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THE SYNTHESIS OF 2,1′-ANHYDRO-, 2,1′:3,6-DIANHYDRO-, AND 2,1′:3,6:3′,6′-TRIANHYDRO-SUCROSE*

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ABSTRACT

1′-*O*-Mesyl-6,6′-di-*O*-tritylsucrose and the corresponding 1′-*O*-tosyl derivative were prepared from 6,6′-di-*O*-tritylsucrose by selective sulphonylation. Both sulphonates underwent intramolecular cyclisation reactions, to give 2,1′-anhydrosucrose in high yields rather than the isomeric 1′,4′-anhydride. Sequential benzoylation, detritylation, and mesylation of the 2,1′-anhydride afforded 2,1′-anhydro-6,6′-di-*O*-mesylsucrose tetrabenzoate which, in the presence of base, gave 2,1′:3,6:3′,6′-trianhydrosucrose that was not identical with the product previously claimed to have this structure. Several derivatives of 2,1′-anhydrosucrose were prepared possessing different functional groups at either the 6,6′- or 4,6′-positions. Dimolar mesitylenesulphonylation of 3,3′,4′,6′-tetra-*O*-acetylsucrose gave the 6,1′-disulphonate, which, in the presence of alkali, gave 2,1′:3,6-dianhydrosucrose, which was transformed into the 2,1′:3,6:3′,6′-trianhydride by sequential bromination at C-6′ (carbon tetrabromide–triphenylphosphine) and base-catalysed cyclisation. Treatment of 3,3′,4′,6′-tetra-*O*-benzoylsucrose with sulphuryl chloride furnished the 4,6,1′-trichloro derivative, which, on alkaline hydrolysis, was converted into 2,1′:3,6-dianhydro-4-chloro-4-deoxy-*galacto*-sucrose.

INTRODUCTION

In 1959, it was reported[1] that a crude tri-*O*-tosylsucrose, thought to be mainly the 1,6,6′-isomer, underwent base-catalysed alcoholysis to give 2,1′:3,6:3′,6′-trianhydrosucrose (**1**). Later work[2,3] established that 6,1′,6′-tri-*O*-tosylsucrose gave the 3,6:1′,4′:3′,6′-trianhydride (**4**) when treated with base, rather than the bridged trianhydride claimed by Lemieux and Barrette[1]. It was suggested that **1** may have arisen from a minor tritosylate present in the crude mixture, such as the 2,6,6′-

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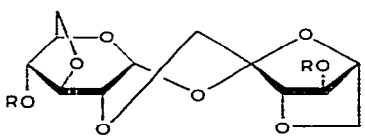
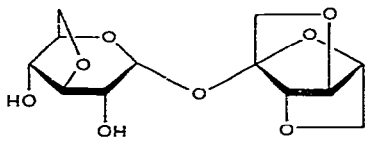
isomer. Ball *et al.*[4] later demonstrated the presence of 2,6,6′-tri-*O*-tosylsucrose in the crude mixture of tritosylates, but they showed that this tritosylate gave a complex mixture when treated with base and could not therefore account for the isolated yield of **1**. These workers also discovered that the 3,6:1′,4′:3′,6′-trianhydride **4** crystallised in two forms, the lower melting of which (m.p. 158–162°) was very similar to **1** (m.p. 163–164.5°). In addition, the physical constants of the diacetate reported by Lemieux and Barrette[1] agreed closely with those reported for the diacetate of 3,6:1′,4′:3′,6′-trianhydrosucrose (**4**). This led Ball and his co-workers[4] to suggest that the product obtained in the earlier work was not **1** but the lower-melting dimorph of **4**, although it is difficult to reconcile the chemical evidence[1] for the structure **1** with structure **4**. However, in the absence of samples from the original work for comparison, an unequivocal synthesis of **1** was considered desirable[5], and we now report two syntheses of **1** and of the intermediary products 2,1′-anhydrosucrose hexa-acetate (**26**) and 2,1′:3,6-dianhydrosucrose (**35**).



1 R = H
2 R = Ac
3 R = Ms



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RESULTS AND DISCUSSION

Examination of molecular models of the two trianhydrides **1** and **4** raised the question as to why the highly strained 1′,4′-anhydro ring should be formed in preference to the seemingly stainless, *cis*-decalin-type, 2,1′-anhydro ring. The formation of anhydro rings proceeds by way of an S_N2 mechanism and therefore a likely answer to this question is provided by consideration of the kinetic factors involved. The relative reactivities of the 6-, 6′-, and 1′-sulphonyloxy groups towards S_N2 reactions are well established and are in the order $6 \approx 6' > 1'$; the lesser reactivity of that at C-1′ being due to the fact that it is adjacent to the anomeric position[6] and is also of the neopentyl type. Hence, it seems likely that the formation of the 3,6- and 3′,6′-anhydro rings would precede the formation of any anhydro ring involving displacement at C-1′. The 3′,6′-anhydrofructose moiety is of the dioxa[1.2.2]bicycloheptane type; this is a very rigid ring structure in which C-1′ and O-4′ are brought into very close proximity (Fig. 1) so that 1′,4′-anhydro ring formation becomes kinetically favourable. The formation of a 2,1′-anhydro link, whilst presumably being thermodynamically favoured, is not kinetically favoured since the sulphonyloxy group would need to adopt an *endo* position with respect to the dioxa[1.2.2]bicycloheptane ring in order to achieve the required colinearity of O-2, C-1′, and O-1′ for the S_N2 transi-

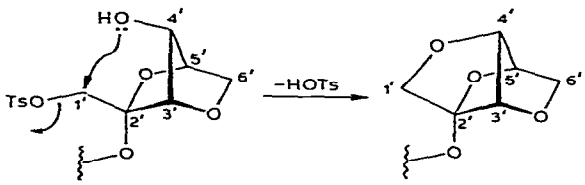


Fig. 1

tion state. It therefore seemed plausible that formation of a 2,1′-anhydro ring could only be achieved in the absence of a 3′,6′-anhydride ring, and therefore any synthesis of the 2,1′:3,6:3′,6′-trianhydride **1** must involve formation of the 2,1′-linkage before the establishment of the 3′,6′-linkage. In order to test this hypothesis, we have synthesised some 1′-sulphonates and examined their reactions with base.

6,6′-Di-*O*-tritylsucrose[7] (**5**) reacted very sluggishly with one molar equivalent

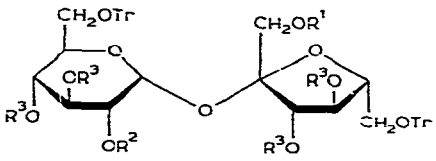
TABLE I

^{1}H-N.M.R. DATA (p.p.m., Hz) FOR SOME SULPHONATE ESTERS AND CHLORINATED DERIVATIVES OF SUCROSE

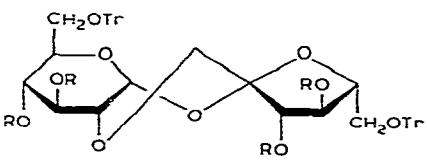
	8[a,e]	**9**[a,e]	**30**[b,e]	**31**[c,f]	**33**[b,e]	**34**[d,e]	**41**[d,f]
H-1	5.85 d	6.01 d	5.87 d	5.41 d	5.85 d	5.63 d	5.79 d
H-2	5.14 m	4.97 dd	4.64 dd	3.74 td[g]	4.63 dd	4.72 dd	
H-3	5.61 m	5.70 m	5.57 t	4.95 t	5.63 t	5.59 t	5.29 dd
H-4			3.79 dt[g]	3.57 dt[g]	5.22 t	5.15 t	4.62 dd
H-5	4.36 m	4.55 m					
H-6a	3.63 dd	3.72 d			4.22 dd		
H-6b	3.48 dd	3.15 dd			4.13 dd		
H-1′a	4.50 d	4.32 d	4.32 d		4.32 d		
H-1′b	4.41 d	4.25 d	4.12 d		4.12 d		
H-3′	5.81 d	5.83 d	5.82 d	5.44 d	5.86 d	5.65 d	6.02 d
H-4′	5.68 t	5.70 m	5.55 t	5.32 t	5.59 t	5.40 t	6.17 dd
H-5′	4.25 q	4.21 q	4.48 m		4.56 m		
H-6′a	3.50 dd	3.58 d			4.47 dd		
H-6′b	3.18 dd						
$J_{1,2}$	3.5	3.5	3.8	4.3	4.0	3.8	4.0
$J_{2,3}$			10.2	9.5	9.3	9.9	10.0
$J_{3,4}$			8.6	9.8	10	9.0	3.5
$J_{4,5}$			9.4		9.2	9.7	1.0
$J_{5,6a}$	~5	~1	9.5		5.0		
$J_{5,6b}$	~2	~3			3.3		
$J_{6a,6b}$	~10	~11			11.0		
$J_{1'a,1'b}$	~11	~10	10.8		10.7		
$J_{3',4'}$	5	7	7.3	6.6	7.1	5.5	7.3
$J_{4',5'}$	5	—	7.1	6.4	7.3	5.5	6.5
$J_{5',6'a}$	5	~6			2.7		
$J_{5',6'b}$	5	~6					
$J_{6'a,6'b}$	~11	—			11.0		

[a]At 220 MHz. [b]At 250 MHz. [c]At 200 MHz. [d]At 90 MHz. [e]In C_6D_6. [f]In $CDCl_3$. [g]Coupling to hydroxylic proton.

of tosyl chloride; even in the presence of an excess of tosyl chloride, substantial amounts of **5** remained. The optimum conditions for the formation of the 1′-tosylate **6** involved the use of three molar equivalents of tosyl chloride, which gave 24% of **6** and 21% of the 2,1′-ditosylate **7**, after chromatographic fractionation. Both products were characterised as their peracetates (**8** and **9**, respectively), the ^{1}H-n.m.r. spectra of which were indicative of their structures (Table I). With the less-bulky mesyl chloride, the yield of the 1′-mesylate **10** could be optimised to ~45%.



5 $R^1 = R^2 = R^3 = H$
6 $R^1 = Ts, R^2 = R^3 = H$
7 $R^1 = R^2 = Ts, R^3 = H$
8 $R^1 = Ts, R^2 = R^3 = Ac$
9 $R^1 = R^2 = Ts, R^3 = Ac$
10 $R^1 = Ms, R^2 = R^3 = H$
11 $R^1 = Ms, R^2 = R^3 = Ac$



12 R = H
13 R = Ac
14 R = Bz

Treatment of the 1′-tosylate **6** or the 1′-mesylate **10** with boiling, methanolic sodium methoxide gave high yields of the required 2,1′-anhydride **12**, which was also characterised as its tetra-acetate **13** and tetrabenzoate **14**. The presence of a 2,1′-anhydride ring was established readily from the ^{1}H-n.m.r. spectra of **13** and **14** (Table II), which were largely first-order; the high-field position (δ ~4) of the H-2 resonance was indicative of its involvement in an anhydro ring. Similarly, the low-field position of the H-3′ and H-4′ resonances revealed the presence of *O*-acyl groups at these positions, which eliminated any possibility of a 1′,4′-anhydro ring. In addition, the $J_{1,2}$, $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ values (Table II) indicated that the $^4C_1$ conformation of the α-D-glucopyranosyl ring had not been perturbed by formation of the 2,1′-anhydro ring.

These studies confirmed that the formation of a 2,1′-anhydro ring was kinetically favoured only in the absence of a 3′,6′-anhydro ring. It was therefore now possible to accomplish a synthesis of the 2,1′:3,6:3′,6′-trianhydride **1**.

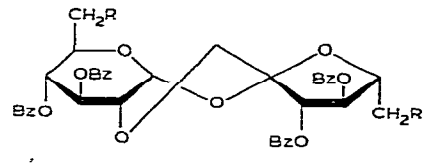
Detritylation of the tetra-acetate **13** with hydrogen bromide in acetic acid was accompanied by extensive 4→6 acetyl migration, to give the 4,6′-diol **24**, which was isolated as its dimesylate **25**, in 32% overall yield, together with only 22% of the required 6,6′-dimesylate. When the crude mixture of diols obtained by this reaction was acetylated, crystalline 2,1′-anhydrosucrose hexa-acetate (**26**) was obtained in 68% overall yield. However, brief treatment of the corresponding tetrabenzoate **14** with hydrogen bromide in acetic acid afforded the 6,6′-diol, which was isolated as its di-*O*-mesyl derivative **15** (76%). The dimesylates **15** and **25** were employed for the

TABLE II

^{1}H-N.M.R. DATA (p.p.m., Hz) FOR SOME 2,1′-ANHYDROSUCROSE DERIVATIVES

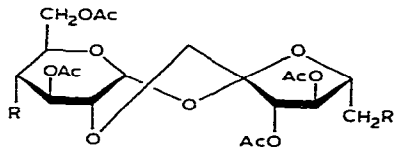
	13[a,f]	14[b,f]	15[b,f]	16[b,f]	17[b,f]	18[b,f]	19[c,f]	20[b,f]	21[c,f]	22[c,f]	23[b,f]	25[d,f]	26[a,e]	27[c,f]	28[b,f]
H-1	5.42 d	5.56 d	5.74 d	5.71 d	5.72 d	5.74 d	5.63 d	5.70 d	5.58 d	5.73 d	5.65 d	5.47 d	5.62 d	5.58 d	5.51 d
H-2	3.84 dd	4.05 dd	4.04 dd	4.04 dd	4.04 dd	4.03 dd	4.01 dd	4.04 dd	3.99 dd	4.05 dd	4.01 dd	3.69 dd	3.64 dd	4.16 dd	4.11 dd
H-3	5.53 t	5.96 t	6.02 t	6.03 t	6.03 t	6.04 t	6.00 t	6.02 t	3.97 t	6.03 t	5.97 t	5.60 t	5.96 t	5.62 dd	5.65 dd
H-4	5.26 t	5.68 t	5.46 t	5.53 t	5.48 t	5.34 t	5.22 t	5.46 t	5.38 t	5.33 t	5.41 t	4.62 t	5.25 t	4.48 d	
H-5	3.91 dt			4.14 dt	4.09 dt	3.76 m	4.03 m	4.11 m	4.06 ddd	4.18 m	4.38 m				
H-6a	3.32 dd	3.19 dd		3.62 dd	3.44 dd	3.23 dd	1.67 d[g]	3.32 m	3.35 dd	3.03 m					3.59 dd
H-6b	3.00 dd	2.90 dd		3.51 dd	3.34 dd	3.11 dd			3.10 dd						3.51 dd
H-1′a	3.98 d	4.80 d		4.56 d	4.57 d	4.57 d	4.53 d	4.55 d	4.54 d	4.58 d	4.43 d	3.90 d	4.25 d		3.95 d
H-1′b	3.48 d	3.70 d	3.75 d	3.74 d	3.73 d	3.76 d	3.67 d	3.73 d	3.67 d	3.77 d	3.67 d	3.43 d	3.46 d		3.52 d
H-3′	5.02 d	5.49 d	5.73 d	5.61 d	5.59 d	5.56 d	5.61 d	5.66 d	5.53 d	5.70 d	5.62 d	5.13 d	5.23 d	5.06 d	5.07 d
H-4′	5.49 t	5.97 t	5.86 t	5.88 dd	5.89 dd	5.87 dd	5.73 t	5.82 dd	5.81 t	5.78 t	5.99 dd	5.36 t	5.70 t	5.43 dd	5.34 dd
H-5′	4.10 q			4.54 dt	4.58 ddd	4.57 dt	4.42 m	4.43 m	4.42 ddd	4.58 m	4.69 dt				4.25 ddd
H-6′a	3.48 dd	3.6 m		4.09 dd	3.90 dd	3.73 dd	1.18 d[g]	3.80 m	3.64 dd	3.72 dd	4.11 dd				4.1 cm
H-6′b	3.36 dd			3.91 dd	3.76 dd	3.61 dd			3.35 dd	3.51 dd	3.78 dd				
$J_{1,2}$	3.5	3.4	3.4	3.7	3.3	3.6	3.5	3.3	3.5	3.5	3.3	3.5	3.5	3.4	3.6
$J_{2,3}$	9.5	9.8	9.8	9.8	10.0	9.8	9.8	9.5	9.8	9.9	9.5	10.0	10.0	10.2	10.3
$J_{3,4}$	9.5	10.4	9.5	9.8	9.5	9.8	9.8	9.5	9.6	9.8	10.0	10.0	9.5	3.5	3.7
$J_{4,5}$	10.0	9.0	9.5	10.0	9.8	9.7	9.7	10.0	9.8	9.8	9.8	9.0	10.0	~1	
$J_{5,6a}$	~1.5	2.5		2.8	3.3	3.0	6.7[g]		3.2	~4					
$J_{5,6b}$	3.5	3.5		4.3	5.1	5.9			6.3	~6					
$J_{6a,6b}$	10.5	10.4		11.9	11.8	11.0	—		14.0						
$J_{1'a,1'b}$	12.5	12.5	12.8	12.9	13.2	12.5	12.6	12.8	12.8	13.1	12.5	13.3	12.2		13.1
$J_{3',4'}$	5.5	4.6	5.5	4.8	4.4	4.0	5.2	5.2	4.6	4.5	5.8	6.7	6.0	5.0	5.3
$J_{4',5'}$	5.5	4.6	5.5	3.7	3.7	3.3	4.4	4.4	4.2	4.0	4.8	4.8	6.5	3.7	4.4
$J_{5',6'a}$	6			6.5	6.6	6.5	7.6[g]		6.0	4.4	5.2				7.5
$J_{5',6'b}$	6			7.5	7.4	8.1			8.0	9.0	8.3				9.4
$J_{6'a,6'b}$	~10			11.25	10.7	10.3			14.0	13.7	14.0				12.8

[a]At 220 MHz. [b]At 250 MHz. [c]At 200 MHz. [d]At 90 MHz. [e]In C_6D_6. [f]In $CDCl_3$. [g]May be interchangeable.

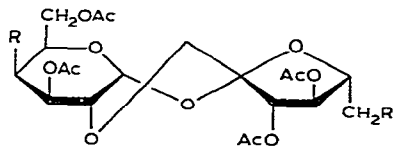


15 R = OMs
16 R = Cl
17 R = Br
18 R = I
19 R = H

20 R = N_3
21 R = SAc
22 R = SCN
23 R = $SC(S)NMe_2$



24 R = OH
25 R = OMs
26 R = OAc



27 R = Cl
28 R = N_3

TABLE III

^{1}H-N.M.R. DATA (p.p.m., Hz) FOR SOME 2,1′:3,6-DIANHYDRO- AND 2,1′:3,6:3′,6′-TRIANHYDRO-SUCROSES

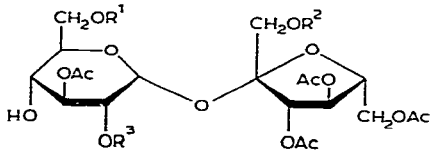
	2[b,f]	3[b,f]	36[b,e]	38[b,f]	42[d,e]
H-1	5.43 d	5.45 d	5.21 d	5.40 d	5.01 d
H-2	3.80 dd	3.86 dd	3.65 t	3.90 dd	3.56 dd
H-3	4.68 m	4.55 t	4.46 t	4.55 t	4.28 d
H-4		4.74 dd	4.38 dd	4.70 dd	4.66 d
H-5	4.58 m	4.64 t	3.87 t	4.43 t	3.97 (br)s
H-6a	4.20 d	4.23 d	3.55 d	4.15 d	4.06 dd
H-6b	3.96 dd	3.99 dd	3.24 dd	3.96 dd	3.89 dd
H-1′a	3.96 d	4.10 d	4.19 d	4.16 d	3.74 d
H-1′b	3.40 d	3.45 d	3.42 d	3.53 d	3.31 d
H-3′	4.83 d	4.87 d	5.54 d	5.42 d	5.46 d
H-4′	5.15 dd	5.12 dd	5.34 t	5.24 dd	5.34 dd
H-5′	4.53 s	4.56 s	4.10 m	4.19 m	
H-6′a	4.08 s	4.10 d	4.52 dd	3.66 dd	4.44 dd
H-6′b		4.04 dd	4.39 dd	3.58 dd	4.26 dd
$J_{1,2}$	2.4	2.4	3.0	2.9	3.0
$J_{2,3}$	5.2	4.4	4.0	4.6	4.5
$J_{3,4}$		4.8	5.0	4.9	0
$J_{4,5}$		2.7	2.5	2.8	1.5
$J_{5,6a}$	0	~0	0	0	3.2
$J_{5,6b}$	3.0	3.1	3.0	2.9	
$J_{6a,6b}$	10.6	11.0	11.0	10.8	10
$J_{1'a,1'b}$	12.3	12.3	11.7	11.9	
$J_{3',4'}$	2.2	2.2	3.6	3.7	4.0
$J_{4',5'}$	0.5	0.7	3.3	3.0	3.0
$J_{5',6'a}$	~0	0	5.5	6.6	6.0
$J_{5',6'b}$	~0	1.3	7.0	7.5	5.0
$J_{6'a,6'b}$		~10	11.0	10.4	11.0

[a]At 220 MHz. [b]At 250 MHz. [c]At 200 MHz. [d]At 90 MHz. [e]In C_6D_6. [f]In $CDCl_3$.

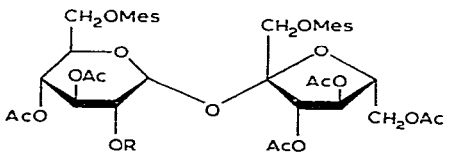
synthesis of several 6,6′- (**16–23**) and two 4,6′-disubstituted 2,1′-anhydrosucroses (**27** and **28**) (see Experimental).

Treatment of the 6,6′-dimesylate **15** with boiling, methanolic sodium methoxide gave crystalline 2,1′:3,6:3′,6′-trianhydrosucrose (**1**), which was also characterised as the crystalline diacetate **2** and dimesylate **3**. The ^{1}H-n.m.r. spectrum of **2** was in accord with its structure (Table III), and the physical constants of **1** {m.p. 189°, $[\alpha]_D$ +54° (methanol)} and **2** {m.p. 297–299° (dec.), $[\alpha]_D$ +68° (chloroform)} are clearly different from those reported by Lemieux and Barrette[1] for their trianhydride {m.p. 163–164.5°, $[\alpha]_D$ +117° (chloroform)*; diacetate, m.p. 181.5–182.5°, $[\alpha]_D$ +128.6° (chloroform)}, showing that their trianhydride was certainly not **1**, but more probably the isomeric 3,6:1′,4′:3′,6′-trianhydride (**4**) as suggested by Ball *et al.*[4].

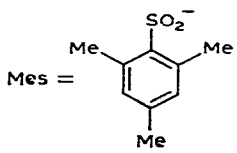
In the foregoing synthesis of **1**, the 2,1′-anhydro linkage was established first. In an alternative synthesis of **1**, we planned to ascertain whether a 2,1′-anhydro ring could be formed in the presence of a 3,6-anhydro linkage. Hence, a convenient synthesis of a 6,1′-disulphonate was sought. A convenient starting-material was 3,3′,4′,6′-tetra-*O*-acetylsucrose[8] (**29**), which is readily available from 2,1′:4,6-di-*O*-isopropylidenesucrose. Selective mesitylenesulphonylation of **29** with three molar equivalents of reagent afforded a mixture of the 2,6,1′-trisulphonate **30** (9%), the 6,1′-disulphonate **31** (52%), and a product thought to be the 6-sulphonate **32**. Initially, the mixture was fractionated by chromatography, but subsequently **31** could be crystallised directly from the crude reaction product. The structures of **30** and **31** were indicated by their ^{1}H-n.m.r. parameters and those of the respective peracetylated derivatives **33** and **34** (Table I). For example, the low-field position (δ 4.64) of the H-2 resonance for the trisulphonate **30** indicated a 2-*O*-sulphonyl group, whereas the H-4 resonance (δ 3.79) showed further coupling to a hydroxylic proton, indicating



29 $R^1 = R^2 = R^3 = H$
30 $R^1 = R^2 = R^3 = Mes$
31 $R^1 = R^2 = Mes, R^3 = H$
32 $R^1 = Mes, R^2 = R^3 = H$



33 R = Mes
34 R = Ac

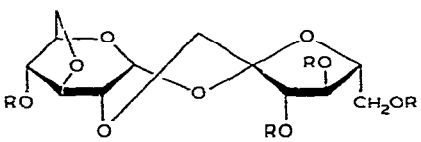


*Our trianhydride was insoluble in chloroform.

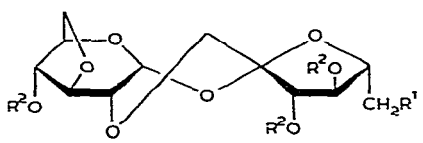
that HO-4 was not substituted. Similarly, the H-2 and H-4 resonances for the disulphonate **31** showed coupling to hydroxylic protons indicating that they were unsubstituted. In agreement with this finding, the mass spectrum showed an intense ion at *m/z* 471 due to $Ac_3MesGlc^+$ and $Ac_3MesFruf^+$ arising from rupture of the two glycosidic linkages; no ion at *m/z* 331 (Ac_4Fruf^+) was present. These results showed that the sulphonyl groups were not on the same glycosyl moiety.

The structure of the monosulphonate **32** could not be established unequivocally, although the ^{1}H-n.m.r. data showed that the sulphonate group was not located at a secondary position. Previous studies of the sulphonylation of sucrose showed that, of the primary positions, HO-1′ has the lowest reactivity[1,4,9]. Hence, the monosulphonate is probably the 6-isomer **32**.

Treatment of 6,1′-di-*O*-mesitylenesulphonylsucrose tetra-acetate (**34**) with boiling, methanolic sodium methoxide afforded 68% of syrupy 2,1′:3,6-dianhydrosucrose (**35**), which was characterised as its crystalline tetra-acetate **36**. The ^{1}H-n.m.r. spectrum of **36** revealed low-field positions (δ 5.54 and 5.34, respectively) for the H-3′ and H-4′ resonances, suggesting that these positions were not involved in anhydro-ring formation. The rather small couplings between the protons of the glucopyranosyl moiety suggested that it existed in the $^1C_4$ conformation, in agreement with the proposed structure. Furthermore, the high-field positions (δ 3.65 and 4.46, respectively) of the H-2 and H-3 resonances showed that C-2 and C-3 were part of the two anhydro rings (Table III).



35 R = H
36 R = Ac



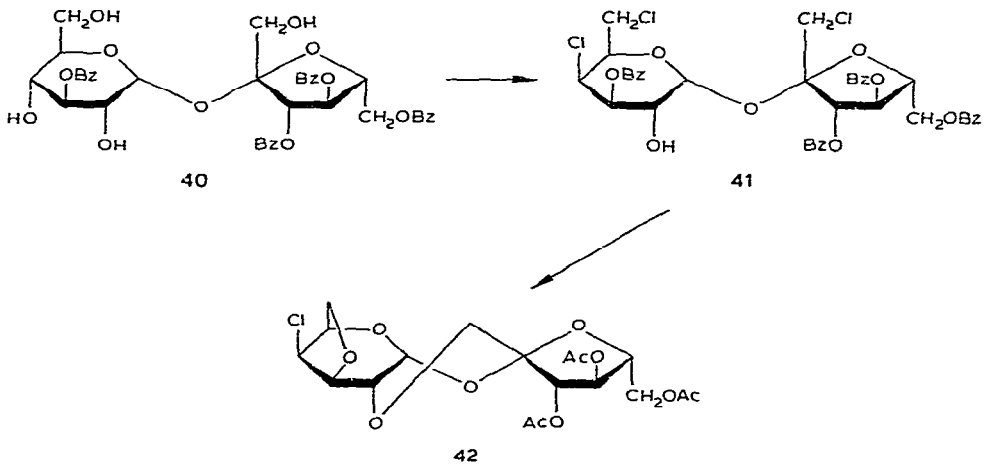
37 R^1 = Br, R^2 = H
38 R^1 = Br, R^2 = Ac
39 R^1 = OTs, R^2 = H

Finally, it was necessary to place a leaving group at C-6′ so that the 3′,6′-anhydro ring could be formed. The reaction of **35** with mesitylenesulphonyl chloride afforded several products, from which a seemingly homogeneous product was isolated in 56% yield. However, the ^{1}H-n.m.r. spectrum revealed that the product was a two-component mixture that could not be separated readily enough to ensure that this was a feasible route to the bridged trianhydride **1**. Treatment of the crude mixture with boiling, methanolic sodium methoxide afforded a mixture of two products which similarly could not be fractionated. Consequently this route was abandoned.

The triphenylphosphine–carbon tetrabromide reagent[10], which can replace primary hydroxyl groups by bromine, was applied to the dianhydride **35**. The syrupy 6′-bromo derivative **37** was isolated (42%), and characterised as its triacetate **38**. When **37** was treated with boiling, methanolic sodium methoxide, followed by acetylation, 2,1′:3,6:3′,6′-trianhydrosucrose diacetate (**2**) was isolated in 65% yield, and

was identical with the product of the previous synthesis. The trianhydride **1** could also be obtained from the dianhydride **35** by selective tosylation at C-6′ followed by the action of base, although the intermediary 6′-tosylate **39** could not be obtained pure.

In a related study, 3,3′,4′,6′-tetra-*O*-benzoylsucrose[8] (**40**) was converted into the 4,6,1′-trichloride **41** by sulphuryl chloride, the structure being indicated by the ^{1}H-n.m.r. spectrum (Table I). When **41** was treated with sodium methoxide, it was transformed into the corresponding 2,1′:3,6-dianhydride, which was isolated as the triacetate **42**.



40 41 42

EXPERIMENTAL

Unless otherwise stated, optical rotations were measured for chloroform solutions ($c \sim 1$). Acetylations, methanesulphonylations, and benzoylations were carried out by dissolution of the compound in pyridine (5–10 mL per mmol), followed by the addition of an excess of either acetic anhydride, methanesulphonyl chloride, or benzoyl chloride, respectively. In the last two cases, the reaction mixture was usually cooled. The reaction mixtures were then processed by pouring into ice–water and extraction into chloroform. The extract was washed with dilute hydrochloric acid (to remove pyridine), saturated, aqueous sodium hydrogencarbonate, and water, dried ($MgSO_4$), and evaporated to dryness. Unless otherwise stated, column chromatography was carried out conventionally on silica gel G (Merck 7734) and t.l.c. was conducted on silica gel G (Merck 5735 or 5554). ^{1}H-N.m.r. spectra were recorded with Bruker HFX-90, Nicolet NT-200, Bruker WM-250, or Perkin–Elmer R-34 spectrometers using tetramethylsilane as internal standard.

6-O-Trityl-α-D-glucopyranosyl 1-O-tosyl-6-O-trityl-β-D-fructofuranoside (**6**). — A solution of tosyl chloride (13.8 g, 72 mmol) in pyridine (100 mL) was added dropwise to an ice-cold, stirred solution of 6,6′-di-*O*-tritylsucrose[7] (**5**; 20 g, 24 mmol) in pyridine. The mixture was stored for 48 h at 0°, and t.l.c. ($CHCl_3$–Me_2CO, 1:1)

then revealed two major and several minor products. The mixture was treated with water (15 mL) and then evaporated to dryness; the last traces of pyridine were removed by co-distillation with toluene, and the resulting residue was fractionated on silica gel. Elution with chloroform–acetone (10:1) afforded the 2,1′-ditosylate **7** (5.9 g, 21%) as a crisp, white foam, $[\alpha]_D$ +22°. Acetylation of **7** afforded the crystalline tetra-acetate **9** (94%), m.p. 101° (from ether–light petroleum), $[\alpha]_D$ +67° (Found: C, 66.4; H, 5.5; S, 4.6. $C_{72}H_{70}O_{19}S_2$ calc.: C, 66.4; H, 5.4; S, 4.9%).

Subsequent elution with chloroform–acetone (4:1) afforded the 1′-tosylate **6** (5.7 g, 24%). m.p. 117° (from ethanol), $[\alpha]_D$ +17° (Found: C, 70.0; H, 5.7; S, 3.3. $C_{57}H_{56}O_{13}S$ calc.: C, 69.8; H, 5.7; S, 3.25%). Acetylation of **6** afforded the penta-acetate **8** (97%), m.p. 100–102° (from ether–light petroleum), $[\alpha]_D$ +49° (Found: C, 67.6; H, 5.7; S, 2.6. $C_{67}H_{66}O_{18}S$ calc.: C, 67.55; H, 5.55; S, 2.7%).

*2,3,4-Tri-*O*-acetyl-6-*O*-trityl-*α*-*D*-glucopyranosyl 3,4-di-*O*-acetyl-1-*O*-mesyl-6-*O*-trityl-*β*-*D*-fructofuranoside* (**11**). — To an ice-cold solution of 6,6′-di-*O*-tritylsucrose (**5**; 11 g, 13.3 mmol) in dry pyridine (150 mL) was added, dropwise, mesyl chloride (1.56 mL, 16 mmol). The temperature was maintained at 0° for the first hour and then allowed to rise to ambient. After 4 h, t.l.c. ($CHCl_3$–Me_2CO, 1:1) indicated a single, major product and some **5**. The mixture was poured into ice–water, and the product was extracted with chloroform in the usual way. Chromatography of the resulting syrup on silica gel ($CHCl_3$–Me_2CO, 3:1) afforded the 1′-mesylate **10** (5.4 g, 45%) as a syrup, which was sufficiently pure for the next stage.

Acetylation of **10** afforded the penta-acetate **11**, m.p. 114–116° (from ethanol), $[\alpha]_D$ +63° (*c* 0.5). (Found: C, 65.2; H, 5.7; S, 2.8. $C_{61}H_{62}O_{18}S$ calc.: C, 65.7; H, 5.55; S, 2.9%).

*2,1′-Anhydro-6,6′-di-*O*-tritylsucrose* (**12**). — A solution of the 1′-tosylate **6** (3 g, 2.5 mmol) in M methanolic sodium methoxide (45 mL) was heated under reflux for 24 h, neutralised with Amberlite IR-120(H^+) resin, and evaporated to dryness, to give **12** (1.6 g, 77%), m.p. 128° (from ethanol), $[\alpha]_D$ +24° (Found: C, 71.2; H, 6.2. $C_{44}H_{48}O_{10}$ calc.: C, 71.75; H, 6.5%).

Acetylation of **12** afforded the tetra-acetate **13**, m.p. 108–109° (from ether–light petroleum), $[\alpha]_D$ +82° (Found: C, 71.25; H, 5.9. $C_{58}H_{56}O_{14}$ calc.: C, 71.3; H, 5.7%).

Benzoylation of **12** afforded the tetrabenzoate **14** in quantitative yield; m.p. 74° (from ethanol), $[\alpha]_D$ +10° (*c* 0.5) (Found: C, 76.55; H, 5.25. $C_{78}H_{64}O_{14}$ calc.: C, 76.5; H, 5.25%).

Very similar results were obtained when the 1′-mesylate **10** was treated with sodium methoxide in the same way.

*2,1′-Anhydro-6,6′-di-*O*-mesylsucrose tetrabenzoate* (**15**). — A solution of 10% (v/v) hydrogen bromide in glacial acetic acid (25 mL) was rapidly added to a stirred, ice-cold solution of **14** (2.5 g, 2.04 mmol) in chloroform (20 mL). After 4 min, the solution was poured into ice–water and the product was extracted with chloroform. The extract was washed thoroughly with water and aqueous sodium hydrogencarbonate, dried ($MgSO_4$), and evaporated to dryness. The 6,6′-diol was freed from triphenylmethanol by chromatography on silica gel and then mesylated in the usual

way, to give **15** (1.4 g, 76%), m.p. 96°, $[\alpha]_D$ +19° (*c* 0.5) (Found: C, 55.8; H, 4.65; S, 6.95. $C_{42}H_{40}O_{18}S_2$ calc.: C, 56.25; H, 4.45; S, 7.1%).

*Detritylation of 2,1′-anhydro-6,6′-di-*O*-tritylsucrose tetra-acetate* (**13**). — A solution of 10% hydrogen bromide in acetic acid (25 mL) was added to a solution of **13** (3 g, 3.07 mmol) in chloroform (20 mL). After 4 min, the mixture was poured into ice–water and the product was isolated in the usual way by chloroform extraction. T.l.c. revealed two products. Elution of the mixture from a column of silica gel with chloroform gave triphenylmethanol. Subsequent elution with chloroform–acetone (6:1) gave, first, the 4,6′-diol **24** as a syrup, which was mesylated in the usual way to give the 4,6′-dimesylate **25** as a monohydrate (0.6 g, 32%), m.p. 101–103° (from ethanol), $[\alpha]_D$ +51° (Found: C, 39.75; H, 5.10; S, 9.25. $C_{22}H_{32}O_{18}S_2 \cdot H_2O$ calc.: C, 39.65; H, 5.10; S, 9.6%). The i.r. spectrum had a broad band at ~1650 cm^{-1} indicative of hydration.

Subsequent fractions from the column gave the 6,6′-diol as a syrup that was mesylated in the usual way, giving 3,4,3′,4′-tetra-*O*-acetyl-2,1′-anhydro-6,6′-di-*O*-mesylsucrose (0.4 g, 22%), m.p. 165° (from ethanol), $[\alpha]_D$ +61° (Found: C, 40.55; H, 5.0; S, 10.05. $C_{22}H_{32}O_{18}S_2$ calc.: C, 40.75; H, 4.95; S, 9.9%.)

2,1′-Anhydrosucrose hexa-acetate (**26**). — The above reaction was repeated using 2 g (2.05 mmol) of **13**, and conventional acetylation of the crude mixture of diols gave the hexa-acetate **26** (0.8 g, 68%), m.p. 141° (from ether), $[\alpha]_D$ +79° (Found: C, 49.9; H, 5.55. $C_{24}H_{32}O_{16}$ calc.: C, 50.0; H, 5.55%).

Nucleophilic displacement reactions of the 6,6′-dimesylate **15**. — (*a*) *With chloride*. The dimesylate **15** (1 g, 1.11 mmol) was heated at 105° for 24 h in *N*,*N*-dimethylformamide (30 mL) containing lithium chloride (2 g) and a small crystal of iodine. Evaporation of the reaction mixture to dryness and elution of the residue from a short column of silica gel with ether–light petroleum (1:1) gave the 6,6′-dichloride **16** (0.7 g, 88%), m.p. 92.5° (from methanol), $[\alpha]_D$ +16° (Found: C, 61.95; H, 4.35; Cl, 8.95. $C_{40}H_{34}Cl_2O_{12}$ calc.: C, 61.85; H, 4.35; Cl, 9.0%).

(*b*) *With bromide*. The reaction in (*a*) was repeated with lithium bromide (3 g), to give the 6,6′-dibromide **17** as an amorphous solid (0.81 g, 84%), m.p. 76–78°, $[\alpha]_D$ +12° (Found: C, 55.0; H, 4.2; Br, 18.5. $C_{40}H_{34}Br_2O_{12}$ calc.: C, 55.45; H, 3.95; Br, 18.5%).

(*c*) *With iodide*. The reaction in (*a*) was repeated with sodium iodide (3 g) in dry butanone (25 mL) and a reaction period of 72 h, to give the 6,6′-di-iodide **18** (0.62 g, 60%), m.p. 96° (from methanol), $[\alpha]_D$ +5° (Found: C, 50.1; H, 3.55; I, 26.85. $C_{40}H_{34}I_2O_{12}$ calc.: C, 50.0; H, 3.55; I, 26.45%).

(*d*) *With azide*. The reaction in (*a*) was repeated with sodium azide (2 g). The isolated diazide **20** (0.6 g, 75%) had m.p. 74° (from methanol), $[\alpha]_D$ +46° (Found: C, 60.6; H, 4.2; N, 9.9. $C_{40}H_{34}N_6O_{12}$ calc.: C, 60.8; H, 4.3; N, 10.6%).

(*e*) *With thioacetate*. The reaction in (*c*) was repeated with potassium thioacetate (2 g) and a reaction period of 48 h. The 6,6′-bis(thioacetate) **21** (89%) had m.p. 79° (from methanol), $[\alpha]_D$ +9° (Found: C, 61.35; H, 4.8; S, 7.3. $C_{44}H_{40}O_{14}S_2$ calc.: C, 61.7; H, 4.65; S, 7.5%).

(*f*) *With thiocyanate.* The reaction in (*a*) was repeated with potassium thiocyanate, to give the 6,6′-bis(thiocyanate) **22** (68%), m.p. 90° (from ethanol), $[\alpha]_D$ +29° (Found: C, 61.15; H, 4.05; N, 3.25; S, 7.55. $C_{42}H_{34}N_2O_{12}S_2$ calc.: C, 61.3; H, 4.15; N, 3.41; S, 7.8%).

(*g*) *With* N,N-*dimethyldithiocarbamate.* The reaction in (*a*) was repeated using sodium *N,N*-dimethyldithiocarbamate (2.5 g), to give the 6,6′-bis(*N,N*-dimethyldithiocarbamate) **23** (95%), m.p. 91–92° (from ethanol), $[\alpha]_D$ +15° (Found: C, 58.2; H, 5.1; N, 3.10. $C_{46}H_{46}N_2O_{12}S_4$ calc.: C, 58.4; H, 4.85; N, 2.95).

2,1′-Anhydro-6,6′-dideoxysucrose tetrabenzoate (**19**). — Approximately two spatula loads of wet Raney nickel were added to a solution of **21** (0.8 g, 0.93 mmol) in ethanol (30 mL). The mixture was heated under reflux for 36 h and then filtered and evaporated to dryness. The product was purified by passage through a column of silica gel (light petroleum–ether, 4:1), to give **19** (0.4 g, 61%) as an amorphous solid, m.p. 48–50°, $[\alpha]_D$ +15.5° (Found: C, 67.85; H, 5.2. $C_{40}H_{36}O_{12}$ calc.: C, 67.8; H, 5.1%).

*3,6-Di-*O*-acetyl-4-chloro-4-deoxy-α-*D*-galactopyranosyl 3,4-di-*O*-acetyl-6-chloro-6-deoxy-β-*D*-fructofuranoside 2,1′-anhydride* (**27**). — A solution of syrupy **24** (0.9 g, 1.83 mmol) in dry pyridine (60 mL) was cooled to ~−40° and treated dropwise with sulphuryl chloride (1.6 mL, 20 mmol), and the temperature was maintained at −40° for 1 h. The mixture was stored at room temperature for 24 h and then diluted with water, and the product was isolated by extraction with chloroform in the usual manner. The crude product was purified by chromatography on silica gel (light petroleum–ether, 10:1), to give amorphous **27**, $[\alpha]_D$ +52° (Found: C, 45.1; H, 4.5; Cl, 13.1. $C_{20}H_{26}Cl_2O_{12}$ calc.: C, 45.35; H, 4.9; Cl, 13.4%).

*3,6-Di-*O*-acetyl-4-azido-4-deoxy-α-*D*-galactopyranosyl 3,4-di-*O*-acetyl-6-azido-6-deoxy-β-*D*-fructofuranoside 2,1′-anhydride* (**28**). — A mixture of the 4,6′-dimesylate **25** (1 g, 1.6 mmol) and sodium azide (3 g) in hexamethylphosphoric triamide (20 mL) was heated at 90° for 3 days. T.l.c. ($CHCl_3$–Me_2CO, 4:1) then showed a fast-moving, major product and several, slower-moving, minor products arising by deacetylation. The mixture was cooled to room temperature and treated with acetic anhydride (2 mL) and pyridine (15 mL). After 18 h, it was diluted with water and the product was isolated by ether extraction in the usual way. The crude product was then purified on a column of silica gel with chloroform–acetone (8:1), to give **28** as a syrup (0.7 g, 72%), $[\alpha]_D$ +50° (Found: C, 43.9; H, 4.8; N, 15.35. $C_{20}H_{26}N_6O_{12}$ calc.: C, 44.3; H, 4.8; N, 15.5%).

*Selective mesitylenesulphonylation of 3,3′,4′,6′-tetra-*O*-acetylsucrose* (**29**). — To an ice-cold solution of **29** (19 g, 37 mmol) in anhydrous pyridine was added, during 30 min, a solution of mesitylenesulphonyl chloride (24.4 g, 110 mmol) in pyridine. The mixture was kept at ~5° for 5 days and then poured into ice–water, and the product was extracted with chloroform in the usual manner. This gave a syrupy mixture (22 g) of two major and one minor products, as indicated by t.l.c. ($CHCl_3$–Me_2CO, 2:1). Chromatography of the mixture on a dry-packed column of

silica gel with ether–light petroleum (10:1) gave, first, a mixture of several trace products that was not investigated further.

Eluted second was the amorphous 2,6,1′-trisulphonate **30** (3.4 g, 8.7%), m.p. 73–75°, $[\alpha]_D$ +41° (Found: C, 53.75; H, 5.95; S, 8.65. $C_{47}H_{60}O_{21}S_3$ calc.: C, 53.4; H, 5.7; S, 9.1%). Acetylation of **30** afforded the penta-acetate **33**, m.p. 168–170° (from ethanol), $[\alpha]_D$ +61° (Found: C, 53.95; H, 5.9; S, 8.45. $C_{49}H_{62}O_{22}S_3$ calc.: C, 53.55; H, 5.65; S, 8.75%).

Eluted third was the 6,1′-disulphonate **31** (17 g, 52%), m.p. 146–147° (from ether), $[\alpha]_D$ +32° (*c* 1) (Found: C, 52.15; H, 5.8; S, 7.15. $C_{38}H_{50}O_{19}S_2$ calc.: C, 52.15; H, 5.7; S, 7.3%). Acetylation of **30** afforded the hexa-acetate **34**, m.p. 145–146° (from ethanol), $[\alpha]_D$ +61° (Found: C, 52.5; H, 5.7; S, 6.45. $C_{42}H_{54}O_{21}S_2$ calc.: C, 52.6; H, 5.65; S, 6.7%).

Elution with acetone then gave a mixture of monosulphonates. A solution of the mixture in 2-propanol deposited crystals of the major component after standing at room temperature for several weeks; the crystalline sulphonate **32** had m.p. 118–120°, $[\alpha]_D$ +22° (Found: C, 49.6; H, 5.8. $C_{29}H_{40}O_{17}S$ calc.: C, 50.3; H, 5.8%).

In later reactions, it was found that **31** could be crystallised directly from the mixture without recourse to chromatography.

2,1′:3,6-Dianhydrosucrose (**35**). — A solution of **31** (13 g, 14.9 mmol) in M methanolic sodium methoxide (140 mL) was heated under reflux for 24 h; t.l.c. ($CHCl_3$–MeOH, 2:1) then showed one fast-moving product and several slow-moving trace-components. The cooled mixture was neutralized with Amberlite IR-120 (H^+) resin and evaporated to dryness. The syrupy residue was purified by passage through a column of silica gel with chloroform–methanol (10:1), to give **35** (3.1 g, 68%) as a syrup, $[\alpha]_D$ +16° (*c* 1, methanol) (Found: C, 47.15; H, 6.5. $C_{12}H_{18}O_9$ calc.: C, 47.05; H, 5.9%).

Acetylation afforded a crystalline tetra-acetate **36**, m.p. 115–116° (from ethanol), $[\alpha]_D$ +39° (Found: C, 50.65; H, 5.6. $C_{20}H_{26}O_{13}$ calc.: C, 50.65; H, 5.5%).

2,1′:3,6-Dianhydro-6′-bromo-6′-deoxysucrose (**37**). — To an ice-cold solution of **35** (3.2 g, 10.5 mmol) in pyridine (30 mL) was added triphenylphosphine (8.2 g, 31.5 mmol) in several small portions. A solution of carbon tetrabromide (5 g, 15 mmol) in pyridine (20 mL) was then added dropwise during 15 min. The mixture was heated at 70° for 2.5 h, and t.l.c. (Me_2CO–$CHCl_3$, 1:3) then indicated one major product with several minor products and some **35**. Methanol (15 mL) was added to the reaction mixture which was then evaporated to dryness. Chromatography of the product on silica gel, initially with chloroform (to remove triphenylphosphine oxide) and then with chloroform–methanol (20:1), afforded syrupy **37** (1.5 g, 39%), $[\alpha]_D$ +10° (*c* 0.7, methanol) (Found: C, 39.7; H, 4.6. $C_{12}H_{17}BrO_8$ calc.: C, 39.05; H, 4.6%), together with **35** (1.2 g, 38%).

Acetylation of **37** afforded the triacetate **38**, m.p. 117–120° (from ether), $[\alpha]_D$ +24° (Found: C, 44.1; H, 4.8; Br, 16.15. $C_{18}H_{23}BrO_{11}$ calc.: C, 43.65; H, 4.65; Br, 16.15%).

2,1′:3,6:3′,6′-Trianhydrosucrose (**1**) *and its diesters* **2** *and* **3**. — (*a*) A solution

of **15** (0.7 g, 0.78 mmol) in M methanolic sodium methoxide (30 mL) was heated under reflux for 24 h, cooled, neutralised with Amberlite IR-120 (H^+) resin, and evaporated. Acetylation of the syrupy residue afforded the 4,4′-diacetate **2** (0.2 g, 69%), m.p. 299° (dec.) (from ethanol), $[\alpha]_D$ +68° (Found: C, 51.8; H, 5.1. $C_{16}H_{20}O_{10}$ calc.: C, 51.6; H, 5.35%).

Deacetylation of **2** with methanolic sodium methoxide afforded the trianhydride **1**, m.p. 188–190° (from methanol–chloroform), $[\alpha]_D$ +54° (*c* 1, methanol) (Found: C, 50.4; H, 5.3. $C_{12}H_{16}O_8$ calc.: C, 50.0; H, 5.55%).

(*b*) A solution of the 6′-bromide **37** (0.6 g, 1.21 mmol) in M methanolic sodium methoxide (15 mL) was heated under reflux for 2.5 h and then processed as in (*a*), to give **2** (0.3 g, 65%), m.p. 303–305° (dec.), $[\alpha]_D$ +73°, which was identical (n.m.r., i.r.) with the product obtained in (*a*).

(*c*) To an ice-cold solution of **35** (6.3 g, 20.5 mmol) in dry pyridine (80 mL) was added, dropwise, a solution of tosyl chloride (4.7 g, 24.7 mmol) in dry pyridine (40 mL). The mixture was then kept at room temperature for 2 days and evaporated to dryness. T.l.c. ($CHCl_3$–MeOH, 4:1) indicated one major, fast-moving product with several slower, minor components and some **35**. The syrupy product was then fractionated on silica gel with chloroform, to give the 6′-tosylate **39** as a syrup (2.1 g, 22%). T.l.c. (Me_2CO–$CHCl_3$, 3:2) indicated that this product was not entirely homogeneous, and no attempt was made at further purification.

The syrup (2.1 g) was then treated with methanolic sodium methoxide as in (*a*), except that neutralisation was effected with acetic acid. The mixture was then evaporated to dryness and the residue was fractionated on a column of silica gel with chloroform, to afford **1**, m.p. 188–190°, $[\alpha]_D$ +57° (*c* 0.5, methanol) identical (i.r., n.m.r.) with the sample obtained in (*a*).

Acetylation of the product afforded **2**, m.p. 303–305° (dec.) (from chloroform–ethanol), $[\alpha]_D$ +73°, identical with the foregoing sample.

Mesylation of **1** afforded the dimesylate **3**, m.p. 165–167°, $[\alpha]_D$ +44° (Found: C, 37.45; H, 4.65; S, 14.45. $C_{14}H_{20}O_{12}S_2$ calc.: C, 37.85; H, 4.5; S, 14.4%).

3-O-Benzoyl-4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 3,4,6-tri-O-benzoyl-1-chloro-1-deoxy-β-D-fructofuranoside (**41**). — Sulphuryl chloride (53 mL, 0.66 mol) was added dropwise during 30 min to a stirred solution of 3,3′,4′,6′-tetra-*O*-benzoylsucrose[8] (**40**; 10 g, 0.013 mol) in a mixture of pyridine (120 mL) and 1,2-dichloroethane (120 mL) at −30°. The temperature of the mixture was then allowed to rise to ambient and, after ~1 h, it was heated at 55–60° (bath) for 16 h. T.l.c. (ether–light petroleum, 3:1) showed the presence of one major product and at least two minor products. The mixture was then poured into ice-cold, 10% sulphuric acid (500 mL), the organic layer was separated, and the aqueous layer was washed with chloroform. The combined organic extracts were then washed with saturated, aqueous sodium hydrogencarbonate, and dried ($MgSO_4$). Evaporation to dryness gave a red syrup that was dissolved in methanol. A catalytic amount of sodium iodide was added, together with sodium carbonate (10 g), in order to effect *O*-dechlorosulphation. The mixture was then filtered, the methanolic solution was evaporated to dry-

ness, and the product was chromatographed on silica gel with ether–light petroleum (1:3), to afford the major product **41** as an amorphous solid (5 g, 47%), m.p. 76–79°, $[\alpha]_D$ +43° (*c* 0.5) (Found: C, 58.85; H, 4.35; Cl, 14.1. $C_{40}H_{35}Cl_3O_{12}$ calc.: C, 59.0; H, 4.3; Cl, 13.1%).

2,1′:3,6-Dianhydro-4-chloro-4-deoxy-galacto-*sucrose triacetate* (**42**). — A solution of **41** (3.7 g, 4.55 mmol) in M methanolic sodium methoxide was heated under reflux for 24 h, cooled, neutralised with Amberlite IR-120 (H^+) resin, and concentrated. Fractionation of the residue on a column of silica gel with chloroform–methanol (8:1) gave the major product as a syrup that was acetylated, in the usual way, to give syrupy **42** (0.7 g, 34%), $[\alpha]_D$ +10° (Found: C, 47.95; H, 5.25; Cl, 7.5. $C_{18}H_{23}ClO_{11}$ calc.: C, 47.95; H, 5.1; Cl, 7.9%).

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