acetate–light petroleum to give a 4,6-*dichloro*-4,6-*dideoxy*-α-D-*galactopyranosyl* 1′,4′,6′-*trichloro*-1′,4′,6′-*trideoxy*-β-D-*hexulofuranoside* 2,3-*sulphate* (9) (0·06 g, 0·2%), m.p. 107—111°, *m/e* (a, b, and c as above) 261 b (10), 217 c (32), 181 b (9), 171 a (20), 151 (12), 144 a (56), 105 (70), 91 a (100), 79 (85), 71 (63), 67 (45), 53 a (27), and 49 a (29) [Found: *m/e* 260·9396 ($C_6H_7Cl_2O_5S$) and 216·9586. Calc. for $C_6H_8Cl_3O_2$: 216·9590].

Component (*A*), found in the later fractions (0·46 g, 2%), m.p. 146—148°, $[\alpha]_D$ +67° (*c* 0·4), was identical (^1H n.m.r. and mass spectra) with that obtained from the lower temperature reaction.

Reaction of 1′,2,3,3′,4,4′,6-*Hepta*-O-*acetylsucrose* (6) *with Mesyl Chloride*–NN-*Dimethylformamide*.—The hepta-acetate [11] (0·25 g) was dissolved *NN*-dimethylformamide (2·5 ml) and the stirred solution was heated to 65° (bath temp.). Mesyl chloride (0·45 g) was added dropwise to the solution, which was then maintained at 65° for 15 h and then concentrated to dryness. The residue was chromatographed on silica gel with ethyl acetate–light petroleum (1 : 1) as eluant to give the 6′-*chloro-hepta-acetate* (4) (0·16 g, 74%), m.p. 116—117° (ethyl acetate–light petroleum), $[\alpha]_D$ +56·3 (*c* 0·4), identical with the product already obtained.

We thank the International Sugar Research Foundation for financial support and the Physico-Chemical Measurements Unit (Harwell) for spectroscopic measurements.

[3/410 *Received*, 22*nd February*, 1973]