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Halogenation reactions of derivatives of D-glucose and sucrose*†

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ABSTRACT

Treatment of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**1**) with triphenylphosphine–carbon tetrachloride–pyridine (reagent *A*) gave methyl 4,6-*O*-benzylidene-2-chloro-2-deoxy-α-D-mannopyranoside (**2**). When reagent *A* was used in excess, a further elimination reaction occurred to give methyl 4,6-*O*-benzylidene-2-chloro- (**6**, 60%) and -3-chloro-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**7**, 16%). Treatment of **1** with triphenylphosphine–carbon tetrabromide–pyridine (reagent *B*) caused little or no elimination, and 47% of methyl 4,6-*O*-benzylidene-2-bromo-2-deoxy-α-D-mannopyranoside (**14**) was obtained. On treatment with reagent *A*, methyl α-D-glucopyranoside (**16**) gave exclusively methyl 2,4,6-trichloro-2,3,4,6-tetradeoxy-α-D-*erythro*-hex-2-enopyranoside (**17**), and methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**19**) gave methyl 4,6-*O*-benzylidene-3-chloro-3-deoxy-β-D-allopyranoside (**20**, 70%). However, with reagent *B*, **19** gave methyl 4,6-*O*-benzylidene-3-bromo-3-deoxy-β-D-glucopyranoside (**23**, 66%), probably by way of double inversion of configuration at C-3. Likewise, with reagent *A*, methyl β-D-glucopyranoside (**25**) gave methyl 2,4,6-trichloro- (**26**) and 3,4,6-trichloro-2,3,4,6-tetradeoxy-β-D-*threo*-hex-2-enopyranoside (**27**), and 4,6-*O*-isopropylidenesucrose (**28**) gave mainly 3-chloro-3-deoxy-4,6-*O*-isopropylidene-α-D-allopyranosyl 1,4,6-trichloro-1,4,6-trideoxy-β-D-*lyxo*-hexulofuranoside (**29**) together with 3-chloro-3-deoxy-4,6-*O*-isopropylidene-α-D-allopyranosyl 1,4,6-trichloro-1,4,6-trideoxy-β-D-fructofuranoside (**30**). The assignment of structure to **29** is tentative.

INTRODUCTION

The potential importance of deoxylhalogeno sugars as intermediates in the synthesis of deoxy, azidodeoxy, aminodeoxy, and thio derivatives has been recognised[2]. Enhancement of the sweetness of sucrose, coupled with the inhibition of the action of invertase, has stimulated interest in the halogenation of sugars[3]. The combinations triphenylphosphine–carbon tetrachloride–pyridine (reagent *A*) and triphenylphosphine–carbon tetrabromide–pyridine (reagent *B*) have been used[4] to replace selectively the primary hydroxyl groups in sugars by halogen. We now report the application of these reagents to some derivatives of D-glucose and sucrose.

* Dedicated to Professor Leslie Hough in the year of his 65th birthday.
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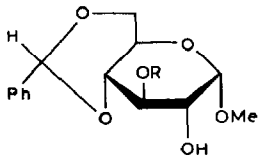
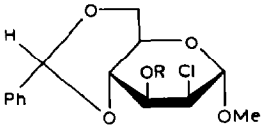
RESULTS AND DISCUSSION

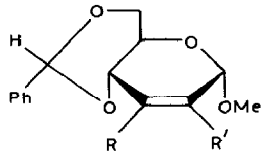
Reaction of methyl 4,6-*O*-benzylidene-*α*-D-glucopyranoside (**1**) with reagent *A* (see Experimental) for 3.5 h at 80° gave, after chromatography, 39% of the 2-chloro-*manno* derivative **2**. Alternatively, treatment of methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (**3**) with reagent *A* gave 88% of the 2-chloro derivative **4**, the ^{1}H-n.m.r. data ($J_{1,2}$ 1.25, $J_{2,3}$ 3.75, $J_{3,4} = J_{4,5} = 10.00$ Hz) of which were in agreement with the *α*-D-*manno* structure and $^4C_1$ conformation. Zemplén debenzoylation of **4** afforded **2**. The resonance (61.5 p.p.m.) of C-2 of **2** was shifted markedly upfield (8.5 p.p.m.) relative to that of C-2 for **1**, confirming that the chlorine substituent was located at C-2. Conventional acetylation of **2** gave the known[5] 3-acetate **5**.



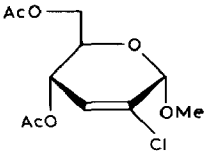
1 R = H
3 R = Bz



2 R = H
4 R = Bz
5 R = Ac



6 R = H, R′ = Cl
7 R = Cl, R′ = H



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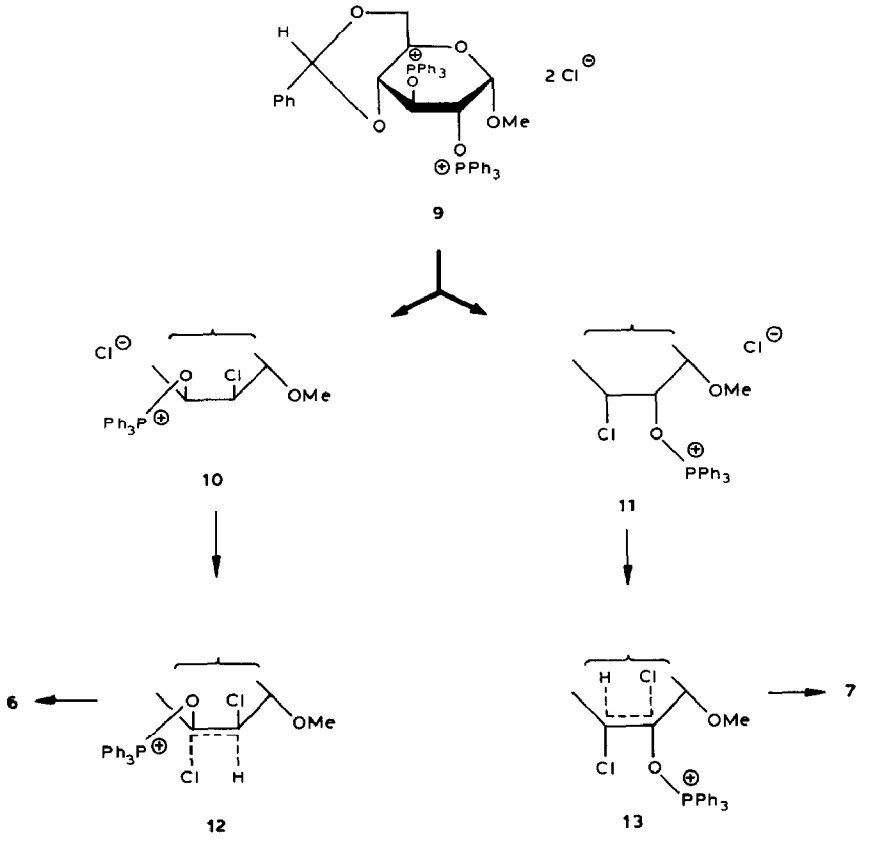
Treatment of **1** with an excess of reagent *A* for 2 h at 50° gave, after chromatography, the 2-chloro-2-ene **6** (60%) and the 3-chloro-2-ene **7** (16%). In the ^{1}H-n.m.r. spectrum of **6**, the signal for H-1 was a singlet (δ 4.78) and that of H-3 was at low field (δ 6.20, $J_{3,4}$ 1.4, $J_{1,3}$ 0.5 Hz). The $J_{3,4}$ value of 1.46 Hz for **6** suggested H-4 to be *quasi*-axial. The resonances (127.6 and 129.2 p.p.m., respectively) of C-2,3 supported the presence of the double bond in **6**. Treatment of **6** with methanolic hydrogen chloride and then with acetic anhydride and pyridine gave **8**, the ^{1}H-n.m.r. spectrum of which contained signals at δ 5.93 (d, $J_{3,4}$ 2.0 Hz, H-3), 4.85 (s, H-1), and 5.37 (d, $J_{4,5}$ 8.8, $J_{1,4}$ 0.5 Hz, H-4) consistent with the $^OH_5$ conformation. Ferrier and his co-workers[6] have determined the conformation of several 2,3-dehydro-3-deoxyaldoses on the basis of ^{1}H-n.m.r. data. Thus, the $J_{3,4}$ (2.0 Hz) and $J_{4,5}$ (8.8 Hz) values were argued to indicate that the conformation of 1,2,4,6-tetra-*O*-acetyl-3-deoxy-*α*-D-*erythro*-hex-2-enopyranose must be close to $^OH_5$. The corresponding *β* anomer ($J_{3,4}$ 5.5, $J_{4,5}$ 1.5 Hz) has been suggested to adopt the ^5H_O conformation.

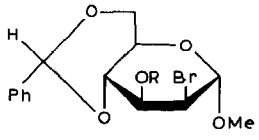
The structure of the 3-chloro-2-ene **7** was elucidated by ^{1}H-n.m.r. spectroscopy. A low-field signal at δ 5.87 (d, $J_{1,3}$ 3.0, $J_{2,4}$ 2.0 Hz) was attributed to H-2 and the resonance due to H-1 appeared at δ 4.90 ($J_{1,2}$ 3.0, $J_{1,4}$ 1.2, $J_{1,5}$ 0.4 Hz). The H-4 signal was identified at δ 4.15 (dd, $J_{4,5}$ 8.8, $J_{2,4}$ 2.0, $J_{1,4}$ 1.2 Hz). The absence of an H-3 resonance, coupled with the mass-spectral data, confirmed the proposed structure for **7**.

Presumably, compounds **6** and **7** were formed from the triphenylphosphonium oxide intermediate **9**, which then underwent an S_N2 reaction by chloride ion at C-2 or C-3, leading to the intermediates **10** or **11**. Further nucleophilic displacement was prevented by the elimination reaction, probably due to polar and steric reasons, which yielded **6** and **7** by way of intermediates **12** and **13**, respectively. The preponderence of **6** over **7** probably reflects the ease of formation of the transition state at C-2, a prerequisite for an S_N2 reaction.

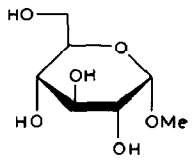


Reaction of **1** with an excess of reagent *B* for 2 h at 85° gave the 2-bromo-*manno* derivative **14** (47%). The resonance of C-2 in **14** was shifted markedly upfield (18 p.p.m.) relative to that of C-2 in **1**. Acetylation of **14** gave **15**, for which the ^{1}H-n.m.r. data ($J_{1,2}$ 1.3, $J_{2,3}$ 4.0, $J_{3,4} = J_{4,5}$ = 9.0, $J_{5,6}$ 8.0 Hz) confirmed the α-D-*manno* structure and the $^4C_1$ conformation.

Treatment of **16** with reagent *A* for 3 h at 90° gave the 2,4,6-trichloro-2-ene **17** (47%), for which the ^{1}H-n.m.r. data ($J_{3,4}$ 5.9, $J_{1,3}$ 0.71, $J_{3,5}$ 2.3, $J_{4,5}$ 2.2, $J_{1,4}$ 0.8 Hz) suggested a conformation close to $^{\circ}H_5$. The low-field resonances at 133.7 and 123.3 p.p.m. were assigned to C-2,3. The resonance for C-6 in **17** was shifted upfield (17 p.p.m.) on chlorination. The upfield shift of 17 p.p.m. for the C-4 resonance was considerably larger than that (5 p.p.m.) of C-4 in the 4,6-dichloride[7] **18**, indicating a β-effect due to the C-2,3 π-bond. Treatment of **18** with reagent *A* gave 61% of **17**, which suggested involvement of the sequence: chlorination at C-6 and then at C-4 and C-2 with inversion of configuration, followed by an E_2C reaction. The lack of chlorination at C-3 is probably due to the 1,3-diaxial interaction and the unfavourable dipole moment associated with the axial Cl-4.



14 R = H
15 R = Ac



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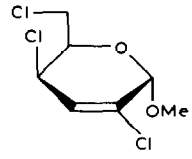

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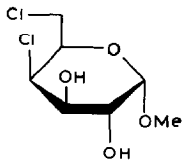

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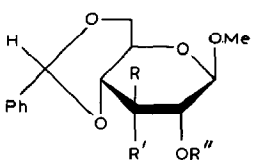
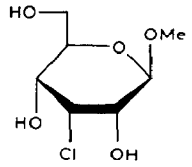


19 R = OH, R′ = R″ = H
20 R = R″ = H, R′ = Cl
23 R = Br, R′ = R″ = H
24 R = Br, R′ = H, R″ = Ac



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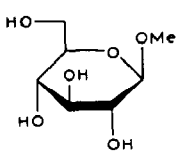
Reaction of **19** with reagent *A* for 3.5 h at 80° gave, after chromatography, the 3-chloro-*allo* compound **20** (71%), the structure of which was supported by the ^{1}H- and ^{13}C-n.m.r. spectra. The resonance of HO-2 appeared at δ 2.88(d), which, on the addition of trichloroacetyl isocyanate to a solution of **20** in deuteriochloroform, was replaced by a signal at δ 8.67(s). ^{1}H-N.m.r. data ($J_{1,2}$ 7.5, $J_{2,3} = J_{3,4}$ = 3.0, $J_{4,5}$ 9.0, $J_{5,6}$ 9.5 Hz) accorded with the β-D-*allo* configuration and $^4C_1$ conformation for **20**. The resonance of C-3 in **20** was shifted upfield (9.6 p.p.m.) compared to that of C-4 in **19**, indicating that the chlorine substituent was located at C-3. Acetylation of **20** afforded **21**, the structure of which was supported by its ^{1}H-n.m.r. spectrum. Treatment of **20** with methanolic hydrogen chloride gave 95% of the glycoside **22** (95%).

Treatment of **19** with reagent *B* gave the 3-bromo-*gluco* derivative **23** (66%), presumably due to double inversion of configuration at C-3 because bromine is a better leaving group than chlorine. The ^{13}C-n.m.r. spectrum of **23** was consistent with the location of the bromine substituent at C-3. Acetylation of **23** afforded the 2-acetate **24**,

for which the ^{1}H-n.m.r. data ($J_{1,2}$ 7.0, $J_{2,3} = J_{3,4} = J_{4,5}$ = 10.0 Hz) confirmed the β-D-*gluco* structure and the $^4C_1$ conformation.

Treatment of **25** with reagent *A* gave, after chromatography, the 2,4,6-trichloro-2-ene **26** (13%) and the 3,4,6-trichloro-2-ene **27** (30%). In the ^{1}H-n.m.r. spectrum of **26**, the signal of H-1 was identified at δ 4.90 ($J_{1,3}$ 2.8, $J_{1,4}$ 0.8 Hz) and that of H-3 at δ 6.20 ($J_{3,4}$ 2.7 Hz). The resonances of C-2,3 in **26** appeared markedly downfield at 128.7 and 126.7 p.p.m., due to charge polarisation of the C-2–C-3 bond. The C-4,6 resonances were shifted upfield (16 and 10 p.p.m., respectively) relative to the corresponding resonances in **25**, which suggested that the chlorine substituents were present at these positions. The ^{1}H-n.m.r. spectrum of **27** contained signals at δ 5.09 (d $J_{1,2}$ 2.4, $J_{1,4}$ 0.92 Hz, H-1) and 6.03 (d, $J_{2,4}$ 2.5 Hz, H-2). The resonances of C-2,3 were identified at 128.7 and 127.8 p.p.m., respectively, which confirmed the presence of the double bond. The signals due to C-4,6 (16 and 19 p.p.m., respectively) were shifted upfield relative to the corresponding signals for **25**.



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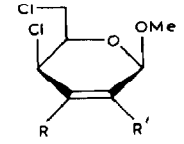
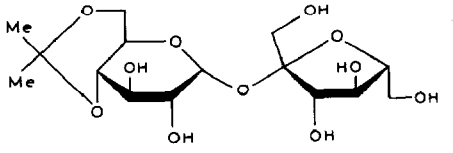
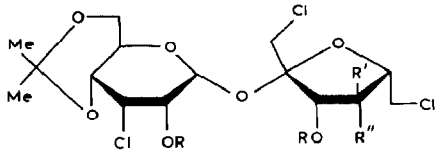


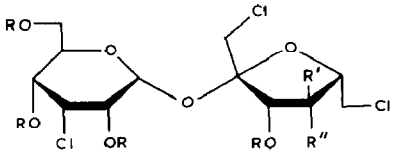
26 R = H, R′ = Cl
27 R = Cl, R′ = H



28



29 R = Ac, R′ = H, R″ = Cl
30 R = Ac, R′ = Cl, R″ = H

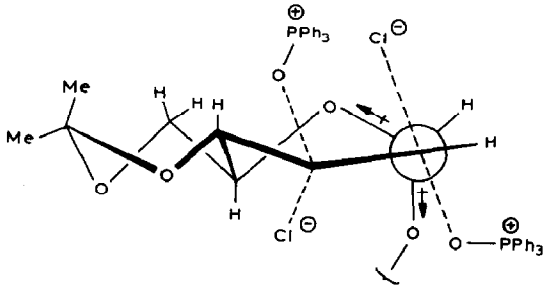


31 R = Ac, R′ = H, R″ = Cl
32 R = R′ = H, R″ = Cl
33 R = Ac, R′ = Cl, R″ = H
34 R = R″ = H, R′ = Cl

Treatment of **28** with reagent *A* for 3 h at 80° gave, after acetylation and chromatography, **29** (43%) and 42% of an inseparable mixture of **29** (major component) and **30**. The ^{1}H-n.m.r. spectrum of **29** contained low-field signals δ 5.56 (d) and 4.94 (t) assigned to H-3′ and H-2, respectively, which indicated that the acetate groups were located at C-2,3′. An upfield shift for the H-3 resonance (0.5 p.p.m.) relative to that of H-3 in 4,6-*O*-isopropylidenesucrose hexa-acetate suggested that one of the chlorine substituents in **29** was located at C-3. The ^{1}H-n.m.r. data ($J_{1,2}$ 4.0, $J_{2,3}$ 4.0, $J_{3,4}$ 5.0 Hz) indicated that the hexopyranosyl ring in **29** had the α-D-*allo* structure and the $^4C_1$ conformation. Although the signal for H-4′ in **29** was not allocated, it was shown by spin-decoupling experiments to be in the region δ 4.12–4.60, and the upfield shift of 0.78–1.18 p.p.m. relative to the corresponding resonance for 4,6-*O*-isopropylidene-

sucrose hexa-acetate suggested that one of the chlorine substituents was located at C-4'. On the basis of the $J_{3',4'}$ value (6.0 Hz) alone, it was not possible to assign the configuration at C-3',4' in **29**. However, a comparison of the $J_{3',4'}$ values for **29** (6.0 Hz), 4-chloro-4-deoxy-α-D-galactopyranosyl 1,4,6-trichloro-1,4,6-trideoxy-β-D-fructopyranoside tetra-acetate (8.8 Hz)[1], 4'-chloro-4'-deoxysucrose hepta-acetate[8] (7.0 Hz), and α-D-glucopyranosyl 4-chloro-4-deoxy-β-D-*xylo*-hexulofuranoside hepta-acetate[8] (4.5 Hz) indicated that the hexulofuranoside ring in **29** probably had the β-D-*lyxo* structure. On the basis of the mechanism proposed for the chlorination at C-4' in **28** (see below), **29** was identified tentatively as 2-*O*-acetyl-3-chloro-3-deoxy-4,6-*O*-isopropylidene-α-D-allopyranosyl 3-*O*-acetyl-1,4,6-trichloro-1,4,6-trideoxy-β-D-*lyxo*-hexulofuranoside. Treatment of **29** with boiling aqueous acetic acid followed by acetylation gave **31**, for which the ^{1}H-n.m.r. data $J_{1,2} = J_{2,3} = J_{3,4} = 4.0$, $J_{4,5}$ 10.0 Hz) indicated the hexopyranosyl moiety to have the α-D-*allo* structure and the $^4C_1$ conformation. The mass spectrum of **31** contained intense peaks at *m/z* 257 (27:27:9:1 quartet) and 305 (3:1 doublet) due to ketofuranosyl and hexopyranosyl cations, respectively. Zemplén deacetylation of **31** gave **32**, the resonances of C-3,4',1',6' of which were shifted markedly upfield (10.5, 13.0, 18.4, and 19.5 p.p.m., respectively) relative to the corresponding resonances in sucrose[9] which indicated the chlorine substituents to be at positions 3,4',1',6'.

Deacetalation of the mixture of **29** and **30** (see above), followed by acetylation, gave **31** (77%) and **33** (7.7%). The ^{1}H-n.m.r. spectrum of **33** was consistent with its structure. The $J_{3,4}$ value (9.0 Hz) indicated the hexofuranosyl ring to have the β-D-*fructo* structure. The α-D-*allo* configuration and $^4C_1$ conformation for the hexopyranosyl moiety was supported by the coupling constants ($J_{1,2} = J_{2,3} = 4.0$, $J_{3,4}$ 3.8, $J_{4,5}$ 10.0 Hz). The mass spectrum of **33** contained intense peaks at *m/z* 259 (27:27:9:1 quartet) and 305 (3:1 doublet) due to ketofuranosyl and hexopyranosyl cations, respectively. Zemplén deacetylation of **33** afforded **34**, the ^{13}C-n.m.r. spectrum of which indicated chlorine substituents at positions 3,1',4',6'.



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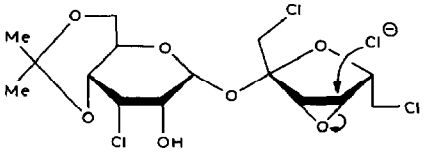
The nucleophilic displacement reaction at positions 1',6',4' in **28** was expected[10], but not the chlorination at C-3. The lack of reactivity at C-2 can be explained on the basis of the unfavourable alignment of dipoles (C-1–O-1 and C-1–O-5) in the transition state **35**. Presumably, chlorination at C-3 in **28** is facilitated by flattening of the

hexopyranosyl ring and reduction of the 1,3-diaxial interactions in the transition state **35**. Chlorination at C-4′ in **28** can be explained by way of the 3′,4′-*lyxo* (**36**) and the 3′,4′-*ribo* (**37**) epoxide intermediates and/or an S_N2 or an S_Ni mechanism. The ring-opening reaction of the epoxides **36** and **37** with chloride ion will lead to the fructofuranoside **34** and the *xylo*-hexulofuranoside **38**, respectively. This mechanism is unlikely because the epoxide intermediates were not detected by t.l.c. Furthermore, in the epoxidation reaction[11], the 3′,4′-*lyxo*-epoxide preponderated over the 3′,4′-*ribo*-epoxide, which, on reaction with chloride ion, would have led to **34** as the major product. However, the *lyxo*-hexulofuranoside **32** was obtained as the major product and the fructofuranoside **34** as the minor product.

Thus, it is concluded that the nucleophilic substitution reaction at position 4′ in **28** either proceeds by an S_N2 process, by way of the intermediate **39**, and/or an S_Ni mechanism (**40** and **41**). The lack of reactivity at C-3′ in **28** probably reflects the effect of the adjacent neopentyl glycosidic carbon[8].



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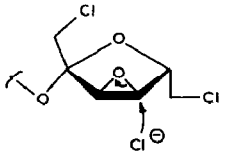

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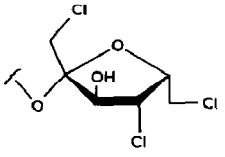

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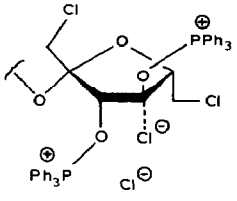

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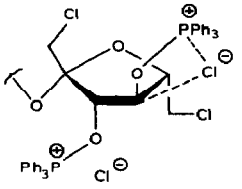

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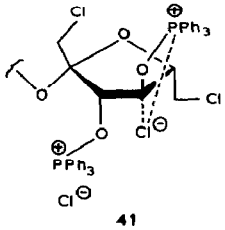

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EXPERIMENTAL

For general experimental details, see ref. 11.

Methyl 4,6-O-benzylidene-2-chloro-2-deoxy-α-D-mannopyranoside (**2**). — A solution of **1** in pyridine (20 mL) was treated with triphenylphosphine (1.8 g, 2 mol. equiv.) and carbon tetrachloride (0.35 mL, 1 mol. equiv.) for 0.5 h at 0°. The mixture was allowed to warm to room temperature and then heated for 3.5 h at 80°. T.l.c. (ethyl acetate–light petroleum, 3:2) showed a fast-moving product. The mixture was diluted with methanol (30 mL) and concentrated to dryness, and the residue was partitioned between water (100 mL) and ether (200 mL). The aqueous layer was further extracted with ether (2 × 50 mL) and the combined ether extracts were dried (Na_2SO_4). Most of

the triphenylphosphine oxide was removed by crystallisation and the mother liquor was concentrated to a syrup which, on column chromatography (silica gel, ether–light petroleum, 1:3), gave **2** (0.4 g, 38.8%), m.p. 89° (from ether–light petroleum), $[\alpha]_D$ +39° (*c* 1, dichloromethane). ^{13}C-N.m.r. data (60 MHz, $CDCl_3$): 102.2 (Ph*C*H), 101.9 (C-1), 78.7 (C-4), 68.6 (C-6), 67.2 (C-3), 64.0 (C-5), 61.5 (C-2), 55.3 (OCH_3). Mass spectrum [(a) 3:1 doublet due to hexopyranosyl cation]: *m/z* 299 (a), 301 (a), 265 (a), 233 (a), 151, 179, 149.

Anal. Calc. for $C_{14}H_{17}ClO_5$: C, 59.9; H, 5.6; Cl, 11.9. Found: C, 60.0; H, 5.7; Cl, 11.5.

*Methyl 3-O-benzoyl-4,6-O-benzylidene-2-chloro-2-deoxy-α-*D*-mannopyranoside* (**4**). — Treatment of **3** (3.25 g) with triphenylphosphine (6.55 g, 2 mol. equiv.) and carbon tetrachloride (1.2 mL, 1 mol. equiv.) in pyridine (30 mL) for 2.5 h at 80°, as described for **2**, gave, after column chromatography (ether–light petroleum, 1:4), **4** (3.0 g, 87.8%), $[\alpha]_D$ +99.5° (*c* 1, chloroform). ^{1}H-N.m.r. data (360 MHz, $CDCl_3$): δ 4.93 (d, 1 H, $J_{1,2}$ 1.25 Hz, H-1), 4.67 (dd, 1 H, $J_{4,5}$ 10.0 Hz, H-2), 5.72 (dd, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 4.37 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.08 (sextet, 1 H, $J_{5,6a}$ 5.0 Hz, H-5), 3.95, 4.28 (dd, 2 H, $J_{6a,6b}$ 10.0 Hz, H-6a,6b), 5.65 (s, 1 H, PhC*H*), 3.48 (s, 3 H, OMe), 7.25–8.20 (aromatic). Mass spectrum [ions (a) correspond to 3:1 doublet due to one chlorine atom]: m/z 403 (a), 373 (a), 255 (a), 133 (a), 149.

Anal. Calc. for $C_{21}H_{21}ClO_6$: C, 62.3; H, 5.2; Cl, 8.8. Found: C, 61.9; H, 5.3; Cl, 8.5.

Conventional debenzoylation of **4** with methanolic sodium methoxide gave **2**, whose physical constants and ^{13}C-n.m.r. and mass spectra were identical to those of the product described above.

Conventional treatment of **2** with acetic anhydride and pyridine gave the known[5] methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-chloro-2-deoxy-α-D-mannopyranoside (**5**).

*Methyl 4,6-O-benzylidene-2-chloro-2,3-dideoxy-α-*D*-*erythro*-hex-2-enopyranoside* (**6**) and *methyl 4,6-O-benzylidene-3-chloro-2,3-dideoxy-α-*D*-*erythro*-hex-2-enopyranoside* (**7**). — A solution of **1** (3 g) in pyridine (30 mL) was treated with triphenylphosphine (16.7 g, 6 mol. equiv.) and carbon tetrachloride (3 mL, 3 mol. equiv.), as described for **2**, to give, after chromatography (silica gel; ethyl acetate–light petroleum, 1:8), **6** (1.8 g, 60%), m.p. 173° (from ethyl acetate–light petroleum), $[\alpha]_D$ +98° (*c* 1, chloroform). ^{1}H-N.m.r. data (200 MHz, $CDCl_3$): δ 4.78 (dd, 1 H, $J_{1,3} = J_{1,4}$ = 0.6 Hz, H-1), 6.20 (dd, 1 H, $J_{3,4}$ 1.4 Hz, H-3), 4.23 (td, 1 H, $J_{4,5}$ 8.8 Hz, H-4), 3.98 (sextet, 1 H, $J_{5,6a}$ 4.0 $J_{5,6b}$ 10.0 Hz, H-5), 3.81, 4.31 (dd, 2 H, $J_{6a,6b}$ 10.0 Hz, H-6a,6b), 5.55 (s, 1 H, PhC*H*), 7.34–7.50 (aromatic). Mass spectrum [ions (a) correspond to 3:1 doublet due to one chlorine atom]: *m/z* 282 (a), 281 (a), 251 (a), 133 (a), 149. ^{13}C-N.m.r. data (60 MHz, $CDCl_3$): δ 129.2, 127.6, (C-2,3), 102.2 (Ph*C*H), 98.2 (C-1), 76.0 (C-4), 69.0 (C-5), 63.9 (C-6), 56.5 (OCH_3).

Anal. Calc. for $C_{14}H_{15}ClO_4$: C, 59.4; H, 5.3; Cl, 12.5. Found: C, 59.4; H, 5.4; Cl, 12.5

Further elution afforded **7** (0.05 g, 16%), m.p. 157° (from ethyl acetate–light petroleum), $[\alpha]_D$ +20° (*c* 1, chloroform). ^{1}H-N.m.r. data (200 MHz, $CDCl_3$): δ 4.95 (dd, 1 H, $J_{1,2}$ 3.0, $J_{1,4}$ 1.2, $J_{1,5}$ 0.4 Hz, H-1), 5.89 (dd, 1 H, $J_{2,4}$ 2.0 Hz, H-2), 4.15 (ddd, 1 H, $J_{4,5}$ 8.7

Hz, H-4), 4.04 (sextet 1 H, $J_{5,6a}$ 4.4, $J_{5,6b}$ 9.8 Hz, H-6a,6b), 5.59 (s, 1 H, PhC*H*), 7.38–7.54 (aromatic), 3.73 (s, 3 H, OMe). Mass spectrum [ions (a) correspond to 3:1 doublet due to one chlorine atom]: *m/z* 282 (a), 281 (a), 251 (a), 133 (a), 149.

Anal. Calc. for $C_{14}H_{15}ClO_4$: C, 59.4; H, 5.3; Cl, 12.5. Found: C, 59.4; H, 5.4; Cl, 12.6.

*Methyl 4,6-di-*O*-acetyl-2-chloro-2,3-dideoxy-*α*-*D*-erythro-hex-2-enopyranoside* (**8**). — A solution of **6** (1 g) in methanol was treated with methanolic 10% hydrogen chloride for 2 h at room temperature. The solution was neutralised with Amberlite IR-45 (HO^-) resin and concentrated, and the resulting syrup was treated with acetic anhydride (3 mL) and pyridine (10 mL) for 3 h at room temperature. Concentration of the solution gave **8** (0.8 g, 82%), $[\alpha]_D$ +87° (*c* 1, chloroform). ^{1}H-N.m.r. data (100 MHz, $CDCl_3$): δ 4.78 (s, 1 H, H-1), 5.98 (d, 1 H, $J_{3,4}$ 2.2 Hz, H-3), 5.34 (dd, 1 H, $J_{4,5}$ 8.0 Hz, H-4), 4.08 (d, 1 H, $J_{5,6a} = J_{5,6b}$ 0.0 Hz, H-5), 4.20 (s, 2 H, $J_{6a,6b}$ 0.0 Hz, H-6a,6b), 3.48 (s, 3 H, Me), 2.08, 2.10 (2 s, 6 H, 2 Ac). Mass spectrum [ions (a) correspond to 3:1 doublet due to the chlorine]: m/z 247 (a), 219 (a), 187 (a), 145 (a), 109.

Anal. Calc. for $C_{11}H_{15}ClO_6$: C, 47.4; H, 5.4; Cl, 12.7. Found: C, 47.6; H, 5.1; Cl, 12.5.

*Methyl 4,6-*O*-benzylidene-2-bromo-2-deoxy-*α*-*D*-mannopyranoside* (**14**). — Compound **1** (6 g) was treated with triphenylphosphine (33.4 g), carbon tetrabromide (21.2 g), and pyridine (120 mL), as described for **2**, to give **14** (3.4 g, 46.5%), m.p. 77–78° (from ether–light petroleum), $[\alpha]_D$ +18° (*c* 1, chloroform). ^{13}C-N.m.r. data (60 MHz, $CDCl_3$): δ 102.2 (C-1, PhCH), 79.5 (C-4), 68.6 (C-6), 66.6 (C-3), 64.5 (C-5), 55.3 (OCH_3), 54.8 (C-2). Mass spectrum [ions (a) correspond to 1:1 doublet due to the bromine]: *m/z* 345 (a), 195 (a), 179 (a), 136 (a), 149.

Anal. Calc. for $C_{14}H_{17}BrO_5$: C, 48.7; H, 4.9; Br, 23.2. Found: C, 48.5; H, 5.2; Br, 22.7.

Conventional acetylation of **14** gave **15**, $[\alpha]_D$ +7.4° (*c* 1, dichloromethane). ^{1}H-N.m.r. data (100 MHz, $CDCl_3$): δ 4.90 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1), 4.56 (dd, 1 H, $J_{3,4}$ 4.0 Hz, H-2), 5.18 (dd, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 4.06 (t, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 6.2 (sextet, 1 H, $J_{5,6a}$ 4.0, $J_{5,6b}$ 5.5 Hz, H-5), 4.2, 3.9 (2 dd, 2 H, $J_{6a,6b}$ 10.0 Hz, H-6a,6b), 5.52 (s, 1 H, PhC*H*), 3.37 (s, 3 H, OMe), 7.1–7.6 (aromatic), 2.08 (s, 3 H, Ac). Mass spectrum [ions (a) correspond to 1:1 doublet due to the bromine]: *m/z* 385 (a), 307 (a), 237 (a), 177 (a), 149.

Anal. Calc. for $C_{16}H_{19}BrO_6$; C, 49.6; H, 4.9; Br, 20.7. Found: C, 49.5; H, 5.2; Br, 20.2.

*Methyl 2,4,6-trichloro-2,3,4,6-tetradeoxy-*α*-*D*-erythro-hex-2-enopyranoside* (**17**). — A solution of methyl α-D-glucopyranoside (**16**, 5 g) in pyridine was treated with triphenylphosphine (40.5 g, 6 mol. equiv.) and carbon tetrachloride (7.5 mL, 3 mol. equiv.), as described for **2**, to give, after chromatography (silica gel, light petroleum), **17** (2.8 g, 47.4%), $[\alpha]_D$ +36° (*c* 1.1, chloroform). N.m.r. data ($CDCl_3$): ^{1}H (200 MHz), δ 4.99 (s, 1 H, $J_{1,2}$ 0.7, $J_{1,4}$ 0.8, $J_{1,5}$ 0.51 Hz, H-1), 6.14 (qdd, 1 H, $J_{3,4}$ 5.9, $J_{3,5}$ 2.3 Hz, H-3), 4.31 (dd, 1 H, $J_{4,5}$ 2.2 Hz, H-4), 4.48 (m, 1 H, H-5), 3.90, 3.92 (sd, 2 H, H-6a,6b), 3.20 (s, 3 H, OMe); ^{13}C (60 MHz), δ 133.7, 123.3 (C-2,3), 100.2 (C-1), 70.7 (C-5), 56.3 (OCH_3), 51.8 (C-4), 44.1 (C-6). Mass spectrum: *m/z* 199 (27:27:9:1, quartet).

Anal. Calc. for $C_7H_9Cl_3O_2$: C, 36.3; H, 3.9; Cl, 46.0. Found: C, 36.5; H, 3.7; Cl, 46.6.

A solution of methyl 4,6-dichloro-4,6-dideoxy-α-D-galactopyranoside[7] (**18**, 4.5 g) was treated with triphenylphosphine (31.4 g), carbon tetrachloride (5.2 g), and pyridine (100 mL), as described for **2**, to give **17** (2.8 g, 61%). The physical constants and the ^{13}C-n.m.r. and mass spectra were identical to those of the compound described above.

Methyl 4,6-O-benzylidene-3-chloro-3-deoxy-β-D-allopyranoside (**20**). — A solution of **19** (6 g) in pyridine (60 mL) was treated with triphenylphosphine (33.4 g) and carbon tetrachloride (6 mL), as described for **2**, to give, after chromatography (silica gel; ether–light petroleum, 1:1), **20** (4.5 g, 70.5%), m.p. 132–133° (from ether), $[\alpha]_D$ +50.5° (*c* 1, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 4.65 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.74 (s, 1 H, H-2), 4.72 (t, 1 H, $J_{2,3} = J_{3,4}$ = 3.0 Hz, H-3), 3.77 (dd, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 4.05 (sextet, 1 H, $J_{5,6a}$ 5.0, $J_{5,6b}$ 10.0 Hz, H-5), 3.74, 4.35 (dd, 2 H, $J_{6a,6b}$ 10.0 Hz, H-6a,6b), 5.55 (s, 1 H, PhC*H*), 7.33–7.56 (aromatic), 4.45 (s, 3 H, OMe), 7.12 (HO-1); after addition of trichloroactyl isocyanate, δ 4.78 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.94 (dd, 1 H, $J_{2,3}$ 3.3 Hz, H-2), 4.76 (t, 1 H, $J_{3,4}$ 3.3 Hz, H-3), 3.87 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.1 (sextet, 1 H, $J_{5,6a}$ 5.0, $J_{5,6b}$ 10.0 Hz, H-6a,6b), 5.64 (s, 1 H, PhC*H*), 7.33–7.56 (aromatic), 3.57 (s, 3 H, OMe), 8.67 (s, 1 H, imino H). Mass spectrum [ions (a) correspond to 3:1 doublet due to the chlorine]: *m/z* 299 (a), 151 (a), 149. ^{13}C-N.m.r. data (60 MHz, $CDCl_3$: δ 101.8 (C-1), 77.2 (C-4), 70.3 (C-6), 68.8 (C-2), 63.8 (C-5), 61.9 (C-3), 57.4 (OCH_3).

Anal. Calc. for $C_{14}H_{17}ClO_5$: C, 59.0; H, 5.6; Cl, 11.9. Found: C, 59.1; H, 5.5; Cl, 10.5.

Conventional acetylation of **20** afforded **21** (97%), $[\alpha]_D$ −94° (*c* 1, dichloromethane). ^{1}H-N.m.r. data (360 MHz, $CDCl_3$): δ 4.83–4.87 (m, 3 H, H-1,2,3), 3.88 (sdd, 1 H, $J_{3,4}$ 2.0, $J_{4,5}$ 9.5 Hz, H-4), 4.12 (sextet, 1 H, $J_{5,6a}$ 5.0, $J_{5,6b}$ 10.0 Hz, H-5), 3.80, 4.42 (dd, 2 H, $J_{6a,6b}$ 10.0 Hz, H-6a,6b), 5.58 (s, 1 H, PhC*H*), 7.35–7.55 (aromatic), 3.57 (s, 3 H, OMe), 2.17 (s, 3 H, Ac). Mass spectrum [ions (a) correspond to 3:1 doublet due to the chlorine): *m/z* 341 (a), 193 (a), 149.

Anal. Calc for $C_{16}H_{19}ClO_6$: C, 56.1; H, 5.6; Cl, 10.3. Found: C, 56.8; H, 5.9; Cl, 10.2.

Methyl 3-chloro-3-deoxy-β-D-allopyranoside (**22**). — A solution of **20** (3.5 g) in methanol was treated with methanolic 10% hydrogen chloride for 2 h at room temperature, then neutralised with Amberlite IR-45 (HO^-) resin, and concentrated. The residue was eluted from a column of silica gel, using ethyl acetate, to give **22** (1.8 g, 95.2%), $[\alpha]_D$ +51° (*c* 1, methanol). ^{13}C-N.m.r. data (60 MHz, D_2O): δ 101.6 (C-1), 74.7 (C-2), 70.0 (C-5), 67.8 (C-4), 66.8 (C-3), 61.6 (C-6), 58.0 (OCH_3).

Anal. Calc. for $C_7H_{13}ClO_5$: C, 39.5; H, 6.1; Cl, 16.7: Found: C, 39.1; H, 6.2; Cl, 16.4.

Methyl 4,6-O-benzylidene-3-bromo-3-deoxy-β-D-glucopyranoside (**23**). — Treatment of **19** (0.5 g) with triphenylphosphine (2.78 g), carbon tetrabromide (1.76 g), and pyridine (20 mL) for 1.75 h at 80°, as described for **2**, gave, after silica gel chromatography (ether–light petroleum, 1:1), **23** (0.4 g, 65.5%), $[\alpha]_D$ +95° (*c* 1, dichloromethane). ^{13}C-N.m.r. data (60 MHz, $CDCl_3$): δ 104.7 (PhCH), 101.8 (C-1), 80.7 (C-4), 75.3 (C-2),

69.2 (C-6), 68.4 (C-5), 57.6 (CH_3), 52.9 (C-3). Mass spectrum [ions (a) correspond to 1:1 doublet due to the bromine]: *m/z* 343 (a), 233 (a), 195 (a), 149.

Anal. Calc. for $C_{14}H_{17}BrO_5$: C, 48.7; H, 4.3; Br, 23.2. Found: C, 48.8, H, 4.4, Br, 23.2.

Conventional acetylation of **23** gave **24** (90%), $[\alpha]_D$ −177° (*c* 0.6, dichloromethane). ^{1}H-N.m.r. data (360 MHz, $CDCl_3$): δ 4.43 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 5.20 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 4.05 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 3.82 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 3.48 (sextet, 1 H, $J_{5,6a}$ 6.0, $J_{5,6b}$ 10.0 Hz, H-5), 4.40, 3.75 (dd, t, 2 H, $J_{6a,6b}$ 10.0 Hz, H-6a,6b), 5.60 (s, 1 H, PhC*H*), 7.32–7.55 (aromatic), 3.55 (s, 3 H, OMe), 2.18 (s, 3 H, Ac). Mass spectrum [ions correspond to 1:1 doublet due to the bromine]: *m/z* 385 (a), 305, 237 (a), 149.

Anal. Calc. for $C_{16}H_{19}BrO_6$: C, 49.6; H, 4.9; Br, 20.7. Found: C, 49.3; H, 4.7; Br, 20.2.

*Methyl 2,4,6-trichloro-2,3,4,6-tetradeoxy-β-*D-threo-*hex-2-enopyranoside* (**26**) *and methyl 3,4,6-trichloro-2,3,4,6-tetradeoxy-β-*D-threo-*hex-2-enopyranoside* (**27**). — Compound **25** (5 g) was treated with triphenylphosphine (40.5 g), carbon tetrachloride (7.5 mL), and pyridine (120 mL), as described for **2**, to afford, after silica gel chromatography (light petroleum), **26** (0.8 g, 13%), $[\alpha]_D$ −33° (*c* 1, dichloromethane). N.m.r. data ($CDCl_3$): ^{1}H (200 MHz), δ 4.90 (s, 1 H, $J_{1,3}$ 2.8, $J_{1,4}$ 0.8 Hz, H-1), 6.20 (d, 1 H, $J_{3,4}$ 2.7 Hz, H-3), 4.27 (td, 1 H, $J_{4,5}$ 4.38 Hz, H-4), 3.68 (d, 1 H, $J_{5,6a} = J_{5,6b} = 0.0$ Hz, H-5), 3.77, 3.81 (2 s, 2 H, $J_{6a,6b}$ 0.0 Hz, H-6a,6b), 3.55 (s, 3 H, OMe); ^{13}C (60 MHz), 128.7, 126.7 (C-2,3), 96.4 (C-1), 78.3 (C-5), 55.9 (OCH_3), (C-4), 43.7 (C-6). Mass spectrum: *m/z* 199 (27:27:9:1:, quartet).

Anal. Calc. for $C_7H_9Cl_3O_2$: C, 36.5; H, 3.9; Cl, 46.0. Found: C, 36.1; H, 3.6; Cl, 46.3.

Further elution afforded **27** (1.2 g, 30%), $[\alpha]_D$ −17° (*c* 1.3, dichloromethane). N.m.r. data ($CDCl_3$): ^{1}H (200 MHz), δ 5.09 (dd, 1 H, $J_{1,2}$ 2.4, $J_{1,4}$ 0.9 Hz, H-1), 6.03 (dd, 1 H, $J_{2,4}$ 2.5 Hz, H-2), 4.55 (ddd, 1 H, $J_{4,5}$ 3.8 Hz, H-4), 3.62 (d, 1 H, $J_{5,6a} = J_{5,6b} = 0.0$ Hz, H-5), 3.73, 3.79 (2 s, 2 H, $J_{6a,6b}$ 0.0 Hz, H-6a,6b), 3.56 (s, 3 H, OMe); ^{13}C (60 MHz), 128.7, 127.8 (C-2,3), 98.5 (C-1), 74.4 (C-5), 57.1 (OCH_3), 54.7 (C-4), 42.3 (C-6). Mass spectrum: *m/z* 199 (27:27:9:1, quartet).

Anal. Calc. for $C_7H_9Cl_3O_2$: C, 36.5; H, 3.9; Cl, 46.0. Found: C, 36.3, H, 3.5; Cl, 46.3.

*2-O-Acetyl-3-chloro-3-deoxy-4,6-O-isopropylidene-α-*D-*allopyranosyl 3-O-acetyl-1,4,6-trichloro-1,4,6-trideoxy-β-*D-lyxo-*hexulofuranoside* (**29**). — Treatment of **28** with triphenylphosphine (41.2 g, 6 mol. equiv.), carbon tetrachloride (7.5 mL, 3 mol), and pyridine (20 mL) for 3 h at 80°, as described for **2**, gave a syrup which was then treated with acetic anhydride (30 mL) and pyridine (200 mL) for 18 h at room temperature. The solution was concentrated by co-distillation with toluene to give a syrup which, on elution from a column of silica gel using ethyl acetate–light petroleum (1:1), afforded **29** (6 g, 42.5%), m.p. 105–107° (from ethyl acetate–light petroleum), $[\alpha]_D$ +44° (*c* 1, dichloromethane). ^{1}H-N.m.r. data (100 MHz, $CDCl_3$: δ 5.32 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.94 (t, 1 H, $J_{2,3}$ 4.0 Hz, H-2), 4.79 (dd, 1 H, $J_{3,4}$ 5.0 Hz, H-3), 4.20–4.60 (m, 5 H),

4.44–3.94 (m, 5 H), 5.56 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3'), 2.09, 2.16 (2 s, 6 H, 2 Ac), 1.42, 1.47 (2 s, 6 H, 2 Me). Mass spectrum [ions (a) correspond to 3:1 doublet due to one chlorine atom, and (b) 27:27:9:1 quartet due to three chlorine atoms]: *m/z* 525 (M + 1), 263 (a), 259 (a), 223 (b), 181 (b), 163 (a), 145 (a).

Anal. Calc. for $C_{19}H_{26}Cl_4O_9$: C, 42.4; H, 4.8; Cl, 26.3. Found: C, 40.7; H, 4.9; Cl, 21.7.

Further elution from the column failed to separate the slower moving component **30** from **29**.

*2,4,6-Tri-*O*-acetyl-3-chloro-3-deoxy-*α*-*D*-allopyranosyl 3-*O*-acetyl-1,4,6-trichloro-1,4,6-trideoxy-*β*-*D*-lyxo-hexulofuranoside* (**31**). — The above mixture (6 g) of **29** and **30** was treated with aqueous 60% acetic acid (25 mL) for 10 min at 90°. The mixture was cooled and extracted with dichloromethane, and the organic layer was washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and concentrated. The residue was treated with acetic anhydride (12 mL) and pyridine (60 mL) at room temperature for 18 h. Conventional work-up followed by silica gel chromatography (ether–light petroleum, 1:1) afforded **31** (5 g, 77%), m.p. 110–111°, $[\alpha]_D$ +60° (*c* 0.9, dichloromethane). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 5.43 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.06 (t, 1 H, $J_{2,3}$ 4.0 Hz, H-2), 4.84 (t, 1 H, $J_{3,4}$ 4.0 Hz, H-3), 4.99 (dd, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.67 (sextet, 1 H, $J_{5,6a}$ 4.0, $J_{5,6b}$ 2.0 Hz, H-5), 4.22, 4.35 (2 dd, 2 H, $J_{6a,6b}$ 12.0 Hz, H-6a,6b), 3.62, 3.72 (2 d, 2 H, $J_{1'a,1'b}$ 12.0 Hz, H-1'a,1'b), 5.60 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3'), 4.87 (t, 1 H, $J_{4',5'}$ 6.0 Hz, H-4'), 4.57 (sxt, 1 H, $J_{5',6'a}$ 3.0, $J_{5',6'b}$ 2.0 Hz, H-5'), 3.84, 3.85 (2 d, 2 H, $J_{6'a,6'b}$ 12.0 Hz, H-6'a,6'b), 2.11, 2.13, 2.14, 2.24 (4 s, 12 H, 4 Ac). Mass spectrum [ions (a) correspond to 3:1 doublet due to one chlorine atom, (b) 9:6:1: triplet due to two chlorine atoms, and (c) 27:27:9:1 quartet due to three chlorine atoms]: *m/z* 307 (a), 257 (c), 221 (b).

Anal. Calc. for $C_{20}H_{26}Cl_4O_{11}$: C, 41.1; H, 4.5; Cl, 24.3. Found: C, 41.2; H, 4.5; Cl, 23.8.

Zemplén deacetylation of **31** (2 g) gave, after conventional work-up, **32** (1.3 g, 96%), $[\alpha]_D$ +55° (*c* 1, water). ^{13}C-N.m.r. data (62.8 MHz, D_2O): δ 96.6 (C-2'), 81.4 (C-1), 73.6 (C-5'), 69.8 (C-3'), 68.0 (C-5), 67.9 (C-2), 67.8 (C-4), 67.1 (C-6), 63.1 (C-3), 62.0 (C-4'), 44.9, 43.9 (C-1',6').

Anal. Calc. for $C_{12}H_{18}Cl_4O_7$: C, 34.6; H, 4.3; Cl, 34.1. Found: C, 34.5; H, 4.6; Cl, 34.2.

*2,4,6-Tri-*O*-acetyl-3-chloro-3-deoxy-*α*-*D*-allopyranosyl 3-*O*-acetyl-1,4,6-trichloro-1,4,6-trideoxy-*β*-*D*-fructofuranoside* (**33**). — Further elution from the column in the preceding experiment afforded **33** (0.5 g, 7.7%), m.p. 135–136° (from ether), $[\alpha]_D$ +42° (*c* 1, dichloromethane). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 5.55 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.07 (t, 1 H, $J_{2,3}$ 4.0 Hz, H-2), 4.84 (d, 1 H, $J_{3,4}$ 3.8 Hz, H-3), 4.89 (dd, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.59 (ddd, 1 H, $J_{5,6a}$ 2.0, $J_{5,6b}$ 12.0 Hz, H-5), 4.14, 4.37 (2 dd, 2 H, $J_{6a,6b}$ 12.0 Hz, H 6a,6b), 3.60, 3.82 (2 d, 2 H, $J_{1'a,1'b}$ 12.0 Hz, H 1'a,1'b), 5.60 (d, 1 H, $J_{3',4'}$ 9.0 Hz, H-3'), 4.36 (m, 1 H, $J_{5',6'a}$ 4.0, $J_{5',6'b}$ 6.0 Hz, H-5'), 3.79, 3.87 (2 dd, 2 H, $J_{6'a,6'b}$ 12.0 Hz, H-6'a, 6'b), 2.11, 2.13, 2.14, 2.20 (4 s, 12 H, 4 Ac). Mass spectrum [ions (a) correspond to 3:1 doublet, (b) 9:6:1 triplet, and (c) 27:27:9:1 quartet due to 1, 2, and 3 chlorine atoms]: *m/z* 307 (a), 257 (c), 221 (b).

Anal. Calc. for $C_{20}H_{26}Cl_4O_{11}$: C, 41.1; H, 4.5; Cl, 24.3. Found: C, 41.1; H, 4.5; Cl, 24.0.

Zemplén deacetylation of **33** (0.5 g) gave, after conventional work-up, **34** (0.34 g, 96%), $[\alpha]_D$ +49° (*c* 0.95, water). ^{13}C-N.m.r. data (62.8 MHz, D_2O): δ 108.3 (C-2′), 96.6 (C-1), 87.8 (C-5′), 83.4 (C-3′), 74.3 (C-5), 72.0 (C-2), 71.4 (C-4,6), 66.3 (C-3′), 65.5 (C-4′), 49.2, 49.0 (C-1′,6′).

Anal. Calc. for $C_{12}H_{18}Cl_4O_7$: C, 34.6; H, 4.3; Cl, 34.1. Found: C, 34.9; H, 4.7; Cl, 34.4.

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