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RING-OPENING REACTIONS OF SUCROSE EPOXIDES: SYNTHESIS OF 4'-DERIVATIVES OF SUCROSE*

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ABSTRACT

The 2,1'-*O*-isopropylidene derivative (**1**) of 3-*O*-acetyl-4,6-*O*-isopropylidene-α-D-glucopyranosyl 6-*O*-acetyl-3,4-anhydro-β-D-*lyxo*-hexulofuranoside and 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranosyl 3,4-anhydro-1,6-di-*O*-trityl-β-D-*lyxo*-hexulofuranoside have been synthesised and **1** has been converted into 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl 1,6-di-*O*-acetyl-3,4-anhydro-β-D-*lyxo*-hexulofuranoside (**2**). The S_N2 reactions of **2** with azide and chloride nucleophiles gave the corresponding 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl 1,3,6-tri-*O*-acetyl-4-azido-4-deoxy-β-D-fructofuranoside (**6**) and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl 1,3,6-tri-*O*-acetyl-4-chloro-4-deoxy-β-D-fructofuranoside (**8**), respectively. The azide **6** was catalytically hydrogenated and the resulting amine was isolated as 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl 4-acetamido-1,3,6-tri-*O*-acetyl-4-deoxy-β-D-fructofuranoside. Treatment of **5** with hydrogen bromide in glacial acetic acid followed by conventional acetylation gave 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl 1,3,6-tri-*O*-acetyl-4-bromo-4-deoxy-β-D-fructofuranoside. Similar S_N2 reactions with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl 1,6-di-*O*-acetyl-3,4-anhydro-β-D-*ribo*-hexulofuranoside (**12**) resulted in a number of 4'-derivatives of α-D-glucopyranosyl β-D-sorbofuranoside. The regiospecific nucleophilic substitution at position 4' in **2** and **12** has been explained on the basis of steric and polar factors.

INTRODUCTION

Sugar epoxides are valuable synthetic intermediates. Several mono- (2,3[2], 3,4[3], and 3',4'[4–6]) and di-epoxides (2,3:3',4'[7]) of sucrose have been synthesised. Most of these epoxides have been synthesised from a vicinal *trans*-hydroxy,sulphonyloxy group. Guthrie and co-workers synthesised α-D-glucopyranosyl 3,4-anhydro-β-D-*lyxo*-hexulofuranoside directly from sucrose in 42% yield by treat-

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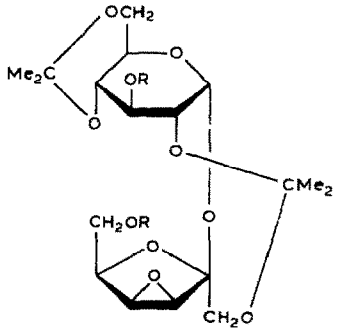
ment of sucrose with diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP) in *N,N*-dimethylformamide and incorporating acetic acid to prevent the formation of 3,6- and 1′,4′-anhydro rings[6]. Ring-opening reactions of some of the sucrose epoxides have been described[2].

We now report on the use of DEAD–TPP in the synthesis of the 3′,4′-*lyxo*-epoxide **2** and the ring-opening reactions of **2** and the 3′,4′-*ribo*-epoxide **12** with various nucleophiles.

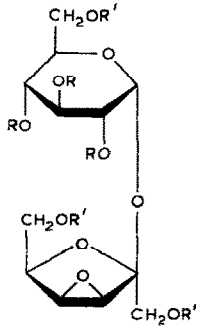
RESULTS AND DISCUSSION

Treatment of 3,6′-di-*O*-acetyl-4,6:2,1′-di-*O*-isopropylidenesucrose with DEAD–TPP in toluene at room temperature for 30 min gave 80% of the crystalline 3′,4′-epoxide **1**. In the ^{1}H-n.m.r. spectrum of **1** (Table I), the resonances due to H-3′,4′ were present, as expected[4], as an AB-like quartet (J 3.0 Hz), the higher field doublet at τ 6.20 being assigned to H-4′ because of coupling (0.8 Hz) with H-5′. Deacetalation of **1** by treatment with boiling aqueous acetic acid followed by acetylation gave the known[4] 3′,4′-*lyxo*-epoxide **2**. In the ^{13}C-n.m.r. spectrum of **2** (Table II), the resonances due to C-3′,4′ were shifted upfield by 20.1 and 18.5 p.p.m., respectively. The β-effect was observed only on C-5′ (−4.6 p.p.m.), whereas γ-effects were observed for C-1′ (+1.0 p.p.m.) and C-6′ (−1.8 p.p.m.). Zemplén deacetylation of **2** gave the *lyxo*-epoxide **3**, treatment of which with 4.7 mol of trityl chloride in pyridine at 70° for 6 h gave the 6,1′,6′-tri-*O*-trityl derivative **4** as the major product. Alternatively, **4** was synthesised (60%) from 6,1′,6′-tri-*O*-tritylsucrose, using DEAD–TPP in toluene. Conventional acetylation of **4** afforded the triacetate **5**, the structure of which was supported by its ^{1}H-n.m.r. spectrum.

Treatment of the 3′,4′-*lyxo*-epoxide **2** with sodium azide in aqueous ethanol



1 R = Ac



2 R = R′ = Ac
3 R = R′ = H
4 R = H, R′ = Tr
5 R = Ac, R′ = Tr

TABLE I

^{1}H-N.M.R. DATA ($CDCl_3$): FIRST-ORDER CHEMICAL SHIFTS (τ VALUES) AND COUPLING CONSTANTS (Hz)

Proton	*Compound*								
	1[a]	**5**	**6**	**7**	**8**	**10**[a]	**13**	**14**	**15**
H-1	4.08 d	4.24 d	4.38 d	4.34 d	4.34 d	4.24 d	4.31 d	4.16 d	4.24 d
H-2	6.05 dd	5.17 dd	5.12 dd	5.09 dd	5.13 dd	5.08 dd	5.14 dd	5.20 dd	5.14 dd
H-3	4.68 t	4.57 t	4.58 dd	4.55 dd	4.60 t	4.92 t	4.55 dd	4.54 dd	4.54 t
H-4	5.6–5.9 m	4.91 t	4.96 t	4.95 t	5.00 t	4.52 t	4.94 t	4.96 t	4.93 t
H-5	—								
H-6a,6b	—	6.60–7.10							
H-1'a, H-1'b	5.96, 6.56 2 d	m							
H-3'	6.17 d	6.02–6.44	4.65 d	4.63 d	4.53 d	4.35 d	4.44 d	4.51 d	4.28 d
H-4'	6.20 sdd	m	5.8	5.39 m	5.60–5.96 m	5.47 t	5.8	5.20 m	5.54–5.86 m
H-5'	6.06 m	—	—	—					
H-6'a,6'b	6.25–6.50 m	6.60–7.10 m	—	—					
CH_3 (Ac)	7.90, 7.96 2 s	8.12, 8.26, 8.42 3 s	7.79–8.00	7.83–8.92		7.90–8.01	7.88–8.00	7.86–7.89	7.80–8.02
CH_3 (Isopropylidene)	8.51, 8.53, 8.62, 8.68	—	—	—					
NHAc	—	—	—	3.83 d				3.64 d	
H Aromatic	—	2.20–3.35 m	—	—					
$J_{1,2}$	3.5	3.5	3.5	3.5	3.5	3.8	3.5	3.8	3.5
$J_{2,3}$	9.5	10.0	10.0	10.0	10.0	10.5	10.0	10.0	10.0
$J_{3,4}$	9.5	—	9.5	9.5	10.0	10.0	9.5	9.5	11.0
$J_{4,5}$	—	—	9.5	9.5	9.0	9.5	9.5	9.5	10.0
$J_{5,6}$	—	—	—	—					
$J_{3',4'}$	3.5	—	7.5	9.0	7.0		3.0	6.5	4.5
$J_{4',5'}$	0.8	—	—	8.5					
$J_{4',NH}$	—	—	—	8.5				7.5	

[a]Measured at 220 MHz, using a Bruker WM 250 spectrometer.

TABLE II

^{13}C-N.M.R. CHEMICAL SHIFTS[a]

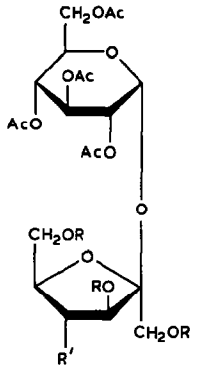
	2	3	8	9	11	12
C-2′	102.9	104.7	102.6	104.7	106.5	104.1
C-1	89.7	93.2	89.2	93.2	94.8	90.4
C-5′	75.2	77.6	80.6	83.5	79.3	78.2
C-3′	56.4	57.3	77.9	75.6	59.0	58.7
C-4′	54.6	56.5	55.6	62.3	58.1	57.6
C-3	70.4	73.8	70.1	73.5	75.3	70.4
C-5	69.9	73.4	69.8	73.5	75.1	69.8
C-2	69.0	72.0	68.7	72.0	73.6	68.5
C-4	68.3	70.6	68.7	70.2	72.1	68.3
C-1′	65.2	64.3	64.3	62.3	66.0	63.3
C-6′	62.4	61.6	62.5	58.9	52.9	63.1
C-6	62.4	61.3	62.5	61.2	63.2	61.9

[a]Expressed in p.p.m. downfield from the signal for Me_4Si; D_2O was used as solvent and sodium 4,4-dimethyl-4-silapentane-1-sulphonate as internal standard.

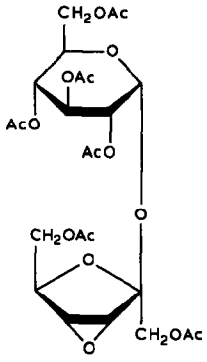
in the presence of ammonium chloride at 80° for 72 h gave, after conventional acetylation and chromatography, 63% of the 4′-azide **6**, for which the ^{1}H-n.m.r. signal for H-4′ (τ 5.8) was at high-field, indicating that the azide group was located at position 4′. Conventional deacetylation of **6** followed by catalytic hydrogenation and reacetylation afforded the 4′-acetamido-4′-deoxy derivative **7**. In the ^{1}H-n.m.r. spectrum of **7**, the multiplet due to H-4′ at τ 5.39 confirmed the presence of an acetamido group at position 4′ and the low-field doublet at 3.83 ($J_{NH,4'}$ 8.5 Hz) was attributed to the acetamido NH.

Treatment of **2** with lithium chloride in *N,N*-dimethylformamide at 120° for 2 h gave, after acetylation and chromatography, 44% of the 4′-chloride **8**, the structure of which was supported by the ^{1}H- and ^{13}C-n.m.r. spectra. In comparison with that of **2**, the resonance of **8** due to H-3′ (τ 4.53) was shifted ~1.8 p.p.m. downfield, consistent with the presence of an acetyl group at position 3′. The H-4′ resonance, identified by spin-decoupling experiments in the region τ 5.40–5.96, was shifted slightly downfield (0.45 p.p.m.), but in comparison with the corresponding signal in sucrose octa-acetate it was shifted upfield (~1.2 p.p.m.). These results indicated that the chlorine substituent in **8** was located at position 4′. The ^{13}C resonance of C-4′ in **8** was markedly shifted upfield (19.4 p.p.m.) compared to the corresponding resonance for sucrose octa-acetate[8]. Zemplén deacetylation of **8** gave the free 4′-chloride **9**, the ^{13}C resonance (62.3 p.p.m.) of C-4′ of which was markedly shifted upfield (12.7 p.p.m.) relative to the corresponding signal for sucrose[9]. These results coupled with the mass-spectral data for **8** confirmed the structures of **8** and **9**.

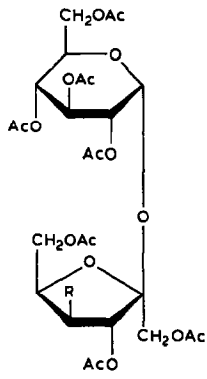
Attempts to cleave the trityl groups in **5** with hydrogen bromide–glacial acetic acid–chloroform at 0° gave, after conventional acetylation, the 4′-bromide **10**. The



6 R = Ac, R′ = N_3
7 R = Ac, R′ = NHAc
8 R = Ac, R′ = Cl
9 R = H, R′ = Cl
10 R = Ac, R′ = Br
11 R = H, R′ = Br



12



13 R = N_3
14 R = NHAc
15 R = Cl

^{1}H-n.m.r. and mass spectra of **10** were consistent with the proposed structure. The ^{13}C resonance for C-4′ of the deacetylated derivative **11** showed a very significant upfield shift (~21 p.p.m.) compared to that of C-4′ in sucrose.

The structure of the 3′,4′-*ribo*-epoxide[4] **12**, whose synthesis from 3′-*O*-tosylsucrose has been described in our earlier report[4], was further elucidated by ^{13}C-n.m.r. spectroscopy. The spectrum revealed, as for the 3′,4′-*lyxo*-epoxides **2** and **3**, large shifts for C-3′ (−17.2 p.p.m.) and C-4′ (−17.6 p.p.m.), with respect to the corresponding signals for sucrose octa-acetate. Unlike **2** and **3**, little or no secondary effects were observed with **12**. This, and the observation that the resonances of C-3′ and C-4′ for **12** appeared at lower fields (2–3 p.p.m.) than for **2**, could be employed to distinguish between a *ribo*- and a *lyxo*-epoxide configuration in a furanose system.

Treatment of **12** with sodium azide in aqueous ethanol in the presence of ammonium chloride at 80° for 72 h gave, after conventional acetylation and chromatography, 82% of the 4′-azide **13**. In comparison with that of sucrose octa-acetate[8], the resonance due to H-4′ in **13** appeared at a comparatively high-field (τ 5.8), indicating that the azide group was located at position 4′. The $J_{3',4'}$ value (4.5 Hz) for **13** was characteristically smaller than the corresponding value (7.5 Hz) for 4′-azido-4′-deoxysucrose hepta-acetate (**6**). Conventional de-esterification of **13**, followed by catalytic hydrogenation and reacetylation, gave the 4′-acetamido-4′-deoxy derivative **14**. When **12** was treated with lithium chloride in *N,N*-dimethylformamide at 120° for 3 days followed by acetylation, 48% of the 4′-chloride **15** was obtained, the structure of which was indicated by the ^{1}H-n.m.r. and mass spectra.

Nucleophilic attack in the 3′,4′-*lyxo*- (**2**) and the 3′,4′-*ribo*-epoxide (**12**)

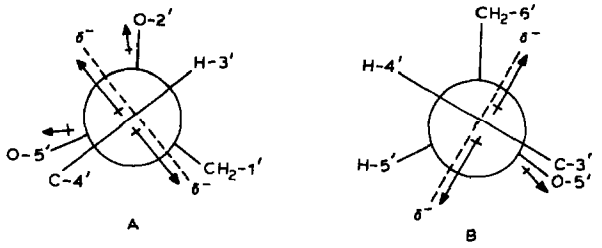


Fig. 1. Newman projections along the C-3'–C-2' bond (A) and the C-4'–C-5' bond (B).

occurred predominantly at position 4', *i.e.*, from the least-hindered side. Similar regioselectivity has been observed by other workers[10]. The lack of reactivity at position 3' in **2** and **12** probably reflects the effect of the adjacent neopentyl glycosidic carbon. This situation can best be visualised by the Newman projections in Figs. 1A (C-3'–C-2') and 1B (C-4'–C-5'). Fig. 1A shows that, for **2** and **12**, the upper bond of the transition states is unfavourably aligned to the two permanent dipoles due to the C-2'–O-2' and C-5'–O-5' bonds. Such a transition state at C-3' would be highly unfavourable. For nucleophilic attack at position 4' in **2** and **12**. Fig. 1B shows that the permanent dipole associated with C-5'–O-5' is approximately at right angles to the temporary dipoles associated with the transitory bonds, thus leading to a transition state of minimum energy.

EXPERIMENTAL

For general experimental details, see ref. 11.

*3,6'-Di-*O*-acetyl-3',4'-anhydro-4,6:2,1'-di-*O*-isopropylidene-*tagato*-sucrose* (**1**). — A solution of 3,6'-di-*O*-acetyl-4,6:2,1'-di-*O*-isopropylidenesucrose (3.0 g, 5.9 mmol) in dry toluene was treated with DEAD (2.2 mL, 14 mmol) followed by TPP (4.6 g, 17.5 mmol) at ambient temperature for 0.5 h. The mixture was then diluted with methanol (10 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) of the residual crude material afforded **1** (2.2 g, 80%), m.p. 95–98° (from ether), $[\alpha]_D$ +9.5° (*c* 1, chloroform).

Anal. Calc. for $C_{22}H_{32}O_{12}$: C, 54.0; H, 6.55. Found: C, 54.2; H, 6.8.

*2,3,4,6-Tetra-*O*-acetyl-α-*D*-glucopyranosyl 1,6-di-*O*-acetyl-3,4-anhydro-β-*D*-*lyxo*-hexulofuranoside* (**2**). — A solution of **1** (2.0 g) in aqueous 60% acetic acid (30 mL) was stored at 80° for 10 min. T.l.c. (dichloromethane–methanol, 4:1) then showed one major slow-moving product. The solution was concentrated to dryness and the residue was treated with pyridine (5 mL) and acetic anhydride (2 mL). Conventional work-up of the mixture gave **2** (2.1 g, 90%), $[\alpha]_D$ +98° (*c* 1 chloroform), the ^{1}H-n.m.r. and mass spectra of which were identical to those of an authentic sample[4].

Conventional deacetylation of **2** (2.0 g) in methanolic sodium methoxide gave

α-D-glucopyranosyl 3,4-anhydro-β-D-*lyxo*-hexulofuranoside (**3**; 1.0 g, 89%), m.p. 107–109° (from ethanol), $[\alpha]_D$ +92.5° (*c* 1, water).

Anal. Calc. for $C_{12}H_{20}O_{10}\cdot H_2O$: C, 42.1; H, 6.4. Found: C, 42.6; H, 6.5.

*6-O-Trityl-α-D-glucopyranosyl 3,4-anhydro-1,6-di-O-trityl-β-D-*lyxo*-hexulofuranoside* (**4**). — (*a*) A solution of **3** (4.0 g, 12.3 mmol) in pyridine (45 mL) was treated with triphenylmethyl chloride (16.0 g, 57.5 mmol) at 70° for 6 h. The mixture was then poured into ice–water, the precipitate was collected and washed well with water, and a solution in dichloromethane was dried (Na_2SO_4) and concentrated. T.l.c. (butyl acetate–pyridine–water, 5:3:1) showed one major spot. Elution of the product from a column of silica gel (200 g) with ether–light petroleum (4:1) gave **4** (7.3 g, 56.3%), m.p. 138–140° (from ethanol), $[\alpha]_D$ +14.5° (*c* 1, chloroform).

Anal. Calc. for $C_{69}H_{62}O_{10}$: C, 78.8; H, 5.9. Found: C, 77.6; H, 6.0.

(*b*) A solution of 6,1′,6′-tri-*O*-tritylsucrose (10 g, 17.2 mmol) in toluene (150 mL) was treated with DEAD (3.6 mL, 22.9 mmol) followed by TPP (7.9 g, 30 mmol) with stirring at room temperature for 15 min. The mixture was then worked-up as described above for **1**, to give a syrup. Column chromatography (ether–light petroleum, 4:1) of the product gave crystalline **4** (6.0 g, 60%), identical with the product in (*a*).

Conventional treatment of **4** (0.5 g) with acetic anhydride (1 mL) and pyridine (5 mL) at ambient temperature for 48 h gave **5** (0.5 g, 89%), m.p. 128–130° (from methanol), $[\alpha]_D$ +51° (*c* 0.9, chloroform).

Anal. Calc. for $C_{75}H_{68}O_{13}$: C, 76.5; H, 5.8. Found: C, 76.1; H, 5.9.

*Reaction of the 3′,4′-*lyxo*-epoxide **2** with azide ion.* — A solution of **2** (2.0 g, 3.5 mmol) in ethanol (40 mL) was treated with sodium azide (2.0 g, 26.6 mmol), ammonium chloride (2.0 g, 37.7 mmol), and water (5 mL) at 80° for 72 h, and then concentrated to dryness. The residue was treated with acetic anhydride (1 mL) and pyridine (5 mL) at room temperature for 16 h when t.l.c. (ether–light petroleum, 4:1) revealed a fast-moving product. The mixture was poured into ice–water, the precipitate was collected and washed well with water, and a solution in dichloromethane was dried (Na_2SO_4) and concentrated. The resulting syrup was eluted from a column of silica gel (30 g) with ether–light petroleum (2:1) to afford 4′-azido-4′-deoxysucrose hepta-acetate (**6**; 1.45 g, 63%), $[\alpha]_D$ +52° (*c* 1, chloroform), ν_{max} 2100 cm^{-1} (azide).

Anal. Calc. for $C_{26}H_{35}N_3O_{17}$: C, 47.2; H, 5.3; N, 6.4. Found: C, 47.3; H, 5.3; N, 6.0.

*4′-Acetamido-2,3,4,6,1′,3′,6′-hepta-*O*-acetyl-4′-deoxysucrose* (**7**). — Compound **6** (0.6 g) was conventionally deacetylated with methanolic sodium methoxide. After 3 h at room temperature, the solution was neutralised with Amberlyst 15 (H^+) resin, filtered, and concentrated. A solution of the dry residue in methanol (10 mL), ethyl acetate (10 mL), and triethylamine (0.1 mL) was hydrogenated (60 p.s.i.) at 35° for 16 h in the presence of 10% Pd/C. Water (10 mL) was then added, the catalyst was collected and washed well with water, and

the combined filtrate and washings were concentrated. The resulting syrup was then treated with acetic anhydride (1 mL) and pyridine (5 mL) at room temperature for 16 h. Conventional work-up gave **7** (0.25 g, 41%), isolated as a syrup, $[\alpha]_D$ +58.5° (*c* 1, chloroform).

Anal. Calc. for $C_{28}H_{39}NO_{18}$: C, 49.6; H, 5.8; N, 2.1. Found: C, 50.0; H, 5.9; N, 1.8.

Reaction of **2** *with chloride ion.* — A solution of **2** (0.4 g, 0.7 mmol) in *N,N*-dimethylformamide (20 mL) was treated with lithium chloride (0.5 g, 11.9 mmol) at 120° for 2 h. T.l.c. (ether–light petroleum, 6:1) then showed one fast-moving product. The solution was concentrated, and the residue was treated with acetic anhydride (2 mL) and pyridine (20 mL) at room temperature for 24 h. The solution was concentrated by co-distillation with toluene, and the resulting syrup was eluted from a column of silica gel (50 g) with ether–light petroleum (3:1) to give 4′-chloro-4′-deoxysucrose hepta-acetate (**8**; 10.2 g, 44%), $[\alpha]_D$ +43° (*c* 1, chloroform). Mass spectrum [(a) indicates ions due to hexopyranosyl cation and (b) due to ketofuranosyl cation (3:1, doublet)]: *m/z* 331 (a), 307 (b), 187 (b), 169 (a), 145 (b), 109 (a).

Anal. Calc. for $C_{26}H_{35}ClO_{17}$: C, 47.7; H, 5.4; Cl, 5.4. Found: C, 47.6; H, 5.4; Cl, 5.6.

Conventional deacetylation of **8** (1.0 g) with methanolic sodium methoxide gave 4′-chloro-4′-deoxysucrose (**9**; 0.35 g, 64%), $[\alpha]_D$ +52° (*c* 0.8, methanol).

Anal. Calc. for $C_{12}H_{21}ClO_{10}\cdot H_2O$: C, 38.0; H, 6.1; Cl, 9.3. Found: C, 37.7; H, 6.2; Cl, 8.5.

*Reaction of the 3′,4′-*lyxo*-epoxide* **5** *with bromide ion.* — A solution of **5** (2 g) in dichloromethane (10 mL) and acetic acid (10 mL) was treated with 45% hydrobromic acid in acetic acid (0.94 mL) at 0° for 2 min. Pyridine (40 mL) was added slowly at 0° followed by acetic anhydride (10 mL). The mixture was allowed to attain room temperature, then diluted with dichloromethane, washed successively with M hydrochloric acid, aqueous sodium hydrogencarbonate, and water, dried (Na_2SO_4), and concentrated. Column chromatography (ether–light petroleum, 1:1) of the resulting syrup gave 4′-bromo-4′-deoxysucrose hepta-acetate (**10**; 0.5 g, 42%), $[\alpha]_D$ +43° (*c* 0.85, chloroform). Mass-spectral data [ions (a) correspond to hexoyranosyl cation and (b) 1:1 doublet due to ketofuranosyl cation]: *m/z* 351 (b), 331 (a).

Anal. Calc. for $C_{26}H_{35}BrO_{17}$: C, 44.7; H, 5.0; Br, 11.5. Found: C, 44.5; H, 4.8; Br, 11.0.

Conventional deacetylation of **10** (0.4 g) with methanolic sodium methoxide gave 4′-bromo-4′-deoxysucrose (**11**; 0.2 g, 87%), $[\alpha]_D$ +40° (*c* 1, water).

*Reaction of 2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl 1,6-di-*O*-acetyl-3,4-anhydro-β-*D*-*ribo*-hexulofuranoside* (**12**) *with azide ion.* — A solution of **12** (0.85 g, 1.5 mmol) in ethanol (20 mL) was treated with sodium azide (0.85 g, 13 mmol), ammonium chloride (0.85 g, 16 mmol), and water (2 mL) at 80° for 72 h. The mixture was concentrated to dryness and the residue was treated with acetic

anhydride (1 mL) and pyridine (5 mL) to give, after working-up as described above for **6**, 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl 1,3,6-tri-*O*-acetyl-4-azido-4-deoxy-β-D-sorbofuranoside (**13**; 0.80 g, 82%), $[\alpha]_D$ +49° (*c* 1, chloroform); ν_{max} 2100 cm^{-1} (azide).

Anal. Calc. for $C_{26}H_{35}N_3O_{17}$: C, 47.2; H, 5.2; N, 6.4. Found: C, 47.5; H, 5.4; N, 5.8.

2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl 4-acetamido-1,3,6-tri-O-acetyl-4-deoxy-β-D-sorbofuranoside (**14**). — Compound **13** (0.60 g) was subjected to deacetylation, hydrogenation, and reacetylation, as described above for **7**, to give **14** (0.18 g, 29%), isolated as a syrup, $[\alpha]_D$ +97° (*c* 1, chloroform).

Anal. Calc. for $C_{28}H_{39}NO_{18}$: C, 49.6; H, 5.8; N, 2.1. Found: C, 50.5; H, 6.0; N, 2.1.

Reaction of **12** *with chloride ion.* — A solution of **12** (0.8 g, 1.4 mmol) in *N,N*-dimethylformamide (40 mL) was treated with lithium chloride (1 g, 23.8 mmol) at 120° for 72 h. The product was treated with acetic anhydride and pyridine, since some deacetylation had occurred. The solution was concentrated, the residue was partitioned between ether and water, the organic layer was dried (Na_2SO_4) and concentrated, and the residue was deacetylated with methanolic sodium methoxide. T.l.c. (butyl acetate–pyridine–water, 5:3:1) revealed one major product which was eluted from a column of silica gel with 1-propanol–water (10:1) to afford, after acetylation with acetic anhydride (1 mL) and pyridine (10 mL), 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl 1,3,6-tri-*O*-acetyl-4-chloro-4-deoxy-β-D-sorbofuranoside (**15**; 0.43 g, 48%), isolated as a syrup, $[\alpha]_D$ +78° (*c* 1.1, chloroform). Mass-spectral data [(a) indicates ions due to hexopyranosyl cation and (b) 3:1 doublet due to ketofuranosyl cation]: *m/z* 331 (a), 307 (b), 169 (a), 145 (b), 109 (a).

Anal. Calc. for $C_{26}H_{35}ClO_{17}$: C, 47.7; H, 5.4; Cl, 5.4. Found: C, 48.5; H, 5.7; Cl, 5.3.

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