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DERIVATIVES OF β-D-FRUCTOFURANOSYL α-D-GALACTOPYRANOSIDE*

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ABSTRACT

De-etherification of 6,6′-di-*O*-tritylsucrose hexa-acetate (**2**) with boiling, aqueous acetic acid caused 4→6 acetyl migration and gave a syrupy hexa-acetate **14**, characterised as the 4,6′-dimethanesulphonate **15**. Reaction of 2,3,3′,4′,6-penta-*O*-acetylsucrose (**5**) with trityl chloride in pyridine gave a mixture containing the 1′,6′-diether **6** and the 6′-ether **9**, confirming the lower reactivity of HO-1′ to tritylation. Subsequent mesylation, detritylation, and acetylation afforded the corresponding 4-methanesulphonate **8** and 1′,4-dimethanesulphonate **11**. Reaction of these sulphonates with benzoate, azide, bromide, and chloride anions afforded derivatives of β-D-fructofuranosyl α-D-galactopyranoside (**29**) by inversion of configuration at C-4. Treatment of the 4,6′-diol **14**, the 1′,4,6′-triol **5**, and the 4-hydroxy-1′,6′-diether **6** with sulphuryl chloride effected replacement of the free hydroxyl groups and gave the corresponding, crystalline chlorodeoxy derivatives. The same 4-chloro-4-deoxy derivative was isolated when the 4-hydroxy-1′,6′-diether **6** was treated with mesyl chloride in *N*,*N*-dimethylformamide.

INTRODUCTION

Prior studies on the nucleophilic substitution of 4-sulphonates of sucrose derivatives have shown that inversion of configuration occurs at C-4 to give galactopyranosyl derivatives[3,20]. The resultant *galacto*-sucroses‡ are of interest, for example, in relation to theories of sweetness and in studies on invertases. Further routes to the synthesis of *galacto*-sucrose derivatives, utilising dityrityl ethers and acetyl-group migrations, are now reported.

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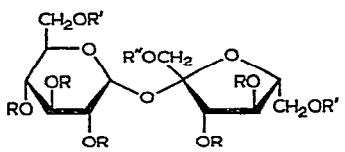
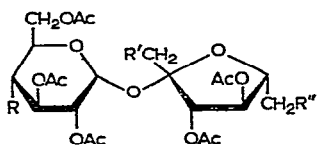
‡The "*galacto*" configuration inserted before "sucrose" implies that the D-glucopyranosyl residue has been changed to the indicated stereochemistry.

RESULTS AND DISCUSSION

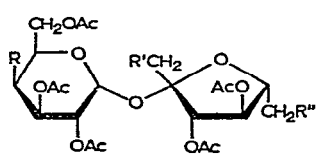
Detritylation of 1',6,6'-tri-*O*-tritylsucrose penta-acetate (**4**) with boiling, aqueous acetic acid afforded crystalline 2,3,3',4',6-penta-*O*-acetylsucrose[2] (**5**), in which the acetyl group at C-4 migrated to C-6, *via* a cyclic acetoxonium ion. Similarly, detritylation of 6,6'-di-*O*-tritylsucrose hexa-acetate (**2**) gave a hexa-acetate (**14**), isolated as a syrup, and characterised as 4,6'-di-*O*-mesylsucrose hexa-acetate (**15**). The occurrence of a C-4→C-6 acetyl migration was established by characterisation of the two products obtained by a benzoate displacement reaction on the 4,6'-dimethanesulphonate **15** in hexamethylphosphoric triamide, as the expected 4,6'-di-*O*-benzoyl-*galacto*-sucrose hexa-acetate (**19**) and the intermediary 6'-*O*-benzoyl-4-*O*-mesylsucrose hexa-acetate (**16**). The p.m.r. spectrum (Table I) of **19** was consistent with its structure, and a narrow, low-field quartet at τ 4.26 was indicative of H-4 of a galactopyranoside. However, the signal for H-3 of **16** was observed as a triplet, which was indicative of an H-2_{ax}, H-3_{ax}, and H-4_{ax} relationship, that is a glucopyranoside. Careful de-esterification of the 4-methanesulphonate **16**, followed



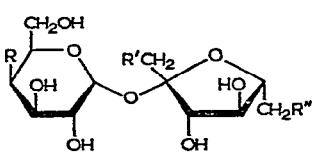
1 R=R"=H, R'=Tr
2 R=R"=Ac, R'=Tr
3 R=H, R'=R"=Tr
4 R=Ac, R'=R"=Tr



5 R=R'=R"=OH
6 R=OH, R'=R"=OTr
7 R=OAc, R'=R"=OTr
8 R=OMs, R'=R"=OTr
9 R=R'=OH, R"=OTr
10 R=R'=OAc, R"=OTr
11 R=R'=OMs, R"=OTr
12 R=OMs, R'=R"=OAc
13 R=R'=OMs, R"=OAc
14 R=R"=OH, R'=OAc
15 R=R"=OMs, R'=OAc
16 R=OMs, R'=OAc, R"=OBz
17 R=OMs, R'=OAc, R"=Br



18 R=Cl, R'=R"=OTr
19 R=R"=OBz, R'=OAc
20 R=R'=OBz, R"=OAc
21 R=OBz, R'=OMs, R"=OAc
22 R=N_3, R'=R"=OAc
23 R=Cl, R'=R"=OAc
24 R=R'=N_3, R"=OAc
25 R=R"=Br, R'=OAc
26 R=R"=N_3, R'=OAc
27 R=R"=Cl, R'=OAc
28 R=R'=R"=Cl



29 R=R'=R"=OH
30 R=R"=OH, R'=OMs
31 R=N_3, R'=R"=OH
32 R=Cl, R'=R"=OH
33 R=R'=N_3, R"=OH
34 R=R"=N_3, R'=OH
35 R=R"=Cl, R'=OH
36 R=R'=R"=Cl

TABLE I

^{1}H-N.M.R. PARAMETERS*: FIRST-ORDER CHEMICAL SHIFTS (τ) AND COUPLING CONSTANTS (Hz) AT 100 MHz

Compound	6[a]	8[a]	9[a]	9[b]	11[a]	16[a]	17[a]	19[a]	20[c]	21[c]	22[a]	24[c]	25[a]	26[a]	27[c]	28[c]
H-1	4.61d	4.10d	4.42d	4.15d	4.35d	4.23d	4.38d	4.25d	3.90d	3.98d	4.33d	4.10d	4.32d	4.28d	4.31d	4.21d
H-2	5.36q	5.24q	5.21q	5.33q	5.28q	4.85q	5.25q	4.77q	4.98q			5.24q	5.23q	5.18q	5.20q	4.44q
H-3	4.92t	4.89t	4.83t	4.94t	4.93t	4.59t	4.57t	4.52q		4.34q	4.83q	4.64q	4.68q	4.55q	4.58q	4.32q
H-4				4.48t	4.41t			4.26q	4.07q	4.17q			4.57q			
H-1′																
H-3′	4.22d	4.64d	4.65d	4.71d	4.66d	4.56d	4.56d		4.12d	4.30d	4.53d	4.18d	4.59d	4.50d	4.55d	4.22d
H-4′	4.53t	4.49t	4.40t	4.72t	4.57t	4.44t	4.40t		4.38t		4.64t	4.36t				4.62t
OAc	7.92–8.10	7.92–8.04	7.85–8.02	7.88–8.02	7.88–7.98	7.84–8.12	7.82–8.00	7.80–8.10	8.14–8.42	8.12–8.38	7.86–7.93	8.14–8.32	7.80–7.95	7.85–8.19	8.14–8.42	7.85–7.92
OTr	2.48–2.84	2.46–2.78	2.50–2.82	2.54–2.78	2.46–2.77											
OMs		7.24			6.90 7.20	6.95	6.89			7.52						
OBz						1.92–2.58		1.84–2.66	2.84–3.07							
$J_{1,2}$	4.0	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	4.0	3.5	3.83	4.0	4.0
$J_{2,3}$	10.0	10.0	9.5	9.5	10.0	10.5	10.0	10.5	10.0	10.0	10.0	10.0	10.0	10.5	10.0	11.0
$J_{3,4}$	10.0	10.0	9.5	9.5	10.0	10.5	10.0	3.8	3.5	3.5	3.8	4.0	3.5	3.8	4.0	3.5
$J_{4,5}$				9.5				1.5	1.5	1.5			1.5			
$J_{3',4'}$	7.0	7.5	6.0	7.5	9.0	6.0	6.5		6.5	5.5	6.5	7.0	6.5	6.5	7.0	7.0
$J_{4',5'}$	7.0	7.5	6.0	7.5	9.0	6.0	6.5		6.5		6.5	7.0				7.0

*Key: d = doublet, t = triplet, q = quartet. The resonances due to H-5, H-5′, H-6, and H-6′ appeared as a complex, overlapped multiplet in the region τ 5.5–6.0. [a]In $CDCl_3$. [b]In $CDCl_3$ after addition of trichloroacetyl isocyanate. [c]In C_6D_6.

by acetylation, afforded the known crystalline 4-*O*-mesylsucrose hepta-acetate[3] (**12**). Similar treatment of the 4,6′-dibenzoate **19** afforded crystalline β-D-fructofuranosyl α-D-galactopyranoside (**29**), first prepared[4] from the action of levan sucrase on raffinose and sucrose, and more recently from a benzoate displacement on 4-*O*-mesylsucrose hepta-acetate[3] (**12**).

Crystalline dibromo (**25**) and monobromo (**17**) derivatives were isolated in yields of 39 and 32%, respectively, when the 4,6′-dimethanesulphonate **15** was treated with lithium bromide in hexamethylphosphoric triamide. The p.m.r. spectrum of the dibromide **25** was in accord with a galactopyranoside, since the narrow, low-field quartet at τ 4.57 ($J_{3,4}$ 3.5 and $J_{4,5}$ 1.5 Hz) was attributed to H-4; consequently, the dibromide was 4,6′-dibromo-4,6′-dideoxy-*galacto*-sucrose hexa-acetate (**25**). Although the H-4 resonance of the monobromide **17** could not be located in the p.m.r. spectrum, H-3 was observed as a triplet at τ 4.57, and since this was indicative of a gluco-pyranoside, the monobromide was identified as 6′-bromo-6′-deoxy-4-*O*-mesylsucrose hexa-acetate (**17**). The structure of **17** was confirmed by a nucleophilic displacement reaction with azide anion in hexamethylphosphoric triamide. Thus, both the 4,6′-dimethanesulphonate **15** and the 6′-bromide-4-methanesulphonate **17** afforded the same diazide. Although the p.m.r. spectrum of the diazide did not show the H-4 resonance, a quartet at τ 4.55 was assigned to H-3, and the small $J_{3,4}$ value, indicative of an *ax–eq* system, characterised the product as 4,6′-diazido-4,6′-dideoxy-*galacto*-sucrose hexa-acetate (**26**). As both the 4,6′-disulphonate **15** and the 6′-bromide **17** afford the diazide **26**, the location of the bromine atom at C-6′ is confirmed.

The reaction of carbohydrates with sulphuryl chloride[5–10] usually results in the replacement of suitably placed hydroxyl groups by chloride, with inversion of configuration when the hydroxyl group is attached to a chiral centre. Initially, the chlorosulphate is formed, which, being an effective leaving-group[11], undergoes nucleophilic displacement with a chloride anion. According to rules enunciated by Richardson[12], all three hydroxyl groups in the 1′,4,6′-triol **5** should be replaced by chloride on reacting with sulphuryl chloride, although HO-1′ should be the least reactive, since it is adjacent to the anomeric position[13–16]. As expected, **5** gave 1′,4,6′-trichloro-1′,4,6′-trideoxy-*galacto*-sucrose penta-acetate (**28**). In the p.m.r. spectrum of **28**, the H-3 resonance at τ 4.32 was a quartet ($J_{2,3}$ 11.0, $J_{3,4}$ 3.5 Hz), which was characteristic of a galactopyranoside. Similar treatment of the 4,6′-diol **14** afforded a crystalline dichloride **27**, whose p.m.r. spectrum showed H-3 as a quartet ($J_{2,3}$ 10.0, $J_{3,4}$ 4.0 Hz) at τ 4.58 and hence characterised the compound as 4,6′-dichloro-4,6′-dideoxy-*galacto*-sucrose hexa-acetate (**27**). The same dichloride **27** was obtained when the 4,6′-disulphonate **15** was treated with lithium chloride in hexamethylphosphoric triamide.

2,3,3′,4′,6-Penta-*O*-acetylsucrose (**5**), previously synthesised by McKeown *et al.*[2], afforded a convenient starting-point to sucrose derivatives substituted at C-4, since Helferich[17] has shown the utility of tritylation for the selective blocking of primary hydroxyl groups. However, tritylation of the penta-acetate **5** gave two products, a mono- and a di-ether, even under forcing conditions. The location of the

trityl groups was ascertained after acetylation, when the di-ether gave 1′,6′-di-*O*-tritylsucrose hexa-acetate[18] (**7**) and the mono-ether gave 6′-*O*-tritylsucrose hepta-acetate[19] (**10**). Tritylation at HO-1′ appears to be subject to steric hindrance about the inter-glycosidic linkage. Thus, it follows that the mono-ether is 2,3,3′,4′,6-penta-*O*-acetyl-6′-*O*-tritylsucrose (**9**) having free 1′,4-hydroxyl groups. However, in the p.m.r. spectrum, the H-4 resonance was overlapped by the H-6 and H-6′ resonances. Addition of trichloroacetyl isocyanate, to form a carbamate with the free hydroxyl groups, caused the overlapped H-4 resonance to move downfield and to appear as a triplet at τ 4.48 ($J_{3,4} = J_{4,5} = 9.5$ Hz), together with two low-field singlets due to the two NH protons of the carbamate groups, confirming that the original compound was a diol. Subsequent mesylation of the di-ether **6** and mono-ether **9** afforded the corresponding 4-methanesulphonate **8** and 1′,4-dimethanesulphonate **11**; their p.m.r. spectra were in accord with the assigned structures.

Detritylation of the trityl-sulphonates **8** and **11**, using 45% hydrobromic acid in glacial acetic acid, followed by acetylation afforded 4-*O*-mesylsucrose hepta-acetate[3] (**12**) and 1′,4-di-*O*-mesylsucrose hexa-acetate (**13**). The p.m.r. spectrum of **13** could not be interpreted due to second-order characteristics, but its structure was confirmed by a study of the benzoate displacement reaction. Thus, treatment of **13** with benzoate anion in hexamethylphosphoric triamide afforded a mono- and a di-benzoate. The p.m.r. spectrum of the dibenzoate was in accord with a galacto-pyranoside, since H-4 appeared as a low-field quartet at τ 4.07 ($J_{3,4}$ 3.5, $J_{4,5}$ 1.5 Hz) and subsequent de-esterification afforded *galacto*-sucrose **29**, thereby identifying the product as 1′,4-di-*O*-benzoyl-*galacto*-sucrose hexa-acetate (**20**). The p.m.r. spectrum of the monobenzoate showed p.m.r. parameters similar to those of the dibenzoate **20**, in that H-4 was seen as a low-field quartet, and also revealed the presence of a mesyloxy group. De-esterification afforded 1′-*O*-mesyl-*galacto*-sucrose[20] (**30**); hence, the monobenzoate is 4-*O*-benzoyl-1′-*O*-mesyl-*galacto*-sucrose hexa-acetate (**21**), and the structure of the 1′,4-dimethanesulphonate **13** was confirmed.

Nucleophilic substitution of the 1′,4-di-*O*-mesyl groups in **13** with sodium azide in hexamethylphosphoric triamide gave a galactopyranoside, as indicated by the p.m.r. spectrum which was consistent with the expected 1′,4-diazido-1′,4-dideoxy-*galacto*-sucrose hexa-acetate (**24**). The 4-methanesulphonate **12** similarly gave 4-azido-4-deoxy-*galacto*-sucrose hepta-acetate (**22**).

The ditrityl ether **6**, having a free hydroxyl group at C-4, lent itself to two methods of chlorination. The same crystalline 4-chloride **18** was isolated after treatment with either sulphuryl chloride at −75° or mesyl chloride in *N*,*N*-dimethylformamide[21] at 65°; it has been shown[22] that prolonged treatment with the latter reagent results in chlorination at secondary positions. The p.m.r. spectrum of this 4-chloride **18** was largely second-order, and structural assignments were therefore based mainly on mass-spectral data. The spectrum showed two oxycarbonium ions at *m/e* 307 and 731, in the ratio 1:3, resulting from the cleavage of the two glycosidic linkages. Previous experience with mass spectrometry of sucrose derivatives has indicated that cleavage of the fructosyl glycosidic bond is the most favoured, initial

fragmentation, since this leads to a tertiary carbonium ion. Hence, the more intense fragment at *m/e* 731 appears to have risen from the fructosyl moiety. The fragmentation pattern of the 4-chloride **18** is shown in Fig. 1. Detritylation of 4-chloro-4-deoxy-1′,6′-di-*O*-trityl-*galacto*-sucrose penta-acetate (**18**), with 45% hydrobromic acid in glacial acetic acid, followed by acetylation gave the 4-chloro-hepta-acetate **23**, which was also isolated when the 4-methanesulphonate **12** was treated with lithium chloride in hexamethylphosphoric triamide. The mass spectrum of **23** was the same for both syntheses, and showed two oxycarbonium ions, at *m/e* 307 and 331, in a ratio of 1:2. The fragmentation pattern of the ion at *m/e* 307 was the same as that for **18**

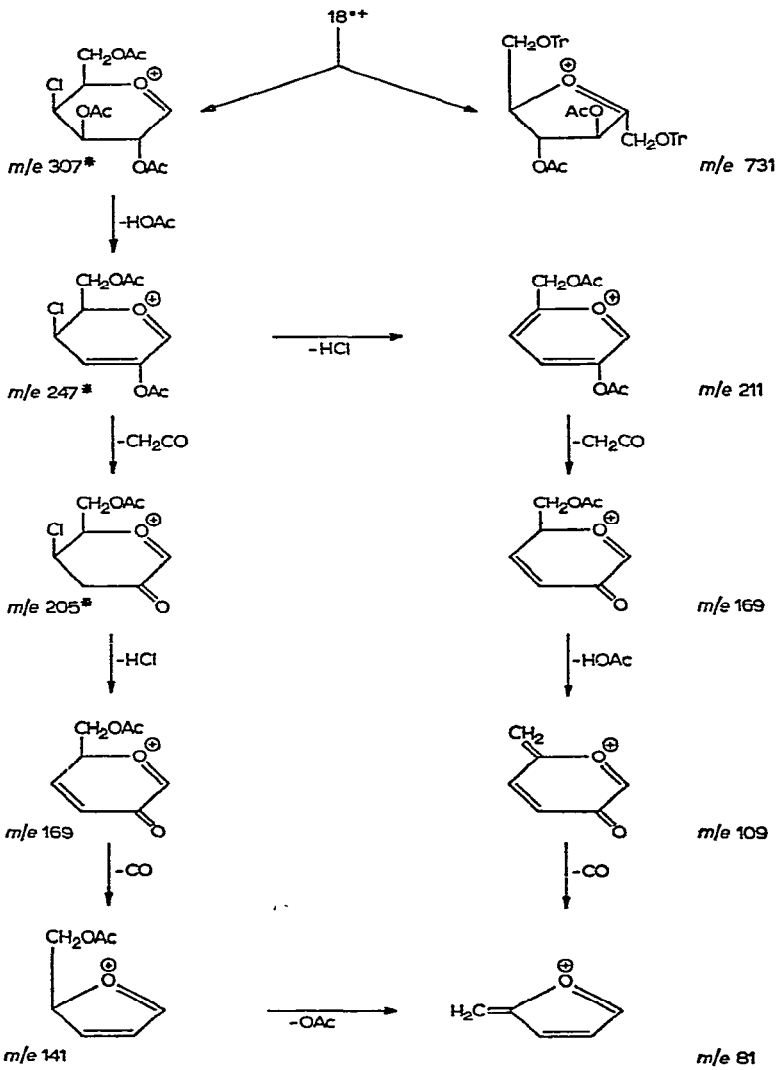


Fig. 1. Fragmentation pattern of the 4-chloride **18**. *Mass based on ^{35}Cl.

(Fig. 1), and since the 4-chloride **23** was isolated from a chloride-anion displacement on the 4-methanesulphonate **12**, it was shown to be 4-chloro-4-deoxy-*galacto*-sucrose hepta-acetate (**23**).

EXPERIMENTAL

For general procedures, see Part VI[23]; dry-column chromatography[24] was performed throughout with silica gel Merck 7734. Light petroleum (b.p. 60–80°) was used throughout. Unless otherwise stated, optical rotations were measured in chloroform at ~20°. Mass spectra were recorded with an A.E.I. M.S.-30 spectrometer.

1,3,4-Tri-O-*acetyl*-β-D-*fructofuranosyl 2,3,6-tri*-O-*acetyl*-α-D-*glucopyranoside* (**14**). — To a boiling solution of the 6,6′-ditrityl ether **2** (10 g) in glacial acetic acid (250 ml), water (5 ml) was added. The solution was heated under reflux for 30 min and cooled, and t.l.c. (chloroform–acetone, 2:1) then showed the presence of triphenylmethanol, the hexa-acetate **14**, and several minor components. The solution was evaporated to a syrup which was fractionated by dry-column chromatography on silica gel (250 g) with chloroform–acetone (4:1). Early fractions contained triphenylmethanol followed by the required hexa-acetate **14** (3.4 g, 65%) as a syrup, $[\alpha]_D$ +32.1° (*c* 1.7) (Found: C, 48.3; H, 5.8. $C_{24}H_{34}O_{17}$ calc.: C, 48.5; H, 5.7%).

1,3,4-Tri-O-*acetyl-6*-O-*mesyl*-β-D-*fructofuranosyl 2,3,6-tri*-O-*acetyl-4*-O-*mesyl*-α-D-*glucopyranoside* (**15**). — The hexa-acetate **14** (5 g) was dissolved in anhydrous pyridine and treated with mesyl chloride (1.7 g). After 24 h, the reaction mixture was poured into ice–water, and the precipitate was filtered off, washed, and recrystallised from ethanol to give **15** (10.5 g, 83%), m.p. 63–65°, $[\alpha]_D$ +47.8° (*c* 1.0) (Found: C, 42.0; H, 5.3; S, 8.4. $C_{26}H_{38}O_{21}S_2$ calc.: C, 41.7; H, 5.1; S, 8.6%).

The reaction of the 4,6′-dimethanesulphonate **15** *with sodium benzoate in hexamethylphosphoric triamide.* — Sodium benzoate (3.0 g) was added to a solution of **15** (3.0 g) in hexamethylphosphoric triamide (15 ml), and the resulting mixture was heated to 85°, with stirring for 3 days. T.l.c. (ethyl acetate–light petroleum, 1:1) then indicated two products moving faster than the starting material, and several minor components. The reaction mixture was diluted with anhydrous pyridine (15 ml) and acetylated *in situ* with acetic anhydride (5 ml). Fractionation on silica gel (100 g) with ethyl acetate–light petroleum (1:3) gave two products. Early fractions afforded 1,3,4-tri-*O*-acetyl-6-*O*-benzoyl-β-D-fructofuranosyl 2,3,6-tri-*O*-acetyl-4-*O*-benzoyl-α-D-galactopyranoside (**19**) (1.9 g, 59%), m.p. 64–66° (from aqueous ethanol), $[\alpha]_D$ +70.4° (*c* 0.2) (Found: C, 56.6; H, 5.2. $C_{38}H_{42}O_{19}$ calc.: C, 56.7; H, 5.2%). Later fractions crystallised from hot methanol to give 1,3,4-tri-*O*-acetyl-6-*O*-benzoyl-β-D-fructofuranosyl 2,3,6-tri-*O*-acetyl-4-*O*-mesyl-α-D-glucopyranoside (**16**) (0.6 g, 19%), m.p. 56–59°, $[\alpha]_D$ +56.6° (*c* 0.9) (Found: C, 49.8; H, 5.2; S, 4.0. $C_{32}H_{40}O_{20}S$ calc.: C, 49.5; H, 5.2; S, 4.1%).

β-D-*Fructofuranosyl* α-D-*galactopyranoside* (**29**). — A solution of the 4,6′-dibenzoate **19** (0.4 g) in dry methanol (10 ml) was treated with M methanolic sodium methoxide until the pH was ~9. The reaction mixture was stood overnight at room

temperature, and t.l.c. (chloroform–ethanol, 2:1) then showed one product, moving slower than the starting material. The solution was neutralised to pH 7 with Amberlite IR-50(H^+) resin and then concentrated to a syrup. Three extractions of the syrup with boiling light petroleum removed methyl benzoate, and crystallisation from ethanol afforded **29** (0.12 g, 80%), m.p. 171–173°, $[\alpha]_D$ +78.5° (*c* 0.8, ethanol); lit.[3] m.p. 179°, $[\alpha]_D$ +81.5° (Found: C, 42.0; H, 6.4. $C_{12}H_{22}O_{11}$ calc.: C, 42.1; H, 6.4%). Paper chromatography of an acid hydrolysate showed the presence of galactose and fructose.

*1,3,4,6-Tetra-*O*-acetyl-β-*D*-fructofuranosyl 2,3,6-tri-*O*-acetyl-4-*O*-mesyl-α-*D*-glucopyranoside* (**12**). — A solution of the 4-methanesulphonate **16** (1.0 g) in dry methanol (25 ml) was adjusted to pH ~9 and de-esterified as described above. The syrupy product (0.42 g, 78%) was acetylated, and crystallisation from aqueous ethanol gave the hepta-acetate (0.55 g, 77%), m.p. 91–93°, $[\alpha]_D$ +51.0° (*c* 0.7); lit.[3] m.p. 94–95°, $[\alpha]_D$ +25.2° (Found: C, 45.5; H, 5.3; S, 4.5. $C_{27}H_{38}O_{20}S$ calc.: C, 45.4; H 5.3; S, 4.5%).

The reaction of the 4,6′-dimethanesulphonate (**15**) *with lithium bromide in hexamethylphosphoric triamide.* — A solution of **15** (2.0 g) in hexamethylphosphoric triamide (10 ml) containing lithium bromide (2.0 g) was heated at 85°, with stirring, for 2 days. T.l.c. (ethyl acetate–light petroleum, 1:1) then showed two major products and some deacetylated products. The reaction mixture was cooled, diluted with anhydrous pyridine (15 ml), and acetylated *in situ* with acetic anhydride (5 ml). The mixture was processed in the usual way and the product fractionated on silica gel (120 g) with ethyl acetate–light petroleum (1:3). The early fractions gave a syrup, which crystallised from aqueous ethanol to give 1,3,4-tri-*O*-acetyl-6-bromo-6-deoxy-β-D-fructofuranosyl 2,3,6-tri-*O*-acetyl-4-bromo-4-deoxy-α-D-galactopyranoside (**25**) (0.74 g, 39%), m.p. 53–55°, $[\alpha]_D$ +40.8° (*c* 0.2) (Found: C, 40.4; H, 4.5; Br, 22.8. $C_{24}H_{32}Br_2O_{15}$ calc.: C, 40.0; H, 4.5; Br, 22.3%). The later fractions yielded a syrup, which crystallised slowly from methanol to give 1,3,4-tri-*O*-acetyl-6-bromo-6-deoxy-β-D-fructofuranosyl 2,3,6-tri-*O*-acetyl-4-*O*-mesyl-α-D-glucopyranoside (**17**) (0.63 g, 32%), m.p. 49–51°, $[\alpha]_D$ +33.2° (*c* 0.3) (Found: C, 41.2; H, 4.8; Br, 11.0; S, 4.0. $C_{25}H_{35}BrO_{18}S$ calc.: C, 40.9; H, 4.8; Br, 10.9; S, 4.3%).

*1,3,4-Tri-*O*-acetyl-6-azido-6-deoxy-β-*D*-fructofuranosyl 2,3,6-tri-*O*-acetyl-4-azido-4-deoxy-α-*D*-galactopyranoside* (**26**). — (*a*) A solution of the 4,6′-dimethanesulphonate **15** (1.0 g) in hexamethylphosphoric triamide (5 ml) containing sodium azide (2.0 g) was heated, with stirring, at 85° for 30 h. The cooled reaction mixture was poured into ice–water and the syrup which formed was extracted with ether (2 × 10 ml). The ethereal solution was washed successively with 2M hydrochloric acid, water, aqueous sodium hydrogen carbonate, and water, and dried (Na_2SO_4). Concentration afforded the 4,6′-diazide **26** (690 mg, 80%) as a syrup, $[\alpha]_D$ +41.3° (*c* 0.5) (Found: C, 44.7; H, 5.3; N, 13.5. $C_{24}H_{32}N_6O_{15}$ calc.: C, 44.7; H, 5.0; N, 13.1%).

(*b*) A solution of the 6′-bromo-4-sulphonate **17** (500 mg) in hexamethylphosphoric triamide (5 ml) containing sodium azide (500 mg) was heated with stirring at 85° for 30 h. The reaction mixture was processed in the usual way, giving a

syrupy product which was purified by p.l.c. (ethyl acetate–light petroleum, 2:3; detection with iodine). The resulting, syrupy diazide (330 mg, 75%) had $[\alpha]_D$ +39.5° (*c* 0.7) and was identical (i.r. spectrum) with the product described in (*a*).

*6-Azido-6-deoxy-β-*D*-fructofuranosyl 4-azido-4-deoxy-α-*D*-galactopyranoside* (**34**). — A solution of the hexa-acetate **26** (250 mg) in dry methanol was adjusted to pH ~9 with M methanolic sodium methoxide. After 12 h, the reaction mixture was processed in the usual manner, and the resulting solution was concentrated to a syrup (120 mg, 70%), $[\alpha]_D$ +63.8° (*c* 0.8, ethanol) (Found: C, 36.1; H, 4.9; N, 21.0. $C_{12}H_{20}N_6O_9$ calc.: C, 36.7; H, 5.1; N, 21.4%).

*3,4-Di-O-acetyl-1,6-dichloro-1,6-dideoxy-β-*D*-fructofuranosyl 2,3,6-tri-O-acetyl-4-chloro-4-deoxy-α-*D*-galactopyranoside* (**28**). — A solution of the triol **5** (2.0 g) in a 2:1 mixture (30 ml) of pyridine and ethanol-free chloroform was cooled to −75° (acetone–solid CO_2), and redistilled sulphuryl chloride (2.0 ml) was then added dropwise, during 15 min. The reaction mixture was stirred at −75° for 4 h and then allowed to attain room temperature. T.l.c. (chloroform–acetone, 9:1) showed the presence of a fast-moving product and some material at the base line. The reaction mixture was poured into ice–2M hydrochloric acid, and the chloroform layer was separated, washed successively with water, aqueous sodium hydrogen carbonate, and water, dried (Na_2SO_4), and concentrated. The syrupy product was fractionated on silica gel (50 g) with chloroform–acetone (12:1). The early fractions were concentrated to a syrup, which crystallised from aqueous ethanol, affording the 1′,4,6′-trichloride **28** (1.5 g, 67%), m.p. 92–94°, $[\alpha]_D$ +66.8° (*c* 0.9) (Found: C, 43.8; H, 4.9; Cl, 17.0. $C_{22}H_{29}Cl_3O_{13}$ calc.: C, 43.5; H, 4.8; Cl, 17.5%).

*1,6-Dichloro-1,6-dideoxy-β-*D*-fructofuranosyl 4-chloro-4-deoxy-α-*D*-galacto-pyranoside* (**36**). — A solution of the penta-acetate **28** (150 mg) in dry methanol was adjusted to pH ~9 with M methanolic sodium methoxide. After 12 h, the reaction mixture was processed in the usual manner, and the resulting solution was concentrated to give a syrup (65 mg, 69%), $[\alpha]_D$ +68.2° (*c* 1.1, ethanol) (Found: C, 36.0; H, 4.7; Cl, 27.3. $C_{12}H_{19}Cl_3O_8$ calc.: C, 36.2; H, 4.8; Cl, 27.1%).

*1,3,4-Tri-O-acetyl-6-chloro-6-deoxy-β-*D*-fructofuranosyl 2,3,6-tri-O-acetyl-4-chloro-4-deoxy-α-*D*-galactopyranoside* (**27**). — (*a*) A solution of the diol **14** (2.0 g) in a 2:1 mixture (30 ml) of pyridine and ethanol-free chloroform was cooled to −75° (acetone–solid CO_2), and redistilled sulphuryl chloride (1.5 ml) was then added dropwise during 15 min. The reaction mixture was stirred at −75° for 4 h and then allowed to attain room temperature. T.l.c. (chloroform–acetone, 9:1) showed the presence of a fast-moving product and some material at the base line. The reaction was processed as before and the syrup crystallised from 2-propanol, affording the 4,6′-dichloride **27** (1.6 g, 75%), m.p. 97–99°, $[\alpha]_D$ +59.5° (*c* 0.4) (Found: C, 45.6; H, 5.1; Cl, 11.1. $C_{24}H_{32}Cl_2O_{15}$ calc.: C, 45.7; H, 5.1; Cl, 11.3%).

(*b*) A solution of the 4,6′-dimethanesulphonate **15** (2.0 g) in hexamethylphosphoric triamide (10 ml) containing lithium chloride (3.0 g) was heated, with stirring, at 85° for 48 h. T.l.c. then indicated one product and some deacetylated products. The reaction mixture was acetylated *in situ*, under the normal conditions.

On pouring into ice–water, a precipitate formed, which was dried *in vacuo* and crystallised from 2-propanol, giving the 4,6′-dichloride **27** (1.2 g, 71%), m.p. 96–98°, $[\alpha]_D$ +59.1° (*c* 0.7), identical (i.r.) with the product from (*a*).

6-Chloro-6-deoxy-β-D-fructofuranosyl 4-chloro-4-deoxy-α-D-galactopyranoside (**35**). — To a solution of the hexa-acetate **27** (250 mg) in dry methanol (10 ml) was added M methanolic sodium methoxide until the pH was ~9. After 12 h, the solution was neutralised and processed as usual to give **35** as a syrup (98 mg, 83%), $[\alpha]_D$ +78.6° (*c* 1.2, ethanol) (Found: C, 37.6; H, 5.1; Cl, 18.2. $C_{12}H_{20}Cl_2O_9$ calc.: C, 38.0; H, 5.3; Cl, 18.8%).

3,4-Di-O-acetyl-β-D-fructofuranosyl 2,3,6-tri-O-acetyl-α-D-glucopyranoside (**5**). — A solution of the tritrityl ether **4** (10 g) in glacial acetic acid (250 ml) was detritylated, and the product was isolated as described above for the hexa-acetate **14**. The penta-acetate (3 g, 70%), crystallised from chloroform–light petroleum, had m.p. 152–154°, $[\alpha]_D$ +19.6° (*c* 1.0); lit.[2] m.p. 155–156°, $[\alpha]_D$ +22.0°.

Reaction of the penta-acetate **5** *with trityl chloride in pyridine.* — A solution of **5**[2] (6.0 g) in anhydrous pyridine (75 ml) was heated to 50°, and trityl chloride (12 g) in anhydrous pyridine (25 ml) was then added dropwise during 15 min. The reaction mixture was maintained at 50° for a further 18 h, with stirring, after which time t.l.c. (chloroform–acetone, 6:1) showed the presence of three products moving faster than the starting material. The reaction mixture was evaporated to a syrup (16.0 g), which was taken up in dichloromethane (100 ml), and the solution was washed successively with 2M hydrochloric acid, water, aqueous sodium hydrogen carbonate, and water, and dried (Na_2SO_4). The mixture was then fractionated on silica gel (250 g) with chloroform–acetone (10:1) to give the following three fractions. *A*: triphenylmethanol, m.p. 161–163°; lit. m.p. 164°; the i.r. spectrum was identical with that of an authentic sample. *B*: 3,4-di-*O*-acetyl-1,6-di-*O*-trityl-β-D-fructofuranosyl 2,3,6-tri-*O*-acetyl-α-D-glucopyranoside (**6**) (7.1 g, 61%), m.p. 105–107° (from 2-propanol), $[\alpha]_D$ +46.9° (*c* 1.0) (Found: C, 69.5; H, 6.1. $C_{60}H_{60}O_{16}$ calc.: C, 69.5; H, 5.8%). *C*: 3,4-di-*O*-acetyl-6-*O*-trityl-β-D-fructofuranosyl 2,3,6-tri-*O*-acetyl-α-D-glucopyranoside (**9**) (2.8 g, 32%), m.p. 146–148° (from methanol), $[\alpha]_D$ +27.1° (*c* 0.9) (Found: C, 61.3; H, 5.8. $C_{41}H_{45}O_{16}$ calc.: C, 62.0; H, 5.8%).

3,4-Di-O-acetyl-1,6-di-O-trityl-β-D-fructofuranosyl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside (**7**). — A solution of the 1′,6′-ditrityl ether **6** (300 mg) in anhydrous pyridine (5 ml) was acetylated in the usual way, and the product was crystallised from ethanol to give the hexa-acetate **7** (250 mg, 80%), m.p. 95–97°, $[\alpha]_D$ +63.6° (*c* 0.6); lit.[18] m.p. 95–98°, $[\alpha]_D$ +65.3°.

1,3,4-Tri-O-acetyl-6-O-trityl-β-D-fructofuranosyl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside (**10**). — A solution of the 6′-trityl ether **9** (300 mg) in anhydrous pyridine (5 ml) was acetylated in the usual way, and the product was crystallised from ethanol to give the hepta-acetate **10** (290 mg, 87%), m.p. 115–117°, $[\alpha]_D$ +55.6° (*c* 0.7); lit.[19] m.p. 118°, $[\alpha]_D$ +55.5°.

3,4-Di-O-acetyl-1,6-di-O-trityl-β-D-fructofuranosyl 2,3,6-tri-O-acetyl-4-O-mesyl-α-D-glucopyranoside (**8**). — Mesyl chloride (1.0 ml) was added dropwise to a

stirred solution of the 1′,6′-ditrityl ether **6** (4.0 g) in anhydrous pyridine (25 ml) at 0°, and the mixture was stirred overnight. Decomposition of the reaction mixture with ice–water afforded a solid, which was washed well with water and dried *in vacuo*. Crystallisation from acetone–methanol afforded the 4-methanesulphonate **8** (3.6 g, 84%), m.p. 111–114°, $[\alpha]_D$ +37.4° (*c* 0.5) (Found: C, 65.6; H, 5.6; S, 2.8. $C_{61}H_{62}O_{18}S$ calc.: C, 65.6; H, 5.6; S, 2.9%).

3,4-Di-O-acetyl-1-O-mesyl-6-O-trityl-β-D-fructofuranosyl 2,3,6-tri-O-acetyl-4-O-mesyl-α-D-glucopyranoside (**11**). — To a stirred solution of the 6′-trityl ether **9** (2.0 g) in anhydrous pyridine (15 ml) at 0°, mesyl chloride (1.0 ml) was slowly added. The reaction mixture was processed as usual and crystallisation from aqueous ethanol afforded **11** (2.0 g, 85%), m.p. 101–103°, $[\alpha]_D$ +51.8° (*c* 0.9) (Found: C, 54.5; H, 5.3; S, 6.6. $C_{43}H_{50}O_{20}S_2$ calc.: C, 54.3; H, 5.3; S, 6.8%).

1,3,4,6-Tetra-O-acetyl-β-D-fructofuranosyl 2,3,6-tri-O-acetyl-4-O-mesyl-α-D-glucopyranoside (**12**). — A stirred solution of the 4-methanesulphonate **8** (3.5 g) in chloroform (15 ml) at 0° was treated with a solution of 45% hydrobromic acid in glacial acetic acid (3 ml). After 20 min, the reaction mixture was poured into ice and aqueous sodium hydrogen carbonate, and the chloroform layer was washed with water, dried (Na_2SO_4), and concentrated to a syrup which was acetylated in the normal manner. Crystallisation from ethanol afforded the hepta-acetate **12** (1.9 g, 84%), m.p. 92–94°, $[\alpha]_D$ +48.7° (*c* 0.5); lit.[3] m.p. 94–95°, $[\alpha]_D$ +25.2°.

3,4,6-Tri-O-acetyl-1-O-mesyl-β-D-fructofuranosyl 2,3,6-tri-O-acetyl-4-O-mesyl-α-D-glucopyranoside (**13**). — The 6′-monotrityl ether **11** (2.0 g), dissolved in chloroform (10 ml), at 0°, was detritylated and then acetylated, as described above. Crystallisation from methanol afforded the hexa-acetate **13** (1.2 g, 76%), m.p. 61–64°, $[\alpha]_D$ +41.7° (*c* 0.8) (Found: C, 41.8; H, 5.3; S, 8.3. $C_{26}H_{38}O_{21}S_2$ calc.: C, 41.6; H, 5.1; S, 8.5%).

The reaction of the 1′,4-dimethanesulphonate **13** *with sodium benzoate in hexamethylphosphoric triamide.* — Sodium benzoate (3.0 g) was added to a solution of **13** (3.0 g) in hexamethylphosphoric triamide (15 ml), and the resulting mixture was heated with stirring at 85° for 3 days. T.l.c. (ethyl acetate–light petroleum, 1:1) indicated the presence of two major products, and some deacetylated products. The reaction mixture was acetylated *in situ*, and t.l.c. then showed only two products, which were fractionated on silica gel (150 g) with ethyl acetate–light petroleum (1:3). The first fractions afforded a syrup, which crystallised from aqueous ethanol to give 3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-β-D-fructofuranosyl 2,3,6-tri-*O*-acetyl-4-*O*-benzoyl-α-D-galactopyranoside (**20**) (1.5 g, 47%), m.p. 59–61°, $[\alpha]_D$ +54.6° (*c* 0.9) (Found, C, 56.4; H, 5.1. $C_{38}H_{42}O_{19}$ calc.: C, 56.7; H, 5.2%). The later fractions gave a syrup, which crystallised from aqueous ethanol to afford 3,4,6-tri-*O*-acetyl-1-*O*-mesyl-β-D-fructofuranosyl 2,3,6-tri-*O*-acetyl-4-*O*-benzoyl-α-D-galactopyranoside (**21**) (0.9 g, 29%), m.p. 64–66°, $[\alpha]_D$ +59.8° (*c* 0.5) (Found: C, 49.9; H, 5.1; S, 4.1. $C_{32}H_{40}O_{20}S$ calc.: C, 49.5; H, 5.2; S, 4.1%).

De-esterification of the dibenzoyl hexa-acetate **20** (500 mg), in the usual way, afforded a syrup which crystallised from ethanol to give β-D-fructofuranosyl α-D-

galactopyranoside (**29**) (180 mg, 85%), m.p. 172–174°, $[\alpha]_D$ +79·8° (*c* 0.8, ethanol).

1-O-Mesyl-β-D-fructofuranosyl α-D-galactopyranoside (**30**). — A solution of the monomethanesulphonate **21** (1.0 g) in dry methanol (25 ml) was adjusted to pH ~9 with M methanolic sodium methoxide, stood overnight at room temperature, then neutralised as usual, and evaporated. The syrupy residue was washed with boiling light petroleum to remove methyl benzoate and then crystallised from hot ethanol to give **30** (0.38 g, 89%), m.p. 156–157°, $[\alpha]_D$ +68.7° (*c* 0.5, ethanol); lit.[20] m.p. 158–161°, $[\alpha]_D$ +70.1°.

3,4,6-Tri-O-acetyl-1-azido-1-deoxy-β-D-fructofuranosyl 2,3,6-tri-O-acetyl-4-azido-4-deoxy-α-D-galactopyranoside (**24**). — A solution of the dimethanesulphonate **13** (2.0 g) in hexamethylphosphoric triamide (10 ml) containing sodium azide (2.0 g) was heated with stirring at 85° for 36 h, after which time t.l.c. (ethyl acetate–light petroleum, 1:1) showed one product moving faster than the starting material. After cooling to room temperature, the reaction mixture was poured into ice–water, and the syrupy product was extracted with ether. The extract was washed successively with 2M hydrochloric acid, water, and aqueous sodium hydrogen carbonate, and dried (Na_2SO_4). Evaporation gave the diazide **24** (1.4 g, 80%) as a syrup, $[\alpha]_D$ +46.0° (*c* 0.2) (Found: C, 44.9; H, 5.1; N, 13.0. $C_{24}H_{32}N_6O_{15}$ calc.: C, 44.7; H, 5.0; N, 13.4%).

1-Azido-1-deoxy-β-D-fructofuranosyl 4-azido-4-deoxy-α-D-galactopyranoside (**33**). — The hexa-acetate **24** (100 mg) was dissolved in dry methanol (5 ml) and treated with M methanolic sodium methoxide until the pH was ~9. The diazide **33** was isolated as a syrup (58 mg, 84%), $[\alpha]_D$ +77.4° (*c* 0.5, ethanol) (Found: C, 36.1; H, 5.0; N, 20.6. $C_{12}H_{20}N_6O_9$ calc.: C, 36.7; H, 5.1; N, 21.4%).

1,3,4,6-Tetra-O-acetyl-β-D-fructofuranosyl 2,3,6-tri-O-acetyl-4-azido-4-deoxy-α-D-galactopyranoside (**22**). — The monomethanesulphonate **12** (2.0 g) was dissolved in hexamethylphosphoric triamide (10 ml), and sodium azide (2.0 g) was added. The reaction mixture was heated at 85°, with stirring, for 24 h, and t.l.c. (ethyl acetate–light petroleum, 1:1) then indicated one product, moving faster than the starting material; no deacetylation was observed. The reaction mixture was processed in the usual way, to give, on crystallisation from aqueous ethanol, the monoazide **22** (1.3 g, 72%), m.p. 97–99°, $[\alpha]_D$ +47.4° (*c* 0.2) (Found: C, 47.4; H, 5.5; N, 6.3. $C_{26}H_{35}N_3O_{17}$ calc.: C, 47.2; H, 5.3; N, 6.4%).

β-D-Fructofuranosyl 4-azido-4-deoxy-α-D-galactopyranoside (**31**). — A solution of the hepta-acetate **22** (500 mg) in dry methanol (20 ml) was adjusted to pH ~9 with M methanolic sodium methoxide. After 12 h, the solution was neutralised with Amberlite IR-50(H^+) resin and evaporated to a syrup, which crystallised from methanol to give the monoazide **31** (230 mg, 83%), m.p. 116–119°, $[\alpha]_D$ +80.1° (*c* 0.6, ethanol) (Found: C, 39.2; H, 5.9; N, 11.5. $C_{12}H_{21}N_3O_{10}$ calc.: C, 39.2; H, 5.7; N, 11.5%).

3,4-Di-O-acetyl-1,6-di-O-trityl-β-D-fructofuranosyl 2,3,6-tri-O-acetyl-4-chloro-4-deoxy-α-D-galactopyranoside (**18**). — (*a*) A solution of the ditrityl ether **6** (2.0 g) in a mixture of pyridine (20 ml) and ethanol-free chloroform (10 ml) was cooled to −75°,

and redistilled sulphuryl chloride (0.5 ml) was added dropwise during 15 min to the stirred solution. After stirring for 4 h at −75°, the mixture was allowed to attain room temperature and then poured into a mixture of M hydrochloric acid and ice. The resulting chloroform layer was washed successively with water, aqueous sodium hydrogen carbonate, and water, dried (Na_2SO_4), and concentrated to dryness. The residue was fractionated on silica gel (50 g) with chloroform–acetone (12:1). The early fractions gave a syrup which crystallised from hot methanol, affording the 4-chloride **18** (1.4 g, 69%), m.p. 101–103°, $[\alpha]_D$ +73.4° (*c* 0.7) (Found: C, 68.7; H, 5.5; Cl, 3.5. $C_{60}H_{59}ClO_{15}$ calc.: C, 68.3; H, 5.6; Cl, 3.4%).

(*b*) To a solution of the trityl ether **6** (0.5 g) in *N*,*N*-dimethylformamide (5 ml) at 65°, mesyl chloride (1.0 g) was added dropwise with stirring. The mixture was maintained at 65° for 15 h and then concentrated to dryness, and the residue was fractionated on silica gel (25 g) with ethyl acetate–light petroleum (1:2). The middle fractions gave a syrup, which crystallised from methanol to afford the 4-chloride **18** (0.3 g, 60%), m.p. and mixture m.p. 99–100°, $[\alpha]_D$ +72.8° (*c* 0.9).

1,3,4,6-Tetra-O-*acetyl*-β-D-*fructofuranosyl 2,3,6-tri*-O-*acetyl-4-chloro-4-deoxy*-α-D-*galactopyranoside* (**23**). — (*a*) To a solution of the 4-chloride **18** (1.0 g) in chloroform (10 ml) cooled to 0°, a solution of 45% hydrobromic acid in glacial acetic acid (2 ml) was added dropwise, and the resulting mixture was stirred at 0°. After 20 min, t.l.c. (chloroform–acetone, 9:1) showed a fast-moving, yellow spot (triphenylmethanol), and a product moving slower than the starting material. The mixture was poured into a mixture of ice and aqueous sodium hydrogen carbonate, and the chloroform layer was washed with water, dried (Na_2SO_4), and concentrated to a syrup, which was acetylated in anhydrous pyridine (10 ml) with acetic anhydride (5 ml). After 24 h, the reaction mixture was poured into ice–water, and the resulting precipitate was dried *in vacuo* and then purified by elution from silica gel (30 g) with chloroform–acetone (12:1). Later fractions contained the hepta-acetate **23** (0.45 g, 73%), m.p. 74–76° (from 2-propanol), $[\alpha]_D$ +56.8° (*c* 0.6) (Found: C, 48.0; H, 5.6; Cl, 5.4. $C_{26}H_{35}ClO_{17}$ calc.: C, 47.7; H, 5.4; Cl, 5.4%).

(*b*) A solution of the monomethanesulphonate **12** (1.0 g) in hexamethylphosphoric triamide (10 ml) containing lithium chloride (2.0 g) was heated, with stirring, at 85° for 3 days. The reaction mixture was acetylated *in situ*, and crystallisation from 2-propanol afforded the hepta-acetate **23** (0.7 g, 73%), m.p. and mixture m.p. 75–77°, $[\alpha]_D$ +57.9° (*c* 0.9).

β-D-*Fructofuranosyl 4-chloro-4-deoxy*-α-D-*galactopyranoside* (**32**). — The hepta-acetate **23** (500 mg) was dissolved in dry methanol (10 ml), and the pH was adjusted to ~9 with M methanolic sodium methoxide. After 12 h, the solution was neutralised in the usual way. The product crystallised from methanol, affording **32** (210 mg, 78%), m.p. 106–108°, $[\alpha]_D$ +84.6° (*c* 0.8, ethanol) (Found: C, 39.8; H, 5.7; Cl, 10.1. $C_{12}H_{21}ClO_{10}$ calc.: C, 39.9; H, 5.8; Cl, 9.9%).

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