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Synthesis and ring-opening reactions of 4-chloro-4-deoxy-α-D-galactopyranosyl 3,4-anhydro-1,6-dichloro-1,6-dideoxy-β-D-*lyxo*-hexulofuranoside*

Riaz Khan, Gita Patel†, and Khizar S. Mufti
Tate & Lyle Research and Technology, Whiteknights, Reading, Berkshire, RG6 2 BX (Great Britain)

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ABSTRACT

Treatment of 4-chloro-4-deoxy-α-D-galactopyranosyl 1,6-dichloro-1,6-dideoxy-β-D-fructofuranoside (**1**) with 2.3 mol. equiv. of diethyl azodicarboxylate (DEAD) and 1.3 mol. equiv. of triphenylphosphine (TPP) in toluene gave a mixture of 3,6-anhydro-4-chloro-4-deoxy-α-D-galactopyranosyl 3,4-anhydro-1,6-dichloro-1,6-dideoxy-β-D-*lyxo*-hexulofuranoside (**2**, 55%) and 4-chloro-4-deoxy-α-D-galactopyranosyl 3,4-anhydro-1,6-dichloro-1,6-dideoxy-β-D-*lyxo*-hexulofuranoside (**3**, 35%). Compound **3** was also synthesised from 6-*O*-*tert*-butyldiphenylsilyl-4-chloro-4-deoxy-α-D-galactopyranosyl 1,6-dichloro-1,6-dideoxy-β-D-fructofuranoside by epoxidation with DEAD–TPP and removal of the silyl ether group with tetrabutylammonium fluoride. The S_N2 reactions of 2,3,6-tri-*O*-acetyl-4-chloro-4-deoxy-α-D-galactopyranosyl 3,4-anhydro-1,6-dichloro-1,6-dideoxy-β-D-*lyxo*-hexulofuranoside (**5**) with fluoride, chloride, bromide, iodide, and azide ions gave the corresponding 4′-derivatives **10**, **12**, **14**, **18**, and **20**, respectively. Reduction of 4-chloro-4-deoxy-α-D-galactopyranosyl 4-bromo-1,6-dichloro-1,4,6-trideoxy-β-D-fructofuranoside (**15**) gave 4-chloro-4-deoxy-α-D-galactopyranosyl 1,6-dichloro-1,4,6-trideoxy-β-D-fructofuranoside (**16**). A similar reduction of 4-chloro-4-deoxy-α-D-galactopyranosyl 4-azido-1,6-dichloro-1,4,6-trideoxy-β-D-fructofuranoside (**21**) gave 4-chloro-4-deoxy-α-D-galactopyranosyl 4-amino-1,6-dichloro-1,4,6-trideoxy-β-D-fructofuranoside (**22**).

INTRODUCTION

In continuation of our studies of sucrose epoxides[2], we now report the synthesis of the 3′,4′-*lyxo*-epoxide **5** from the 4,1′,6′-trichloride **1**, using diethyl azodicarboxylate–triphenylphosphine (DEAD–TPP), and its ring opening reactions with various nucleophiles.

RESULTS AND DISCUSSION

Treatment of the 4,1′,6′-trichloride[3] **1** with DEAD–TPP in toluene for 30 min at reflux gave, after chromatography, the 3,6:3′,4′-dianhydride **2** (55%) and the desired 3′,4′-*lyxo*-epoxide **3** (35%). In the ^{1}H-n.m.r. spectrum of **2**, the resonance at δ 4.42 was

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†Present address: School of Pharmacy, Department of Pharmacognosy, 29–39 Brunswick Square, London WC1N 1AX.

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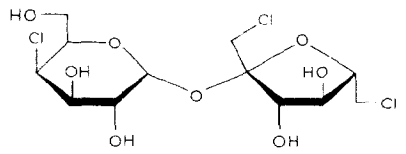
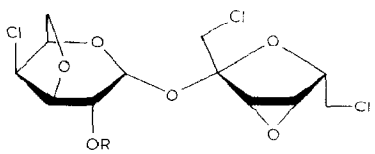
attributed to H-3, indicating that C-3 was involved in the presumed ether linkage. Addition of trichloroacetyl isocyanate to the n.m.r. sample of **2** in $CDCl_3$ generated a singlet at δ 8.55 due to the imino proton and also caused the reappearance of signals for H-2 at δ 5.06, which confirmed that the hydroxyl group in **2** was located at C-2. The rather small coupling constants ($J_{1,2}$ 2.8, $J_{2,3}$ 5.0, $J_{3,4}$ 0.0, and $J_{4,5}$ 1.5 Hz) confirmed the $^1C_4$ conformation for the galactopyranosyl moiety in **2**. Conventional acetylation of **2** afforded the 2-acetate **4**, the structure of which was in accord with its ^{1}H-n.m.r. spectrum. The resonances for H-3′,4′ in **4** were identified at δ 3.86 and 3.94, respectively, as an "AB-like" quartet ($J_{3',4'}$ 2.8 Hz) supporting the presence of 3′,4′-anhydro ring in **4**. The *lyxo* configuration for the 3′,4′-anhydrohexulofuranosyl moiety was based on the fact that the reaction of DEAD–TPP with *trans*-vicinal diols in furanoses and hexulofuranoses leads exclusively to epoxides with the *lyxo* configuration[3,4].

Acetylation of the 3′,4′-*lyxo*-epoxide **3** gave the triacetate **5**, the structure of which was supported by its ^{1}H-n.m.r. spectrum. The coupling constants ($J_{1,2}$ 4.0, $J_{2,3}$ 10.7, $J_{3,4}$ 3.7, and $J_{4,5}$ 1.1 Hz) confirmed the α-D-*galacto* configuration and $^4C_1$ conformation of the hexopyranosyl ring in **5**. The resonances due to H-3′,4′ appeared, as expected[3], as an "AB-like" quartet at δ 3.93 and 3.90, respectively.

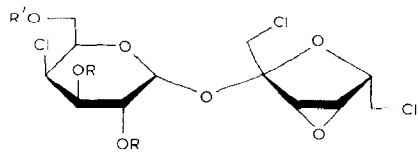
It was necessary to block HO-6 in **1** in order to avoid the formation of **2**. Treatment of **1** with 1.1 mol. equiv. of *tert*-butyldiphenylsilyl chloride in pyridine in the presence of 4-dimethylaminopyridine gave the 6-silyl ether **6** (87%). Conventional acetylation of **6** afforded the tetra-acetate **7**, the structure of which was supported by its ^{1}H-n.m.r. spectrum. Treatment of **6** with DEAD–TPP in toluene for 30 min at room temperature gave, after chromatography, the 3′,4′-*lyxo*-epoxide **8** (88%) which, on acetylation, gave the diacetate **9**. In the ^{1}H-n.m.r. spectrum of **9**, the pattern of the



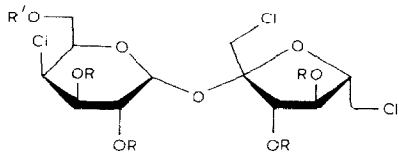
1



2 R = H
4 R = Ac



3 R = R′ = H
5 R = R′ = Ac
8 R = H, R′ = ^{t}BuPh$_2$Si
9 R = Ac, R′ = ^{t}BuPh$_2$Si

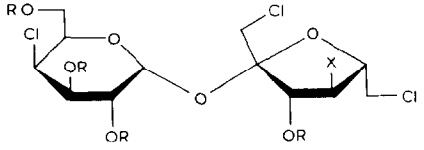


6 R = H, R′ = ^{t}BuPh$_2$Si
7 R = Ac, R′ = ^{t}BuPh$_2$Si

H-3′,4′ resonances and their chemical shifts were typical of protons attached to an epoxide ring fused to a larger ring. Desilylation of **9** with tetrabutylammonium fluoride in tetrahydrofuran followed by acetylation afforded **5**, the ^{1}H-n.m.r. and mass spectra of which were identical with those of a sample prepared previously.

Reaction of **5** with potassium hydrogen fluoride and sodium fluoride in ethylene glycol for 72 h at 90° afforded, after deacetylation and chromatography, the 4′-fluoride **10** (66%), the ^{13}C-n.m.r. spectrum of which contained a resonance for C-4′ (d, $J_{F,4'}$ 185.5 Hz) at 98.9, which was shifted downfield by 24.0 p.p.m., compared to the corresponding signal in sucrose[5]. The signals for C-3′ (δ 77.5, $J_{F,3'}$ 22.0 Hz) and C-5′ (δ 81.7, $J_{F,5'}$ 26.0 Hz) were doublets. The C-2′ resonance (δ 106.8, $J_{F,2'}$ 11.2 Hz) appeared as a small doublet, indicating a long-range interaction. Acetylation of **10** gave the tetra-acetate **11**, the ^{1}H-n.m.r. spectrum of which was complex and could not be analysed fully. The signals at δ 5.76 (dd, $J_{3',4'}$ 5.5, $J_{F,3'}$ 18.0 Hz) and 5.19 (td, $J_{4',5'}$ 5.5, $J_{F,4'}$ 53.0 Hz) were assigned to H-3′ and H-4′, respectively. The complexity of the signal for H-5′ in the region δ 4.35–4.47 suggested the involvement of $J_{F,5'}$ couplings in addition to vicinal proton couplings. The ^{19}F-n.m.r. spectrum of **11** contained, as expected, a double triplet at −38.68 p.p.m. ($J_{F,H-4'}$ 53.0, $J_{F,H-3'} = J_{F,H-5'} = 18.0$ Hz) relative to internal trifluoroacetic anhydride.

Treatment of **5** with lithium chloride in *N*,*N*-dimethylformamide for 4 h at 90° gave, after acetylation and chromatography, 56% of the 4,1′,4′,6′-tetrachloride **12**, for which the ^{1}H-n.m.r. signal (δ 5.65) for H-3′ was 1.72 p.p.m. to lower field than the corresponding proton resonance for **5**, consistent with the presence of an acetyl group at C-3′. The H-4′ resonance, identified by spin-decoupling experiments at δ 4.58, was shifted slightly downfield (0.68 p.p.m.), but, in comparison with the corresponding signal for sucrose octa-acetate[6], it was shifted upfield (0.78 p.p.m.). These results suggested that the chlorine substitution in **12** had occurred at position 4′. Zemplén deacetylation of **12** gave the free 4,1′,4′,6′-tetrachloride **13**, the resonance (59 p.p.m.) of C-4′ of which was shifted markedly upfield (16 p.p.m.) relative to the corresponding



10 R = H, X = F
11 R = Ac, X = F
12 R = Ac, X = Cl
13 R = H, X = Cl
14 R = Ac, X = Br
15 R = H, X = Br
16 R = H, X = H
17 R = Ac, X = H
18 R = Ac, X = I
19 R = H, X = I
20 R = Ac, X = N_3
21 R = H, X = N_3
22 R = H, X = NH_2

signal for the 4,1′,6′-trichloride **1**. These results, coupled with the mass-spectral data for **12**, confirmed the structures of **12** and **13**.

Reaction of the 3′,4′-*lyxo*-epoxide **5** with lithium bromide in *N,N*-dimethylformamide at 80° for 24 h gave, after acetylation and chromatography, the 4′-bromide **14** (70%). Alternatively, **14** was synthesised by the treatment of **5** with hydrobromic acid in glacial acetic acid followed by acetylation. The ^{1}H-n.m.r. spectrum of **14** was consistent with its assumed structure. Zemplén deacetylation of **14** gave the free 4′-bromide **15**, the resonance (52 p.p.m.) of C-4′ of which was shifted upfield significantly (21 p.p.m.) relative to the signal for C-4′ for sucrose[5]. Catalytic hydrogenation of **15** gave the 4′-deoxy derivative **16**, for which the resonance of C-4′ (33.7 p.p.m.) showed a large upfield shift (10.3 p.p.m.) relative to the corresponding signal for sucrose[5]. Conventional acetylation of **16** gave **17**, the ^{1}H-n.m.r. spectrum of which showed the characteristic multiplets at δ 2.05 and 2.61 due to H-4′a and H-4′b. The mass spectrum was consistent with the structure of **17**.

Treatment of **5** with sodium iodide in acetic acid and sodium acetate buffer in acetone at reflux gave, after acetylation and chromatography, the 4′-iodide **18**. The ^{1}H-n.m.r. and mass spectra of **18** were consistent with the proposed structure. The resonance for C-4′ of the deacetylated derivative **19** showed a significant upfield shift (55 p.p.m.) compared to that of C-4′ in sucrose[5].

Reaction of **5** with sodium azide in aqueous ethanol in the presence of ammonium chloride for 72 h at 70° gave, after acetylation, 74% of the 4′-azide **20**. In comparison with that of sucrose octa-acetate[6], the resonance due to H-4 in **20** appeared at comparatively high field (δ 4.2), indicating that the azide group was located at position 4′. The $J_{3',4'}$ value (11.0 Hz) for **20** was significantly larger than that (7.5 Hz) for 4′-azido-4′-deoxysucrose hepta-acetate[3]. Conventional deacetylation of **20** gave the free 4′-azide **21** which, on catalytic hydrogenation, afforded the 4′-amino-4′-deoxy derivative **22**. The resonance for C-4′ of **22** revealed an upfield shift (15.1 p.p.m.) compared to that of C-4′ in sucrose[5].

An interesting correlation between the nature of the 4′-substituent in **1** and the $J_{3',4'}$ value was observed. For example, the $J_{3',4'}$ values for the 4′-fluoride **11**, the chloride **12**, the bromide **14**, the iodide **18**, and the azide **20** were 5.50, 8.82, 9.28, 10.5, and 11.00 Hz, respectively. When these values were plotted against the electronegativities (fluorine, 4.0; chlorine, 3.0; bromine, 2.8; and iodine, 2.0), a straight line was obtained.

EXPERIMENTAL

For general experimental details, see ref. 7.

Reaction of 4′,1′,6′-trichloro-4,1′,6′-trideoxy-galacto-*sucrose* (**1**) *with DEAD and TPP.* — A solution of **1** (10 g) in dry toluene (250 mL) was treated with DEAD (12 mL, 2.3 mol. equiv.) followed by TPP (19 g, 1.3 mol. equiv.) for 2.5 h at reflux. The mixture was diluted with methanol (50 mL) and concentrated to a syrup which was dissolved in ether. Most of the triphenylphosphine oxide was removed by crystallisation. Column chromatography (silica gel; ether–light petroleum, 1:1) of the residual crude material

afforded 3,6-anhydro-4-chloro-4-deoxy-α-D-galactopyranosyl 3,4-anhydro-1,6-dichloro-1,6-dideoxy-β-D-*lyxo*-hexulofuranoside (**2**; 5 g, 55%), m.p. 107–110° (from ether), $[\alpha]_D$ +6.5° (*c* 1, chloroform). ^{1}H-N.m.r. data (100 MHz, $CDCl_3$): δ 5.58 (d, 1 H, $J_{1,2}$ 2.5 Hz, H-1), 4.88 (sd, 1 H, $J_{3,4}$ 0.0, $J_{4,5}$ 1.5 Hz, H-4), 4.30–4.70 (m, 5 H), 3.60–4.1 (m, 6 H), 2.68 (bs 1 H, H-2); after addition of trichloroacetyl isocyanate: δ 5.75 (d, 1 H, $J_{1,2}$ 2.5 Hz, H-1), 5.06 (dd, 1 H, $J_{2,3}$ 5.0 Hz, H-2), (sd, 1 H, $J_{3,4}$ 0.00, $J_{4,5}$ 1.5 Hz, H-4), 4.60–4.80 (m, 3 H), 4.30–4.55 (t, 2 H, H-3′4′), 3.60–4.20 (m, 6 H). Mass spectrum [(a) 3:1 doublet due to hexopyranosyl cation, (b) 9:6:1 triplet due to ketofuranosyl cation]: *m/z* 181 (b), 165 (b), 163 (a).

Anal. Calc. for $C_{12}H_{15}Cl_3O_6$: C, 39.8; H, 4.1; Cl, 29.5. Found: C, 40.2; H, 4.2; Cl, 28.5.

Further elution gave 4-chloro-4-deoxy-α-D-galactopyranosyl 3,4-anhydro-1,6-dichloro-1,6-dideoxy-β-D-*lyxo*-hexulofuranoside (**3**; 3 g, 35%), $[\alpha]_D$ +117.5° (*c* 1, chloroform).

Conventional treatment of **2** (2 g) with acetic anhydride (3 mL) in pyridine (20 mL) gave 2-*O*-acetyl-3,6-anhydro-4-chloro-4-deoxy-α-D-galactopyranosyl 3,4-anhydro-1,6-dichloro-1,6-dideoxy-β-D-*lyxo*-hexulofuranoside (**4**) as a syrup (2 g, 90%), $[\alpha]_D$ +5.5° (*c* 1, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 5.53 (d, 1 H, $J_{1,2}$ 2.75 Hz, H-2), 5.06 (dd, 1 H, $J_{2,3}$ 5.0 Hz, H-2), 4.42 (bd, 1 H, $J_{3,4}$ 0.0 Hz, H-3), 4.63 (sd, 1 H, $J_{4,5}$ 1.5 Hz, H-4), 4.91 (m, 1 H, H-5), 4.12–4.26 (2 bd, 2 H, $J_{6a,6b}$ 12.0 Hz, H-6a,6b), 3.56, 3.68 (2 d, 2 H, $J_{1'a,1'b}$ 10.0 Hz, H-1′a,1′b), 3.86 (d, 1 H, $J_{3',4'}$ 5.5 Hz, H-3′), 3.94 (dd, 1 H, $J_{4',5'}$ 1.0 Hz, H-4′), 4.32 (s, 1 H, H-5′), 3.52, 3.64 (2 d, 2 H, $J_{6'a,6'b}$ 12.0 Hz, H-6′a,6′b), 2.07 (s, 3 H, Ac). Mass spectrum [(a) 3:1 doublet due to hexopyranosyl cation, (b) 9:6:1 triplet due to ketofuranosyl cation]: *m/z* 205 (a), 181 (b), 165 (b), 163 (a).

Anal. Calc. for $C_{14}H_{17}Cl_3O_7$: C, 41.6; H, 4.2; Cl, 26.4. Found: C, 41.2; H, 4.1; Cl, 25.2.

Conventional treatment of **3** (2 g) with acetic anhydride and pyridine gave 2,3,6-tri-*O*-acetyl-4-chloro-4-deoxy-α-D-galactopyranosyl 3,4-anhydro-1,6-dichloro-1,6-dideoxy-β-D-*lyxo*-hexulofuranoside (**5**; 2.1 g, 95%), m.p. 133–134° (from ether–light petroleum), $[\alpha]_D$ +116° (*c* 1, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 5.82 (d, 1 H, $J_{1,2}$ 4.04 Hz, H-1), 5.12 (dd, 1 H, $J_{2,3}$ 10.66 Hz), 5.31 (dd, 1 H, $J_{3,4}$ 3.67 Hz, H-3), 4.60 (dd, 1 H, $J_{4,5}$ 1.09 Hz, H-4), 4.51 (bt, 1 H, $J_{5,6a}$ 6.25, $J_{5,6b}$ 5.51 Hz, H-5), 4.20, 4.29 (2 dd, 2 H, $J_{6a,6b}$ 11.39 Hz, H-6a,6b), 3.51, 3.67 (2 d, 2 H, $J_{1'a,1'b}$ 11.76 Hz, H-1′a,1′b), 3.93 (d, 1 H, $J_{3',4'}$ 2.57 Hz, H-3′), 3.90 (dd, 1 H, $J_{4',5'}$ 0.73 Hz, H-4′), 4.18 (ddd, 1 H, $J_{5',6'a}$ 8.08, $J_{5',6'b}$ 5.51 Hz, H-5′), 3.52, 3.61 (2 dd, 2 H, $J_{6'a,6'b}$ 11.35 Hz, H-6′a,6′b), 2.03, 2.07, 2.13 (s, 9 H, 3 Ac). Mass spectrum [(a) 3:1 doublet due to hexopyranosyl cation, (b) 9:6:1 triplet due to ketofuranosyl cation]: *m/z* 307 (a), 247 (a), 187 (a), 181 (b), 165 (b).

Anal. Calc. for $C_{18}H_{23}Cl_3O_{10}$: C, 42.3; H, 4.5; Cl, 21.1. Found: C, 43.0; H, 4.6; Cl, 20.8.

6-O-tert-Butyldiphenylsilyl-4-chloro-4-deoxy-α-D-galactopyranosyl 1,6-dichloro-1,6-dideoxy-β-D-fructofuranoside (**6**). — A solution of **1** (8 g) in dry pyridine (80 mL) was treated with *tert*-butyldiphenylsilyl chloride (5.6 mL, 1.1 mol) and 4-dimethylaminopyridine (200 mg) at room temperature for 18 h. T.l.c. (ethyl acetate–acetone–water,

10:10:1) then revealed one major product together with **1**. The mixture was poured into ice–water and extracted with ethyl acetate, and the extract was washed successively with M HCl, aq. sodium hydrogen carbonate, and water, dried (Na_2SO_4), and concentrated. Crystallisation of the residue from ethanol gave **6** (10.5 g, 82.6%), m.p. 95–97°, $[\alpha]_D$ +39° (*c* 1, chloroform).

Anal. Calc. for $C_{28}H_{37}Cl_3O_8Si$: C, 52.8; H, 5.8; Cl, 16.8. Found: C, 52.3; H, 5.8; Cl, 16.3.

Conventional treatment of **6** (1 g) with acetic anhydride and pyridine gave 2,3-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-4-chloro-4-deoxy-α-D-galactopyranosyl 3,4-di-*O*-acetyl-1,6-dichloro-1,6-dideoxy-β-D-fructofuranoside (**7**; 1.3 g, 96%), $[\alpha]_D$ +43° (*c* 1, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 4.32 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.29 (dd, 1 H, $J_{2,3}$ 11.0 Hz, H-2), 5.40 (dd, 1 H, $J_{3,4}$ 3.0 Hz, H-3), 4.75 (dd, 1 H, $J_{4,5}$ 1.5 Hz, H-4), 4.47 (t, 1 H, $J_{5,6a} = J_{5,6b} = 6.0$ Hz, H-5), 4.21 (dd, 1 H, $J_{6a,6b}$ 12.0 Hz, H-6a), 3.74–3.85 (m, 2 H, H-5′,6b), 3.59, 3.73 (2 d, 2 H, $J_{1'a,1'b}$ 12.0 Hz, H-1′a,1′b), 5.70 (d, 1 H, $J_{3',4'}$ 6.5 Hz, H-3′), 5.39 (t, 1 H, $J_{4',5'}$ 6.5 Hz, H-4′), 3.66 (d, 2 H, $J_{6'a,6'b}$ 0.0 Hz, H-6′a,6′b), 2.10, 2.13, 2.16 (3 s, 12 H, 4 Ac), 7.30–7.80 (m, aromatic). Mass spectrum [(a) 3:1 doublet due to hexopyranosyl cation, (b) 9:6:1 triplet due to ketofuranosyl cation]: *m/z* 503(a), 283(b), 247(a), 223(b), 205(a), 187(b), 145(a).

Anal. Calc. for $C_{36}H_{45}Cl_3O_{12}Si$: C, 53.6; H, 5.6; Cl, 13.2. Found: C, 53.3; H, 5.2; Cl, 13.3.

Reaction of **6** *with DEAD and TPP.* — Treatment of **6** (10 g) in dry toluene (250 mL) with DEAD (12 mL, 2.3 mol. equiv.) and TPP (19 g, 1.3 mol. equiv.), as described for **2** and **3**, gave 6-*O*-*tert*-butyldiphenylsilyl-4-chloro-4-deoxy-α-D-galactopyranosyl 3,4-anhydro-1,6-dichloro-1,6-dideoxy-β-D-*lyxo*-hexulofuranoside (**8**; 8.5 g, 87.6%), $[\alpha]_D$ +107° (*c* 1, chloroform). Mass spectrum [(a) 3:1 doublet due to hexopyranosyl cation, (b) 9:6:1 triplet due to ketofuranosyl cation]: *m/z* 419(a), 181(b), 165(b), 163(a).

Conventional treatment of **8** (1 g) with acetic anhydride and pyridine gave 2,3-di-*O*-acetyl-6-*O*-*tert*-butyl-diphenylsilyl-4-chloro-4-deoxy-α-D-galactopyranosyl 3,4-anhydro-1,6-dichloro-1,6-dideoxy-β-D-*lyxo*-hexulofuranoside (**9**; 1.1 g, 95%), $[\alpha]_D$ +104.5° (*c* 1, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 5.80 (d, 1 H, $J_{1,2}$ 4.04 Hz, H-1), 5.11 (dd, 1 H, $J_{2,3}$ 10.66 Hz, H-2), 5.35 (dd, 1 H, $J_{3,4}$ 3.67 Hz, H-3), 4.70 (sdd, 1 H, $J_{4,5}$ 1.10 Hz, H-4), 4.43 (bt, 1 H, $J_{5,6a}$ 6.25, $J_{5,6b}$ 6.1 Hz, H-5), 3.76, 3.83 (2 dd, 2 H, $J_{6a,6b}$ 11.39 Hz, H-6a,6b), 3.50, 3.63 (2 d, 2 H, $J_{1'a,1'b}$ 11.76 Hz, H-1′a,1′b), 3.77 (d, 1 H, $J_{3',4'}$ 2.57 Hz, H-3′), 3.20 (dd, 1 H, $J_{4',5'}$ 0.73 Hz, H-4′), 4.14 (m, 1 H, $J_{5',6'a}$ 8.08, $J_{5',6'b}$ 5.88 Hz, H-5′), 3.47, 3.54 (2 dd, 2 H, $J_{6'a,6'b}$ 11.03 Hz, H-6′a,6′b), 2.04, 2.14 (2 s, 6 H, 2 Ac), 7.54–7.68 (m, aromatic), 1.04 (s, 9 H, CMe_3). Mass spectrum [(a) 3:1 doublet due to hexopyranosyl cation, (b) 9:6:1 triplet due to ketofuranosyl cation]: *m/z* 503(a), 247(a), 187(a), 181(b), 165(b), 145(a).

Anal. Calc. for $C_{32}H_{39}Cl_3O_9Si$: C, 54.7; H, 5.7; Cl, 15.2. Found: C, 54.4; H, 5.7; Cl, 14.4.

Conversion of **9** *into* **5**. — A solution of **9** (7 g) in tetrahydrofuran (150 mL) was treated with M tetrabutylammonium fluoride (14.2 mL, 1.5 mol. equiv.) for 18 h at room

temperature. The solution was concentrated, and the residue was treated with acetic anhydride (7 mL) and pyridine (50 mL) for 4 h at room temperature. The mixture was concentrated with toluene, and the resulting syrup was eluted through a short column of silica gel to give 2,3,6-tri-*O*-acetyl-4-chloro-4-deoxy-α-D-galactopyranosyl 3,4-anhydro-1,6-dichloro-1,6-dideoxy-β-D-*lyxo*-hexulofuranoside (**5**; 3.4 g, 85.2%).

4-Chloro-4-deoxy-α-D-galactopyranosyl 1,6-dichloro-1,4,6-trideoxy-4-fluoro-β-D-fructofuranoside (**10**). — A solution of **5** (4 g) in 1,2-ethanediol (40 mL) was treated with potassium hydrogen difluoride (4 g) and sodium fluoride (2 g) for 72 h at 90°. The mixture was extracted with ethyl acetate (4 × 100 mL), the combined extracts were concentrated to a syrup, the residue was deacetylated conventionally with methanolic sodium methoxide, and the product was eluted from a column of silica gel with dichloromethane–methanol (20:1) to afford **10** (2.7 g, 66%), m.p. 66–68° (from acetone–ether), $[\alpha]_D$ +83° (*c* 1, water). ^{13}C-N.m.r. data (60 MHz, D_2O): δ 106.64 ($J_{2',F}$ 11.2 Hz, C-2'), 98.90 ($J_{4',F}$ 185.5 Hz, C-4'), 95.50 (C-1), 81.70 ($J_{5',F}$ 26 Hz, C-5'), 77.5 ($J_{3',F}$ 22.00 Hz, C-3'), 73.40 (C-2), 70.64 (C-3), 70.18 (C-5), 65.60 (C-6), 63.98 (C-4), 46.55 (C-1'), 45.92 (C-6').

Anal. Calc. for $C_{12}H_{18}Cl_3FO_7$: C, 36.0; H, 4.5; Cl, 26.7; F, 4.7. Found: C, 36.0; H, 4.8; Cl, 25.8; F, 4.1.

Conventional treatment of **10** (0.5 g) with acetic anhydride and pyridine gave 2,3,6-tri-*O*-acetyl-4-chloro-4-deoxy-α-D-galactopyranosyl 3-*O*-acetyl-1,6-dichloro-1,4,6-trideoxy-4-fluoro-β-D-fructofuranoside (**11**; 1,2 g, 94.4%), m.p. 104–105° (from acetone–ether), $[\alpha]_D$ +78° (*c* 0.8, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 5.73 (bs, 1 H, H-1), 5.24–4.35 (m, 2 H, H-2,3), 4.58 (bs, 1 H, H-4), 4.53 (t, 1 H, $J_{5,6a}$ 6.0, $J_{5,6b}$ 5.0 Hz, H-5), 4.15–4.33 (m, 2 H, $J_{6a,6b}$ 12.0 Hz, H-6a,6b), 3.77, 3.55 (2 d, 2 H, $J_{1'a,1'b}$ 12.5 Hz, H-1'a,1'b), 5.76 (dd, 1 H, $J_{3',4'}$ 5.5, $J_{3',F}$ 18.0 Hz, H-3'), 5.10 (td, 1 H, $J_{4',5'}$ 5.5, $J_{4',F}$ 53.0 Hz, H-4', 4.35–4.47 (m, 1 H, H-5'), 3.67–3.87 (m, 2 H, H-6'a,6'b), 2.06–2.20 (4 s, 12 H, 4 Ac). ^{19}F [250 MHz, $CDCl_3$, relative to $(CCl_3FO)_2O$]: 38.66 (td, $J_{F,4'}$ 53.0, $J_{F,3'} = J_{F,5'} = 18.0$ Hz). Mass spectrum [(a) 3:1 doublet due to hexopyranosyl cation, (b) 9:6:1 triplet due to ketofuranosyl cation] : *m/z* 307(a), 247(a), 243(b), 223(b), 187(a), 181(b).

Anal. Calc. for $C_{20}H_{26}Cl_3FO_{11}$: C, 42.3; H, 4.5; Cl, 18.5; F, 3.3. Found: C, 42.2; H, 4.6; Cl, 18.3; F, 3.0.

*2,3,6-Tri-*O*-acetyl-4-chloro-4-deoxy-α-D-galactopyranosyl 3-O-acetyl-1,4,6-trichloro-1,4,6-trideoxy-β-D-fructofuranoside* (**12**). — A solution of **5** (4 g) in *N,N*-dimethylformamide (50 mL) was treated with lithium chloride (4 g) for 5 h at 90°. The mixture was poured into ice–water and extracted with ether. The extract was dried (Na_2SO_4) and concentrated to a syrup, which was reacetylated with acetic anhydride (4 mL) in pyridine (20 mL). Conventional work-up of the mixture gave **12** (2.6 g, 56.2%), m.p. 103–104° (from ether–light petroleum), $[\alpha]_D$ +75° (*c* 1, chloroform), ^{1}H-N.m.r. data (250 MHz, $CDCl_3$), δ 5.70 (d, 1 H, $J_{1,2}$ 3.53 Hz, H-1), 5.24 (dd, 1 H, $J_{2,3}$ 10.61 Hz, H-2), 5.31 (dd, 1 H, $J_{3,4}$ 3.30 Hz, H-3), 4.58 (dd, 1 H, $J_{4,5}$ 1.8 Hz, H-4), 4.55 (m, 1 H, $J_{5,6a}$ 4.41, $J_{5,6b}$ 6.98 Hz, H-5), 4.28, 4.19 (2 dd, 2 H, $J_{6a,6b}$ 11.76 Hz, H-6a,6b), 3.72, 3.57 (2 d, 2 H, $J_{1'a,1'b}$ 11.76 Hz, H-1'a,1'b), 5.65 (d, 1 H, $J_{3',4'}$ 8.82 Hz, H-3'), 4.58 (t, 1 H, $J_{4',5'}$ 8.82 Hz, H-4'), 4.33 (m, 1 H, $J_{5',6'a}$ 3.67, $J_{5',6'b}$ 3.67 Hz, H-5'), 3.86, 3.79 (2 dd, 2 H, $J_{6'a,6'b}$ 12.13 Hz,

H-6'a,6'b), 2.20, 2.12, 2.11, 2.08 (4 s, 12 H, 4 Ac). Mass spectrum [(a) 3:1 doublet (one chlorine substituent) due to hexopyranosyl cation, (b) 27:27:9:1 quartet and (c) 9:6:1 triplet due to ketofuranosyl cation]: *m/z* 307(a), 259(b), 247(a), 223(c), 187(a), 181(c), 145(a).

Anal. Calc. for $C_{20}H_{26}Cl_4O_{11}$: C, 41.1; H, 4.5; Cl, 24.3. Found: C, 42.0; H, 4.6; Cl, 23.8.

Conventional deacetylation of **12** (2.5 g) with methanolic sodium methoxide at room temperature gave 4-chloro-4-deoxy-α-D-galactopyranosyl 1,4,6-trichloro-1,4,6-trideoxy-β-D-fructofuranoside (**13**; 1.9 g, 93.5%), m.p. 58–60° (from acetone–ether), $[\alpha]_D$ +72° (*c* 1, water). ^{13}C-N.m.r. data (60 MHz, D_2O): δ 103.70 (C-2'), 93.09 (C-1), 82.59 (C-5'), 77.7 (C-3'), 71.04 (C-2), 68.52, 68.05 (C-3,5), 63.42 (C-6), 61.89 (C-4), 59.49 (C-4'), 44.36 (C-1'), 44.01 (C-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, 4.5; Cl, 34.2.

2,3,6-Tri-O-acetyl-4-chloro-4-deoxy-α-D-galactopyranosyl 3-O-acetyl-4-bromo-1,6-dichloro-1,4,6-trideoxy-β-D-fructofuranoside (**14**). — (*a*) A solution of **5** (4 g) in *N,N*-dimethylformamide (40 mL) was treated with lithium bromide (4 g) for 24 h at 80°. The mixture was worked-up as described for **12** to give, after chromatography on silica gel (ether–light petroleum, 1:1), **14** (3.5 g, 70%), m.p. 110–111° (from ether–light petroleum), $[\alpha]_D$ +59° (*c* 1, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): 5.71 (d, 1 H, $J_{1,2}$ 3.53 Hz, H-1), 5.27 (dd, 1 H, $J_{2,3}$ 10.61 Hz, H-2), 5.32 (dd, 1 H, $J_{3,4}$ 3.53 Hz, H-3), 4.58 (dd, 1 H, $J_{4,5}$ 1.3 Hz, H-4), 4.55 (m, 1 H, $J_{5,6a}$ 4.86, $J_{5,6b}$ 7.07 Hz, H-5), 4.28, 4.20 (2 dd, 2 H, $J_{6a,6b}$ 11.49, H-6a,6b), 3.73, 3.58 (2 d, 2 H, $J_{1'a,1'b}$ 11.5 Hz, H-1'a,1'b), 5.71 (d, 1 H, $J_{3',4'}$ 9.28, H-3'), 4.32 (t, 1 H, $J_{4',5'}$ 9.28 Hz, H-4'), 4.42 (m, 1 H, $J_{5',6'a}$ 3.53, $J_{5',6'b}$ 5.75 Hz, H-5'), 3.87, 3.80 (2 dd, 2 H, $J_{6'a,6'b}$ 12.38 Hz, H-6'a,6'b), 2.21, 2.13, 2.08, 1.57 (4 s, 12 H, 4 Ac). Mass spectrum [(a) 3:1 doublet due to hexopyranosyl cation, (b) 28:46:21:2 quartet (due to two chlorine and one bromine substituents), (c) 9:6:1 triplet due to ketofuranosyl cation]: *m/z* 307(a), 303(b), 247(a), 223(c), 187(a).

Anal. Calc. for $C_{20}H_{26}BrCl_3O_{11}$: C, 38.2; H, 4.1; Cl, 16.9; Br, 12.7. Found: C, 38.4; H, 4.3; Cl, 16.8; Br, 12.1.

(*b*) A solution of **5** (4 g) in dichloromethane (40 mL) was treated with 45% hydrobromic acid in acetic acid (1.4 mL) for 5 min at 0°. The mixture was then stirred with pyridine (40 mL) followed by acetic anhydride (5 mL) for 2 h at room temperature, and co-concentrated with toluene. The residue was eluted from a column of silica gel using ether–light petroleum (1:1) to afford **14** (4 g, 81%).

Conventional deacetylation of **14** (6 g) with methanolic sodium methoxide at 0° gave **15** (2.7 g, 61%), m.p. 78–80° (from acetone–ether), $[\alpha]_D$ +63° (*c* 1, water). ^{13}C-N.m.r. data (60 MHz, D_2O): δ 104.13 (C-2'), 93.56 (C-1), 84.25 (C-3'), 72.02 (C-2), 69.23, 69.19 (C-3,5), 64.91 (C-6), 63.20 (C-4), 50.63 (C-4'), 45.02 (C-1'), 44.63 (C-6').

Anal. Calc. for $C_{12}H_{18}BrCl_3O_7$: C, 31.3; H, 3.9; Cl, 23.1; Br, 17.4. Found: C, 31,0; H, 3.9; Cl, 24.2; Br, 15.2.

4-Chloro-4-deoxy-α-D-galactopyranosyl 1,6-dichloro-1,4,6-trideoxy-β-D-fructofuranoside (**16**). — A solution of **15** (2 g) in methanol (20 mL) and triethylamine (2 mL)

was hydrogenated (50 p.s.i.) for 4 h at room temperature in the presence of 10% Pd–C (0.2 g). The mixture was filtered and concentrated, and the resulting syrup was eluted from a column of silica gel (dichloromethane–methanol, 20:1) to afford **16** (1.2 g, 72%), m.p. 78–80° (from acetone–ether), $[\alpha]_D$ +91.7° (*c* 1, water).

Anal. Calc. for $C_{12}H_{19}Cl_3O_7$: C, 37.9; H, 5.0; Cl, 27.6. Found: C, 37.60; H, 5.1; Cl, 26.3.

Conventional treatment of **16** (0.4 g) with acetic anhydride and pyridine gave 2,3,6-tri-*O*-acetyl-4-chloro-4-deoxy-α-D-galactopyranosyl 3-*O*-acetyl-1,6-dichloro-1,4,6-trideoxy-β-D-fructofuranoside (**17**; 0.5 g, 86%), m.p. 109–110° (from ether–light petroleum), $[\alpha]_D$ +74° (*c* 1.1, chloroform). ^{1}H-N.m.r. data; ^{1}H (250 MHz, $CDCl_3$), δ 5.61 (d, 1 H, $J_{1,2}$ 3.07 Hz, H-1) 5.26 (dd, 1 H, $J_{2,3}$ 10.71 Hz, H-2), 5.32 (dd, 1 H, $J_{3,4}$ 3.26 Hz, H-3), 4.59 (dd, 1 H, $J_{4,5}$ 2.88 Hz, H-4), 4.56 (m, 1 H, $J_{5,6a}$ 4.58, $J_{5,6b}$ 6.85 Hz, H-5), 4.27 (2 dd, 2 H, $J_{6a,6b}$ 11.75 Hz, H-6a,6b), 3.66, 3.49 (2 d, 2 H, $J_{1'a,1'b}$ 11.76 Hz, H-1′a,1′b), 5.59 (dd, 1 H, $J_{3',4'a} = J_{3',4'b} = 7.34$ Hz, H-3′), 2.61, 2.05 (2 m, 2 H, H-4′a,4′b), 4.33 (m, 1 H, $J_{5',6'a}$ 5.64, $J_{5',6'b}$ 7.47 Hz, H-5′), 3.76, 3.63 (2 dd, 2 H, $J_{6'a,6'b}$ 10.82 Hz, H-6′a,6′b), 2.00–2.20 (4 s, 12 H, 4 Ac); ^{13}C (60 MHz, $CDCl_3$), δ 170.9–170.3 (carbonyl carbons), 105.2 (C-2′), 90.4 (C-1), 79.1 (C-5′), 73.3 (C-3′), 68.9 (C-2), 68.2 (C-3), 67.5 (C-5), 64.6 (C-6), 59.7 (C-4), 46.1 (C-1′), 45.8 (C-6′), 33.7 (C-4′), 21.3 (methyl carbons). Mass spectrum [(a) 3:1 doublet due to hexopyranosyl cation, (b) 9:6:1 triplet due to ketofuranosyl cation]: *m/z* 307(a), 247(a), 225(b), 187(a), 165(b), 145(a).

Anal. Calc. for $C_{20}H_{27}Cl_3O_{11}$: C, 43.8; H, 4.9; Cl, 19.2. Found: C, 43.8; H, 5.0; Cl, 19.5.

*2,3,6-Tri-*O*-acetyl-4-chloro-4-deoxy-α-D-galactopyranosyl 3-*O*-acetyl-1,6-dichloro-1,4,6-trideoxy-4-iodo-β-D-fructofuranoside* (**18**). — A solution of **5** (5 g) in acetone (50 mL) was treated with sodium iodide (5 g), acetic acid (20 mL). and sodium acetate (5 g) at reflux temperature for 9 h, then concentrated, and extracted with ether. The extract was washed with aq. sodium hydrogen carbonate, dried (Na_2SO_4), and concentrated. The resulting syrup was treated with acetic anhydride (4 mL) and pyridine for 4 h at room temperature. T.l.c. (ether–light petroleum, 4:1) then showed a fast-moving product. The solution was concentrated and extracted with ether, and the extract was washed successively with M hydrochloric acid, aq. sodium hydrogen carbonate, and water, dried (Na_2SO_4), and concentrated. Crystallisation of the residue from ether–light petroleum gave **18** (6.0 g, 89.5%), m.p. 95–97° (from ether), $[\alpha]_D$ +66° (*c* 1, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 4.27 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 5.27 (dd, 1 H, $J_{2,3}$ 11.0 Hz, H-2), 5.34 (dd, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 4.59 (dd, 1 H, $J_{4,5}$ 1.8 Hz, H-4), 4.56 (m, 1 H, $J_{5,6a}$ 4.5, $J_{5,6b}$ 7.0 Hz, H-5), 4.25, 4.22 (2 dd, 2 H, $J_{6a,6a}$ 11.5 Hz, H-6a,6b), 3.74, 3.59 (2 d, 2 H, $J_{1'a,1'b}$ 12.0 Hz, H-1′a,1′b), 5.74 (*d*, 1 H, $J_{3',4'}$ 10.5 Hz, H-3′), 4.26 (*t*, 1 H, $J_{4',5'}$ 10.5 Hz, H-4′), 4.49 (m, 1 H, $J_{5',6'a}$ 3.3, $J_{5',6'b}$ 5.5 Hz, H-5′), 3.92, 3.82 (2 dd, 2 H, $J_{6'a,6'b}$ 12.2 Hz, H-6′a,6′b), 2.24, 2.16, 2.15, 2.12 (4 s, 12 H, 4 Ac). Mass spectrum [(a) 3:1 doublet due to hexopyranosyl cation, 9:6:1 triplet due to ketofuranosyl cation]: *m/z* 351 (b), 307 (a), 247 (a), 233 (b), 187 (a), 181 (b).

Anal. Calc. for $C_{20}H_{26}Cl_3IO_{11}$: C, 35.7; H, 3.8; Cl, 15.6; I, 18.7. Found: C, 35.5; H, 3.6; Cl, 15.3; I, 18.0.

Conventional deacetylation of **18** (2 g) at 0°, using methanolic sodium methoxide, gave 4-chloro-4-deoxy-α-D-galactopyranosyl 1,6-dichloro-1,4,6-trideoxy-4-iodo-β-D-fructofuranoside (**19**; 1 g, 68%), $[\alpha]_D$ +53° (*c* 0.95, water). ^{13}C-N.m.r. data (60 MHz, D_2O): δ 105.83 (C-2'), 95.26 (C-1), 86.65 (C-5'), 81.99 (C-3'), 73.35 (C-2), 70.64 (C-3), 70.16 (C-5), 65.53 (C-6), 64.04 (C-4), 46.35 (C-1'), 46.07 (C-6'), 24.25 (C-4').

Anal. Calc. for $C_{12}H_{18}Cl_3IO_7$: C, 28.5; H, 3.6; Cl, 20.8; I, 25.0. Found: C, 28.3; H, 3.5; Cl, 20.2; I, 20.4.

*2,3,6-Tri-*O*-acetyl-4-chloro-4-deoxy-α-*D*-galactopyranosyl 3-*O*-acetyl-4-azido-1,6-dichloro-1,4,6-trideoxy-β-*D*-fructofuranoside* (**20**). — To a warm (60°) solution of **5** (5 g) in ethanol (50 mL) was added sodium azide (5 g), ammonium chloride (5 g), and water (5 mL). The mixture was heated for 72 h at 70°, then concentrated to dryness. The residue was treated with acetic anhydride (15 mL) and pyridine (50 mL) at room temperature for 16 h. Conventional work-up gave **20** (4.3 g, 74%), $[\alpha]_D$ +77.5° (*c* 0.94, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 5.65 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.27 (dd, 1 H, $J_{2,3}$ 12.0 Hz, H-2), 5.32 (dd, 1 H, $J_{3,4}$ 3.0 Hz, H-3), 4.59 (dd, 1 H, $J_{4,5}$ 2.0 Hz, H-4), 4.55 (m, 1 H, $J_{5,6a}$ 7.0, $J_{5,6b}$ 6.8 Hz, H-5), 4.09, 4.07 (2 dd, 2 H, $J_{6a,6b}$ 11.4 Hz, H-6a,6b), 3.71, 3.56 (2 d, 2 H, $J_{1'a,1'b}$ 15.0 Hz, H-1'a,1'b), 5.54 (d, 1 H, $J_{3',4'}$ 11.0 Hz, H-3'), 4.20 (t, 1 H, $J_{4',5'}$ 11.0 Hz, H-4'), 4.24 (qt, 1 H, H-5'), 3.82, 3.79 (2 s, 2 H, H-6'a,6'b), 2.26, 2.18, 2.17, 2.10 (4 s, 2 H, 4 Ac). Mass spectrum [(a) 3:1 doublet due to hexopyranosyl cation, (b) 9:6:1 triplet due to ketofuranosyl cation]: *m/z* 307(a), 166(b), 297(a), 223(b), 187(a), 181(b), 145(a).

Anal. Calc. for $C_{20}H_{26}Cl_3N_3O_{11}$: C, 40.6; H, 4.4; Cl, 18.0; N, 7.1. Found: C, 41.0; H, 4.4; Cl, 18.0; N, 7.1.

Conventional deacetylation of **20** (4 g), using methanolic sodium methoxide, gave 4-chloro-4-deoxy-α-D-galactopyranosyl 4-azido-1,6-dichloro-1,4,6-trideoxy-β-D-fructofuranoside (**21**; 2.5 g, 89.3%), $[\alpha]_D$ +55° (*c* 0.9, water). ^{13}C-N.m.r. data (60 MHz, D_2O): δ 106.0 (C-2'), 95.2 (C-1), 82.2 (C-5'), 78.0 (C-3'), 73.5 (C-2), 70.6 (C-5), 70.1 (C-3), 68.1 (C-4'), 65.5 (C-6), 64.2 (C-4), 46.8 (C-6'), 45.9 (C-1').

Anal. Calc. for $C_{12}H_{18}Cl_3N_3O_7$: C, 34.1; H, 4.3; Cl, 25.2; N, 9.9. Found: C, 34.1; H, 4.6; Cl, 24.8; N, 9.9.

*4-Chloro-4-deoxy-α-*D*-galactopyranosyl 4-amino-1,6-dichloro-1,4,6-trideoxy-β-*D*-fructofuranoside* (**22**). — A solution of **21** (2 g) in dry methanol (20 mL) and triethylamine (2 mL) was hydrogenated (50 p.s.i.) in the presence of 10% Pd–C (200 mg) for 5.5 h at room temperature. T.l.c. (dichloromethane–methanol, 2:1) then revealed a slow-moving product which gave a positive reaction with ninhydrin. The catalyst was removed and the filtrate was concentrated to yield **22** (1.6 g, 94.1%), $[\alpha]_D$ +75° (*c* 1, water). ^{13}C-N.m.r. data (60 MHz, D_2O): δ 106.06 (C-2'), 95.20 (C-1), 85.15 (C-5'), 79.48 (C-3'), 73.34 (C-2), 70.70 (C-3), 70.24 (C-5), 65.69 (C-6), 64.04 (C-4), 59.80 (C-4'), 47.85 (C-1'), 46.13 (C-6').

Anal. Calc. for $C_{12}H_{20}Cl_3NO_7$: C, 36.3; H, 5.4; Cl, 26.8; N, 3.5. Found: C, 35.4; H, 5.5; Cl, 25.3; N, 3.3.

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