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THE USE OF PIVALIC ESTERS OF SUCROSE FOR THE SYNTHESIS OF CHLORO, AZIDO, AND ANHYDRO DERIVATIVES*

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ABSTRACT

2,3,6,1′,2′,3′,6′-Hepta-*O*-pivaloylsucrose, readily available from sucrose, has been converted into 4-chloro-4-deoxy-*galacto*-sucroses, 4-amino-4-deoxy-*galacto*-sucrose, and 4-deoxysucrose, *via* nucleophilic displacement reactions. Similarly, 3,6,1′,3′,4′,6′-hexa-*O*-pivaloylsucrose and other readily available hexa-, penta-, and tri-pivalates have been converted into chloro and azido derivatives and also into various epoxides.

INTRODUCTION

The selective pivaloylation of sucrose under a variety of conditions afforded several partially pivaloylated sucroses in reasonably good yields[1]. We now report on their potential as starting materials in the synthesis of sucrose analogues.

RESULTS AND DISCUSSION

The 2,3,6,1′,3′,4′,6′-heptapivalate **1** is readily available (50% yield from sucrose[1]) and HO-4 reacted readily with sulphuryl chloride with inversion of configuration, to give 92% of the crystalline 4-chloro-4-deoxy-*galacto*-sucrose derivative **3**. Alternatively, **3** could be prepared from the 4-mesylate **2** by reaction with lithium chloride in *N,N*-dimethylformamide. *O*-Depivaloylation of **3** afforded 92% of crystalline 4-chloro-4-deoxy-*galacto*-sucrose (**8**). Similarly, reaction of **2** with sodium azide in hexamethylphosphoric triamide afforded 92% of the syrupy 4-azide **4**, *O*-depivaloylation of which gave crystalline 4-azido-4-deoxy-*galacto*-sucrose (**5**) in quantitative yield. The melting points of both **8** and **5** are at variance with, but higher than, the reported values[2]. However, the ^{1}H-n.m.r. spectra of **3** and **4** (Table I) indicate beyond doubt the structures of the products. A subsequent direct comparison of **5** (m.p. 193–195°) with the product (m.p. 116–119°) prepared previ-

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TABLE I

^{1}H-N.M.R. (220 MHz) PARAMETERS (δ AND Hz) FOR SOLUTIONS IN HEXADEUTERIOBENZENE

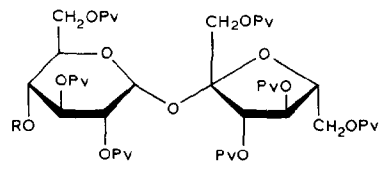
	3[a]	**4**	**13**	**14**	**15**	**16**	**21**	**22**	**24**
H-1	5.74d	5.89d	5.99d	5.56d	5.87d	6.06d	6.14d	6.04d	5.96d
H-2	5.26dd	5.44dd	5.36dd	4.40dd	5.19dd	5.37dd	5.63dd	5.47dd	5.07dd
H-3	5.39dd	5.83dd	5.59dd	5.39dd	5.57dd	5.68dd	5.68dd	5.60dd	5.60dd
H-4	4.60dd		4.82dd	4.69dd	4.06dd	4.86m	4.98bd	4.90dd	
H-5	4.74t		4.91br t	4.77t	4.70t		4.90t	4.81t	
H-6a							4.72dd		
H-6b							4.35dd		
H-1′a	4.01d			4.56d		4.68d	4.63d	4.68d	4.68d
H-1′b	3.94d			4.37d		4.46d	4.42d	4.35d	4.44d
H-3′	5.56d	4.17s	5.88d	5.67d	5.80d	5.58d	5.59d	5.52d	5.62d
H-4′	5.40t		5.68t	5.60t	5.62t	5.83t	5.87t	5.72t	5.44t
H-5′						4.23td	4.14td	4.14td	
H-6′a							4.50dd		
H-6′b							4.30dd		
$J_{1,2}$	3.5	3.0	3.5	3.5	3.5	3.5	3.0	3.5	4.0
$J_{2,3}$	10.5	8.5	10.5	10.5	10.5	11	10.5	11	10.0
$J_{3,4}$	4.0	3.5	3.5	3.5	3.5	3.5	3.0	3.5	4.0
$J_{4,5}$	1		1.5	1.5	1.5			1.5	
$J_{5,6a}$				6	6		5.5	6	
$J_{5,6b}$				6	6		5.0	6	
$J_{6a,6b}$							10.5		
$J_{1'a,1'b}$	11.0			11.0		12.5	11.8	12.0	12.0
$J_{3',4'}$	8.0		7.0	7.0	7.5	7.5	8.0	7.5	7.0
$J_{4',5'}$	8.0		7.0	7.0	7.5	7.5	8.0	7.5	7.0
$J_{5',6'a}$	6					7.5	5.5	7.5	
$J_{5',6'b}$	6					3	2.5	3.5	
$J_{6'a,6'b}$							12.5		

[a] In $CDCl_3$

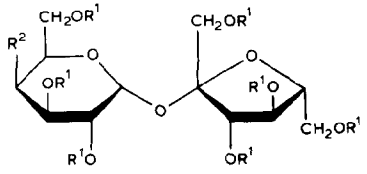
ously indicated that they were identical (i.r.), but, in both cases, the m.p. had risen to 201–203°. It is possible that **5** may exist in two forms and that the lower-melting form may slowly be converted into the higher-melting form on storage. Unfortunately, a direct comparison of the two samples of **8** was not possible.

Reductive dehalogenation of 4-chloro-4-deoxy-*galacto*-sucrose (**8**) by hydrogenation with Raney nickel in methanolic potassium hydroxide afforded 77% of crystalline 4-deoxysucrose (**9**), and catalytic hydrogenation of the 4-azide **5** yielded 81% of crystalline 4-amino-4-deoxy-*galacto*-sucrose (**6**), which afforded a syrupy octa-actate **7**.

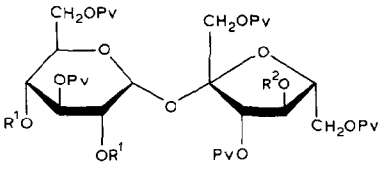
3,6,1′,3′,4′,6′-Hexa-*O*-pivaloylsucrose (**10**) was also readily available[1] and reacted selectively with sulphuryl chloride, as expected, only at O-4 to give the 4-chloro derivative **14** in good yield. Likewise, the 2,4-dimesylate **11** also underwent selective displacement at C-4 with lithium chloride in *N*,*N*-dimethylformamide to give the 4-chloride **13** in which the 2-*O*-sulphonyl group was still present. The lack of reactivity of sulphonate groups located adjacent to the anomeric position is



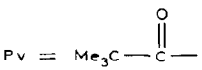
1 R = H
2 R = Ms



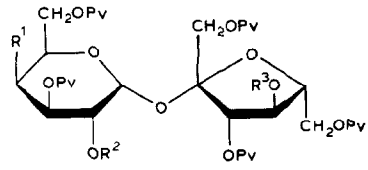
3 R^1 = Pv, R^2 = Cl
4 R^1 = Pv, R^2 = N_3
5 R^1 = H, R^2 = N_3
6 R^1 = H, R^2 = NH_2
7 R^1 = Ac, R^2 = NHAc
8 R^1 = H, R^2 = Cl
9 R^1 = R^2 = H



10 R^1 = H, R^2 = Pv
11 R^1 = Ms, R^2 = Pv
12 R^1 = R^2 = Ms



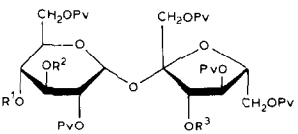
Pv = Me_3C—C(=O)—



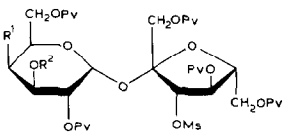
13 R^1 = Cl, R^2 = Ms, R^3 = Pv
14 R^1 = Cl, R^2 = H, R^3 = Pv
15 R^1 = N_3, R^2 = Ms, R^3 = Pv
16 R^1 = Cl, R^2 = R^3 = $MeSO_2$

well known[3]. As anticipated, **11** underwent selective displacement with the azide anion to give the syrupy 4-azide **15**.

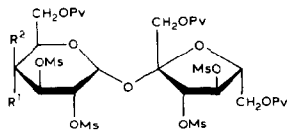
The other mesylated pivalates which were readily available from the selective pivaloylation, namely, 2,4,4′-tri-*O*-mesylsucrose pentapivalate (**12**), 3,4,3′-tri-*O*-mesylsucrose pentapivalate (**19**), and 2,3,4,3′,4′-penta-*O*-mesylsucrose tripivalate (**23**), each underwent selective displacement at the 4-position with either chloride or azide to give the appropriate derivatives **16, 22,** and **24** in good yields (80–95%); no other products were detected.



17 R^1 = R^3 = H, R^2 = Pv
18 R^1 = R^3 = Ms, R^2 = Pv
19 R^1 = R^2 = R^3 = Ms
20 R^1 = Pv, R^2 = R^3 = Ms



21 R^1 = Cl, R^2 = Pv
22 R^1 = Cl, R^2 = Ms



23 R^1 = OMs, R^2 = H
24 R^1 = H, R^2 = Cl

3′,4′-Anhydro derivatives of sucrose have been synthesised[4] by conventional procedures from 3′- and 4′-tosylates and from the 3′,4′-ditosylate, and directly[5,6] by reaction of either sucrose 2,3,4,6,1′,6′-hexabenzoate, and 4,6:2,1′-di-*O*-isopropylidenesucrose with triphenylphosphine–diethyl azodicarboxylate. A 3′,4′-epoxide was also produced directly from sucrose by the same reagent, except that HO-6 was selectively blocked by the incorporation of acetic acid into the reaction mixture. In each reaction, the corresponding derivative of 3,4-anhydro-β-D-tagatofuranosyl α-D-glucopyranoside was produced as the only 3′,4′-anhydride. Therefore, it was of interest to see whether the mesylated pivalic esters could function as convenient precursors of other oxiranes, although isomerisation to other anhydro derivatives might be expected.

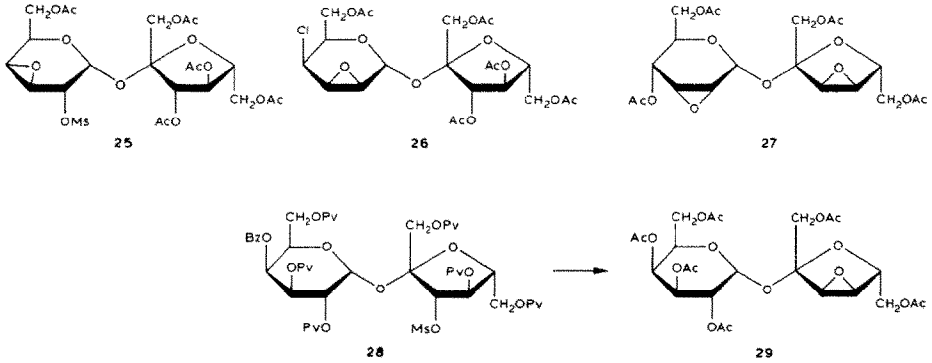
Treatment of the 2,4-dimesylate **11** with an excess of sodium methoxide at room temperature gave a complex mixture of products. Acetylation and then column chromatography gave one major component **25** in 25% yield; no other pure products were isolated. The ^{1}H-n.m.r. spectrum of **25** indicated that the 2-*O*-mesyl group was still intact (δ 2.43) because the H-1 resonance appeared as a doublet (δ 5.51, $J_{1,2}$ 4.0 Hz). Had there been a 2,3-anhydro group, the *cis* relationship of H-1,2 would have given rise to a near-zero coupling[7]. Similarly, the lack of H-2,3 coupling indicated that these protons were *trans* and that H-3 was attached to the oxirane ring. The remainder of the spectrum was in complete accord with the structure proposed; in particular, the high-field positions of the H-3 and H-4 doublets at δ 3.2 and 2.78, respectively, indicated that they were attached to an

TABLE II

^{1}H-N M R (220 MHz) DATA (δ AND Hz) FOR ANHYDRIDES[a]

	25	**26**	**27**	**29**
H-1	5 51d	5.74s	5.32d	5.88d
H-2	4.67d	2 82d	3 04dd	5 50dd
H-3	3 20d	2.90dd	3.26d }	5.71m
H-4	2.78dd	3 96dd	5 12dd }	
H-5				4.44t
H-1′a			4 66d	4.58d
H-1′b			4.33d	4.30d
H-3′	5.73d	5.69d	3.76d	3 72d
H-4′	5 58t		3.38d	3 37d
$J_{1,2}$	4.0	0	3 0	4.0
$J_{2,3}$	0	3.5	4 0	10.0
$J_{3,4}$	4 5	6.0	1 5	4 0
$J_{4,5}$	1 5	3.5	10.0	1
$J_{5,6a}$				6
$J_{5,6b}$				6
$J_{1'a,1'b}$			12 5	12 5
$J_{3',4'}$	6.0		3.0	2 5
$J_{4',5'}$	6 0		0	0

[a]In hexadeuteriobenzene



oxirane ring (Table II). The formation of the D-*galacto*-3,4-epoxide rather than the D-*manno*-2,3-epoxide was not unexpected since it is well known[3] that displacements at C-4 are much more favourable than those at C-2, although the formation of some of the 2,3-epoxide cannot be excluded.

Treatment of the 4-chloro-2-mesylate **13** with base resulted in a much cleaner reaction, affording, after *O*-acetylation, 67% of the crystalline D-*talo*-2,3-epoxide **26**. The overlap of signals in the ^{1}H-n.m.r. spectrum of **26** prevented complete interpretation, but the signals for H-1,2,3,4 were clearly observed and in complete accord with the structure (Table II). The high yield of the 2,3-epoxide **26** was undoubtedly due to the fact that the 2,3-epoxide was unable to rearrange into the 3,6-anhydride because of its *cis* relationship to C-6.

The reaction of the 3,3′-dimesylate **20** with base afforded the 2,3:3′,4′-diepoxide which was isolated as the syrupy tetra-*O*-acetyl derivative **27** (37% yield after column chromatography). The structure of **27** was confirmed by its ^{1}H-n.m.r. spectrum in which four high-field C*H* resonances in the range δ 3.04–4.76 were indicative of two oxirane rings. The $J_{1,2}$ and $J_{3,4}$ couplings (3.0 and 1.8 Hz, respectively) were indicative of H-1,2 and H-3,4 being *cis* (Table II).

3-*O*-Mesyl-1,4,6-tri-*O*-pivaloyl-β-D-fructofuranosyl 4-*O*-benzoyl-2,3,6-tri-*O*-pivaloyl-α-D-galactopyranoside (**28**) is readily available by treatment of the 4,3′-dimesylate **18** with benzoate anion in *N*,*N*-dimethylformamide[1]. Brief reaction of **28** with boiling methanolic sodium methoxide followed by *O*-acetylation afforded 71% of the syrupy D-*ribo*-3′,4′-epoxide **29**, the structure of which was indicated by its ^{1}H-n.m.r. spectrum in which the oxirane ring resonances at δ 3.72 and 3.37 closely corresponded to the values found for H-3′,4′ in the spectrum of the diepoxide **27**, indicating that the furanoside ring was identical in both compounds.

EXPERIMENTAL

For general procedures, see ref. 1.

4-Chloro-4-deoxy-2,3,6-tri-O-*pivaloyl-*α-D-*galactopyranosyl 1,3,4,6-tetra*-O-*pivaloyl-*β-D-*fructofuranoside* (**3**). — (*a*) To a stirred solution of the 4-mesylate[1] **2**

(3 g, 3 mmol) in dry *N,N*-dimethylformamide (30 mL) was added an excess of lithium chloride (3 g) and a trace of iodine as catalyst. The mixture was stirred at 120–125° for 24 h, when t.l.c. (ether–light petroleum, 1:1) indicated that the reaction was complete and that a faster-moving compound had been formed. The mixture was then cooled and poured into ice–water, and the precipitated product was extracted with ether. The extract was washed well with water, dried ($MgSO_4$), and concentrated to dryness. Recrystallisation of the residue from light petroleum gave **3** (2.5 g, 89%), m.p. 95–96°, $[\alpha]_D$ +58° (*c* 1, methanol) (Found: C, 60.0; H, 8.3; Cl, 4.0. $C_{47}H_{77}ClO_{17}$ calc.: C, 59.5; H, 8.1; Cl, 3.8%). Mass spectrum: *m/z* 499 (6%), 435 (4), 433 (12), 331 (4), 297 (1), 295 (11), 211 (5), 109 (3), 85 (32), 57 (100).

(*b*) To a solution of the heptapivalate[1] **1** (3 g) in pyridine (30 mL) at −30° was added sulphuryl chloride (3 mL) dropwise with stirring. The reaction mixture was then allowed to attain room temperature. After 6 h, t.l.c. (ether–light petroleum, 1:1) indicated that the reaction was complete and that a faster-moving material had been formed. The mixture was then poured into ice-cold, aqueous 10% sulphuric acid, and the precipitated product was extracted with dichloromethane. The extract was washed well with aqueous sodium hydrogencarbonate and water, dried ($MgSO_4$), and concentrated to dryness. Recrystallisation of the residue afforded **3** (2.75 g, 90%).

O-Depivaloylation in the usual way with sodium methoxide initially afforded a syrup which crystallised after column chromatography (ethyl acetate–methanol, 10:1) to give 4-chloro-4-deoxy-α-D-galactopyranosyl β-D-fructofuranoside (**8**; 0.35 g, 92%), m.p. 146–148° (from ethyl acetate–methanol), $[\alpha]_D$ +67° (*c* 0.8, ethanol); lit.[2] m.p. 106–108°, $[\alpha]_D$ +84.6° (ethanol) (Found: C, 39.5; H, 5.8; Cl, 9.6. $C_{12}H_{21}ClO_{10}$ calc.: C, 40.0; H, 5.8; Cl, 9.9%).

*4-Azido-4-deoxy-2,3,6-tri-*O*-pivaloyl-α-*D*-galactopyranosyl 1,3,4,6-tetra-*O*-pivaloyl-β-*D*-fructofuranoside* (**4**). — Sodium azide (1 g) was added to a solution of **2** (1 g) in hexamethylphosphoric triamide (10 mL), and the mixture was then stirred at 85° for 12 h, when t.l.c. (ether–light petroleum, 1:1.5) indicated that the reaction was complete. The mixture was then cooled and extracted with ether, and the extract was washed well with water, dried ($MgSO_4$), and concentrated to dryness. The resulting syrupy **4** (0.85 g, 85%) had $[\alpha]_D$ +31° (*c* 1, methanol) (Found: C, 59.1; H, 8.1; N, 4.0. $C_{47}H_{77}N_3O_{17}$ calc.: C, 59.1; H, 8.1; N, 4.4%). Mass spectrum: *m/z* 499 (6%), 440 (0.2), 296 (3), 295 (18), 211 (9), 195 (2), 109 (7), 85 (31), 57 (100).

O-Depivaloylation of **4** in the usual way with sodium methoxide afforded 4-azido-4-deoxy-α-D-galactopyranosyl β-D-fructofuranoside (**5**, 91%), m.p. 201–203° (from ethanol), $[\alpha]_D$ +82° (*c* 0.6, ethanol); lit.[2] m.p. 112–115°, $[\alpha]_D$ +80° (ethanol) (see Discussion Section) (Found: C, 39.7; H, 5.5; N, 11.3. $C_{12}H_{21}N_3O_{10}$ calc.: C, 39.2; H, 5.7; N, 11.5%).

*4-Amino-4-deoxy-α-*D*-galactopyranosyl β-*D*-fructofuranoside* (**6**). — To a solution **5** (0.2 g) in ethanol was added 10% Pd/C, and the mixture was then hydro-

genated at 60 p.s.i. for 2 h, when t.l.c. (water–ethanol–ethyl acetate, 8:1:1) indicated that the reaction was complete and that one slower-moving compound had been formed. The mixture was then filtered through Celite and concentrated to dryness, and the residue was crystallised from ethanol to give **6** (0.15 g, 81%), m.p. 120–122°, $[\alpha]_D$ +43° (*c* 1, methanol) (Found: C, 41.9; H, 6.7; N, 4.0. $C_{12}H_{23}NO_{10}$ calc.: C, 42.2; H, 6.8; N, 4.1%). Mass spectrum (of the trimethylsilylated compound): *m/z* 451 (7%), 378 (43), 361 (23), 288 (1), 271 (4), 198 (1), 73 (100).

Conventional treatment of **6** with acetic anhydride–pyridine gave 4-acetamido-2,3,6-tri-*O*-acetyl-4-deoxy-α-D-galactopyranosyl tetra-*O*-acetyl-β-D-fructofuranoside (**7**) as a syrup (74%), $[\alpha]_D$ +57° (*c* 1, chloroform) (Found: C, 54.0; H, 5.8; N, 2.4. $C_{28}H_{39}NO_{18}$ calc.: C, 54.5; H, 6.3; N, 2.3%). Mass spectrum: *m/z* 331 (11%), 330 (8), 271 (1), 270 (2), 211 (16), 169 (9), 43 (100).

*4-Deoxy-α-*D-xylo-*hexopyranosyl β-*D-*fructofuranoside* (**9**). — A solution of the 4-chloride[1] **8** (0.5 g) in methanolic 1.65% potassium hydroxide (30 mL) was hydrogenated at 60 p.s.i. for 120 h in the presence of Raney nickel. The mixture was then filtered and concentrated to dryness. Recrystallisation of the residue from ethanol gave **9** (0.35 g, 77%), m.p. 181–182°, $[\alpha]_D$ +54° (*c* 1, methanol) (Found: C, 44.2; H, 6.3. $C_{12}H_{22}O_{10}$ calc.: C, 44.2; H, 6.7%). Mass spectrum (of the trimethylsilylated derivative): *m/z* 451 (4%), 361 (23), 273 (4), 271 (4), 85 (1), 73 (100).

*4-Chloro-4-deoxy-2-*O*-methanesulphonyl-3,6-di-*O*-pivaloyl-α-*D*-galactopyranosyl 1,3,4,6-tetra-*O*-pivaloyl-β-*D*-fructofuranoside* (**13**). — To a stirred solution of the 2,4-dimesylate[1] **11** (1 g) in dry *N,N*-dimethylformamide (15 mL) was added lithium chloride (1 g) and a trace of iodine. The mixture was then stirred at 120–125° for 12 h, when t.l.c. (ether–light petroleum, 1:1) indicated that the reaction was complete and that a more mobile product had been formed. The mixture was then poured into ice–water, the precipitated product was extracted with ether, and the extract was washed well with water, dried ($MgSO_4$), and concentrated to dryness. The 4-chloride **13** was obtained as a syrup (0.9 g, 95%), $[\alpha]_D$ +47° (*c* 1, methanol) (Found: C, 55.3; H, 7.8; Cl, 3.9; S, 3.7. $C_{43}H_{71}ClO_{18}S$ calc.: C, 54.8; H, 7.5; Cl, 3.8; S, 3.4%). Mass spectrum: *m/z* 499 (8%), 429 (3), 427 (11), 327 (3), 325 (8), 295 (8), 211 (3), 109 (5), 85 (33), 81 (2), 57 (100).

*4-Chloro-4-deoxy-3,6-di-*O*-pivaloyl-α-*D*-galactopyranosyl 1,3,4,6-tetra-*O*-pivaloyl-β-*D*-fructofuranoside* (**14**). — To a cooled (−30°) and stirred solution of the hexapivalate[1] **10** in anhydrous pyridine (15 mL) was added dropwise an excess of sulphuryl chloride (2 mL, 20 molar equiv.) in anhydrous pyridine. The mixture was then allowed to attain room temperature and, after 6 h, t.l.c. (ether–light petroleum, 1:1) indicated that **10** had been converted into a faster-moving compound. The mixture was then poured into ice-cold, aqueous 10% sulphuric acid (200 mL) and extracted with dichloromethane, and the extract was washed well with aqueous sodium hydrogencarbonate and water, dried ($MgSO_4$), and concentrated to dryness to give **14** (0.8 g, 78%) as a syrup, $[\alpha]_D$ +52° (*c* 1, methanol) (Found: C, 59.0; H, 8.4; Cl, 4.2. $C_{42}H_{69}ClO_{16}$ calc.: C, 58.3; H, 8.0; Cl, 4.1%).

Mass spectrum: *m/z* 499 (7%), 351 (2), 349 (8), 295 (8), 211 (4), 109 (4), 85 (39), 57 (100).

*4-Azido-4-deoxy-2-*O*-methanesulphonyl-3,6-di-*O*-pivaloyl-α-*D*-galactopyranosyl 1,3,4,6-tetra-*O*-pivaloyl-β-*D*-fructofuranoside* (**15**). — To a stirred solution of **11** (2 g) in dry *N,N*-dimethylformamide (20 mL) was added sodium azide (2 g), and the mixture was stirred at 100° for 48 h, when t.l.c. (ether–light petroleum, 1:2) indicated that **11** had been converted into a faster-moving compound. The mixture was cooled, poured into ice-cold water, and extracted twice with ether. The combined extracts were washed well with water, dried ($MgSO_4$), and concentrated to dryness, to give **15** as a syrup (1.6 g, 84%), $[\alpha]_D$ +27° (*c* 1, methanol) (Found: C, 54.6; H, 7.6; N, 4.4; S, 3.7. $C_{43}H_{71}N_3O_{18}S$ calc.: C, 54.4; H, 7.5; N, 4.4; S, 3.4%). Mass spectrum: *m/z* 499 (11%), 434 (9), 332 (3), 295 (10), 211 (4), 109 (4), 85 (31), 57 (100).

*4-Chloro-4-deoxy-2,3,6-tri-*O*-pivaloyl-α-*D*-galactopyranosyl 3-*O*-methanesulphonyl-1,4,6-tri-*O*-pivaloyl-β-*D*-fructofuranoside* (**21**). — A mixture of the 4,3′-dimesylate[1] **18** (1 g), lithium chloride (1 g), a trace of iodine, and hexamethylphosphoric triamide (10 mL) was stirred at 80–85° for 24 h, when t.l.c. (ether–light petroleum, 1:1) indicated completion of the reaction. The mixture was then cooled and poured into ice–water, and twice extracted with ether. The combined extracts were washed well with water, dried ($MgSO_4$), and concentrated to dryness to give the 4-chloride **21** as a syrup (0.9 g, 96%), $[\alpha]_D$ +59° (*c* 1, chloroform) (Found: C, 55.3; H, 7.8; Cl, 3.9; S, 3.7. $C_{43}H_{71}ClO_{18}S$ calc.: C, 54.8; H, 7.5; Cl, 3.8; S, 3.4%). Mass spectrum: *m/z* 493 (5%), 435 (1), 433 (4), 333 (1), 331 (3), 289 (9), 211 (3), 109 (8), 85 (28), 57 (100).

*4-Chloro-4-deoxy-2-*O*-methanesulphonyl-3,6-di-*O*-pivaloyl-α-*D*-galactopyranosyl 4-*O*-methanesulphonyl-1,3,6-tri-*O*-pivaloyl-β-*D*-fructofuranoside* (**16**). — A solution of the 2,4,4′-trimesylate[1] **12** (1 g) in hexamethylphosphoric triamide (10 mL) containing lithium chloride (1 g) and a trace of iodine as catalyst was stirred at 90° for 12 h, when t.l.c. (ether–light petroleum, 3:1) indicated that **12** had been transformed into a faster-moving product. The mixture was processed as described above using ether, and **16** was obtained as a syrup (0.85 g, 90%), $[\alpha]_D$ +58° (*c* 1, chloroform) (Found: C, 49.5; H, 6.7; Cl, 3.5; S, 6.8. $C_{39}H_{65}ClO_{19}S_2$ calc.: C, 50.0; H, 7.0; Cl, 3.8; S, 6.8%). Mass spectrum: *m/z* 493 (5), 429 (2), 427 (7), 327 (2), 325 (5), 289 (8), 211 (3), 109 (9), 85 (27), 57 (100).

*4-Chloro-4-deoxy-3-*O*-methanesulphonyl-2,6-di-*O*-pivaloyl-α-*D*-galactopyranosyl 3-*O*-methanesulphonyl-1,4,6-tri-*O*-pivaloyl-β-*D*-fructofuranoside* (**22**). — To a stirred solution of the 3,4,3′-trimesylate[1] **19** (2 g) in hexamethylphosphoric triamide (10 mL) was added lithium chloride (2 g) and a catalytic amount of iodine. The mixture was heated at 90° for 36 h, when t.l.c. (ether–light petroleum, 1:1) indicated that the reaction was complete and that a faster-moving product had been formed. The mixture was then processed as described above to give **22** (1.5 g, 80%), m.p. 101–102°, $[\alpha]_D$ +51° (*c* 1, chloroform) (Found: C, 50.2; H, 6.9; Cl, 3.8; S, 6.8. $C_{39}H_{65}ClO_{19}S_2$ calc.: C, 50.0; H, 7.0; Cl, 3.8; S, 6.8%). Mass spectrum: *m/z*

493 (4), 429 (4), 427 (10), 289 (9), 211 (3), 109 (8), 85 (24), 57 (100).

4-Chloro-4-deoxy-2,3-di-O-methanesulphonyl-6-O-pivaloyl-α-D-galactopyranosyl 3,4-di-O-methanesulphonyl-1,6-di-O-pivaloyl-β-D-fructofuranoside (**24**). — To a stirred solution of the pentamesylate[1] **23** (1 g) in hexamethylphosphoric triamide (10 mL) was added lithium chloride (1 g) and a catalytic amount of iodine. The mixture was then heated at 90° for 24 h, when t.l.c. (chloroform–methanol, 20:1) indicated that the reaction was complete and that one product had been formed. The mixture was then processed as described above, to give **24** (0.8 g, 89%), m.p. 101–103°, $[\alpha]_D$ +45° (*c* 1, chloroform) (Found: C, 42.2; H, 6.1; Cl, 4.0; S, 13.9. $C_{31}H_{53}ClO_{21}S_4$ calc.: C, 41.6; H, 5.9; Cl, 4.0; S, 14.3%). Mass spectrum: *m/z* 487 (0.2%), 423 (0.4). 421 (2), 313 (0.3), 295 (1), 211 (2), 109 (7), 85 (18), 57 (100).

6-O-Acetyl-3,4-anhydro-2-O-methanesulphonyl-α-D-galactopyranosyl 1,3,4,6-tetra-O-acetyl-β-D-fructofuranoside (**25**). — To a solution of **11** (1 g) in ethanol (20 mL) was added methanolic sodium methoxide (5 mL). The mixture was stirred at room temperature for 48 h, then neutralised with Amberlite IR-120(H^+) resin, and concentrated to dryness. The residue was acetylated in the usual way (acetic anhydride–pyridine), to give a syrup which was shown by t.l.c. (chloroform–acetone, 15:2) to contain one major slower-moving component and several minor products. The mixture was fractionated by column chromatography (dichloromethane–acetone, 75:1). None of the minor components was isolated pure, but the major component **25** was isolated as a chromatographically pure syrup (0.15 g, 25%), $[\alpha]_D$ +5° (*c* 0.55, methanol) (Found: C, 45.8; H, 5.5; S, 5.1. $C_{23}H_{32}O_{17}S$ calc.: C, 45.1; H, 5.2; S, 5.2%). Mass spectrum: *m/z* 331 (13%), 271 (0.2), 265 (25), 229 (1), 211 (20), 185 (1), 169 (12), 109 (18), 85 (4), 81 (8), 43 (100).

6-O-Acetyl-2,3-anhydro-4-chloro-4-deoxy-α-D-talopyranosyl 1,3,4,6-tetra-O-acetyl-β-D-fructofuranoside (**26**). — To a stirred solution of **13** (2.3 g) in ethanol (30 mL) was added methanolic M sodium methoxide (5 mL). The solution was kept for 1 week at room temperature, then neutralised with Amberlite IR-120(H^+) resin, and concentrated to dryness. The residue was acetylated in the usual way (acetic anhydride–pyridine), to give **26** (0.9 g, 67%), m.p. 101–104° (from ethanol–light petroleum), $[\alpha]_D$ +44° (*c* 1, methanol) (Found: C, 48.1; H, 5.2; Cl, 6.4. $C_{22}H_{29}ClO_{14}$ calc.: C, 47.8; H, 5.3; Cl, 6.4%). Mass spectrum: *m/z* 331 (2%), 207 (5), 205 (16), 109 (7), 81 (1), 43 (100).

2,3,4,6-Tetra-O-acetyl-α-D-galactopyranosyl 1,6-di-O-acetyl-3,4-anhydro-β-D-ribo-hexulopyranoside (**29**). — To a solution of the 3′-mesylate[1] **28** (2 g) in ethanol (50 mL) was added methanolic M sodium methoxide (5 mL). The mixture was heated under reflux for 15 min, and then processed as described above. The residue was acetylated in the usual way (acetic anhydride–pyridine), to give **29** as a syrup (0.8 g, 71%), $[\alpha]_D$ +56° (*c* 1, chloroform) (Found: C, 49.6; H, 5.2. $C_{24}H_{32}O_{16}$ calc.: C, 50.0; H, 5.6%). Mass spectrum: *m/z* 331 (10%), 229 (33), 169 (16), 109 (40), 81 (3), 43 (100).

4,6-Di-O-acetyl-2,3-anhydro-α-D-allopyranosyl 1,6-di-O-acetyl-3,4-anhydro-

β-D-ribo-*hexulofuranoside* (**27**). — A solution of the 3,3′-dimesylate[1] **20** (2 g) in methanol (30 mL) was treated with methanolic M sodium methoxide (5 mL), and the mixture was heated under reflux for 15 min and then processed as described above. The residue was acetylated in the usual way (acetic anhydride–pyridine), and the product was shown by t.l.c. (chloroform–acetone, 15:2) to contain one major component and several minor components. The major component (0.35 g, 37%) was isolated by column chromatography (dichloromethane–acetone, 75:1) to give syrupy **27**, $[\alpha]_D$ +60° (*c* 1, chloroform) (Found: C, 50.2; H, 5.9. $C_{20}H_{26}O_{13}$ calc.: C, 50.5; H, 5.5%). Mass spectrum: *m/z* 229 (16%), 169 (23), 109 (23), 81 (6), 43 (100).

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