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SYNTHESIS OF 6,1′,3′-, 2,6,1′-, 1′,3′,6′-, AND 2,1′,6′-TRI-*O*-BENZOYL-SUCROSE

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ABSTRACT

6,1′,3′-Tri-*O*-benzoylsucrose (**1**) has been synthesised by three routes. Monobenzoylation of 3,6′-di-*O*-acetyl-2,1′:4,6-di-*O*-isopropylidenesucrose[1–3] gave 3,6′-di-*O*-acetyl-3′-*O*-benzoyl-2,1′:4,6-di-*O*-isopropylidenesucrose. Removal of the acetal groups and dibenzoylation gave 3,6′-di-*O*-acetyl-6,1′,3′-tri-*O*-benzoylsucrose (**5**). Selective deacetylation of **5** using trifluoroacetic acid gave **1**. 6′-*O*-*tert*-Butyldiphenylsilyl-2,1′:4,6-di-*O*-isopropylidenesucrose was converted into **1** by a reaction sequence similar to the above. A three-step synthesis of **1** involved tribenzoylation of 6′-*O*-*tert*-butyldiphenylsilylsucrose[4]. 2,6,1′-Tri-*O*-benzoylsucrose was also synthesised by this route. 1′,3′,6′-Tri-*O*-benzoylsucrose and 2,1′,6′-tri-*O*-benzoylsucrose were synthesised by tribenzoylation of 4,6-*O*-isopropylidenesucrose.

INTRODUCTION

The partial benzoylation of sucrose[5] gave three sucrose tribenzoates having two primary benzoate groups and one secondary benzoate group. ^{1}H-N.m.r. spectroscopy indicated that the secondary benzoate group was located at C-2 in two compounds and at C-3′ in the third. In order to confirm these structures, several sucrose tribenzoates esterified at either C-2 or C-3′ and two of the three primary positions have been synthesised. The synthesis of 6,3′,6′-tri-*O*-benzoylsucrose (**12**) has been described[6] and we now report syntheses of 6,1′,3′- (**1**), 2,6,1′- (**8**), 1′,3′,6′- (**9**), and 2,1′,6′-tri-*O*-benzoylsucrose (**10**).

DISCUSSION

Treatment[2] of 2,1′:4,6-di-*O*-isopropylidenesucrose tetra-acetate (**2**) with methanolic ammonia at 5° gave, among other products, 35% of 3,6′-di-*O*-acetyl-2,1′:4,6-di-*O*-isopropylidenesucrose (**3**). We have obtained partially acetylated products during a Zemplén deacetylation of **2** and, in particular, one major component which had an R_F value in t.l.c. indicative of a diacetate. Treatment of **2** with

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TABLE I

^{1}H-N M R DATA FOR COMPOUNDS **4, 13, 14, 16, 17, 41, 42,** AND **45**

Compound[a]	*Chemical shifts (δ) (first-order couplings, Hz, in parentheses)*										
	H-1 ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-3'* ($J_{3',4'}$)	*H-4'* ($J_{4',5'}$)	*H-2–6 H-1',H-3'–6' OH*	*Aryl*	*OAc*		CMe_2	
4	6.16d		5.41t	4.89d		3.40–4.65m	7.40–8.35m	2.07	2.07	1.28	1.33
	(3.5)	(9.6)	(9.6)	(6.2)						1.45	1.48
13[b]	6.40d		5.62t		5.45dd	3.20–4.95m		1.77	1.79	1.19	1.26
	(3.8)	(9.5)	(9.5)	(7.0)	(5.5)			1.80		1.32	1.38
14	6.08d		5.23t	4.86d		3.20–4.50m		2.06	2.07	1.27	1.40
	(3.7)	(9.2)	(9.2)	(6.8)				2.26		1.45	1.46
16	6.16d		5.15t	5.23d	5.62–5.78m	3.40–4.70m	7.30–8.30m	2.00	2.05	1.28	1.32
	(3.5)	(9.5)	(9.5)	(5.2)						1.43	1.47
17	6.12d		5.13t	5.32d	5.39–5.56m	3.40–4.60m	7.30–8.30m	2.00	2.06	1.27	1.32
	(3.6)	(9.6)	(9.6)	(5.2)				2.10		1.42	1.46
41	5.69d	4.87dd	5.33t	5.83d	5.67t	3.35–5.00m	7.25–8.20m	1.87	2.00	1.30	1.40
	(3.7)	(10.0)	(10.0)	(6 4)	(6.4)			2.05			
42	6.24d		5.26t		5.50–5.90m	3.45–5.14m	7.20–8.30m	1.94	1.98	1.27	1.30
	(3.5)	(9.2)	(9.2)					2.07			
45	5.78d	5.08dd				2.75–4.75m	7.15–8.15m			1.39	1.47
	(3.8)	(10.0)									

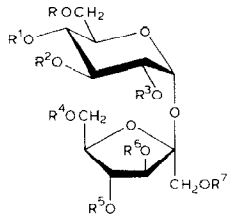
[a]In $CDCl_3$ unless otherwise stated. [b]In C_6H_6/CD_3OD.

methanolic 0.1M sodium methoxide for ~1.5 h, followed by chromatography, gave **3** in excellent yield. An early fraction contained **2** and the triacetates **13** and **14** which were subsequently isolated pure. The ^{1}H-n.m.r. spectra (Table I) confirmed the structures assigned[2] to **13** and **14** in admixture. Thus, **13**, which showed low-field signals at δ 5.62 (t, $J_{3,4}$ 9.5 Hz) and 5.45 (dd, $J_{3',4'}$ 7.0, $J_{4',5'}$ 5.5 Hz), was the 3,4',6'-triacetate, and **14**, which showed low-field signals at δ 5.23 (t, $J_{3,4}$ 9.2 Hz) and 4.86 (d, $J_{3',4'}$ 6.8 Hz), was the 3,3',6'-triacetate.

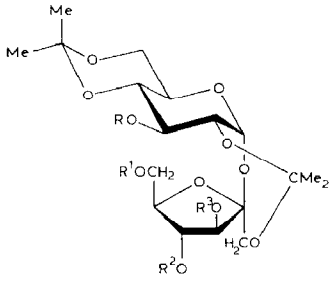
Monobenzoylation of **3** gave **4** in good yield, which showed low-field signals in the ^{1}H-n.m.r. spectrum for the anomeric proton (δ 6.16, d), H-3 (δ 5.41, t, $J_{3,4}$ 9.6 Hz), and H-3' (δ 4.89, d, $J_{3',4'}$ 6.2 Hz). Removal of the acetal groups from **4**, in the normal manner, gave crystalline **18** which could be prepared, in the same overall yield, by combining the partial deacetylation, monobenzoylation, and deacetalation steps. Dibenzoylation of **18** gave a product which showed (t.l.c.) a major and several minor components. Column chromatography of the mixture gave the tetrabenzoate **20** (16%), and then the major product **5** (47%). The ^{1}H-n.m.r. spectrum (Table II) of **20** indicated that it was a tetrabenzoate; since the only extra low-field signal was at δ 5.87 (dd, $J_{3',4'}$ 6.0, $J_{4',5'}$ 5.5 Hz), characteristic of substitution at H-4', **20** is a 6,1',3',4'-tetrabenzoate. This assignment was supported by the mass spectrum (Table III) of the tetra-acetate **21** which contained fragment ions at *m/z* 517 and 393 indicating the presence of three benzoate groups on one ring and one on the second. The ^{1}H-n.m.r. spectrum of the major product **5** showed that it was a tribenzoate and, since there were no extra low-field signals, benzoylation must have occurred at the two primary positions, namely, 6 and 1'.

Treatment of **5** with aqueous methanolic trifluoroacetic acid selectively hydrolysed the acetate groups to give the tribenzoate **1**[5], which was isolated in a yield of 43%. The only other low-field signal, apart from the anomeric signal, in the ^{1}H-n.m.r. spectrum of **1** was at δ 5.80 (d, $J_{3',4'}$ 8.5 Hz), confirming that the only secondary benzoate was located at position 3'. Compound **1** and its acetylated derivative **22** (Table IV) were clearly different from the other two possible tribenzoates having benzoate groups at position 3' and two of the primary positions, namely 6,3',6'-tri-*O*-benzoylsucrose[6] (**12**) and 1',3',6'-tri-*O*-benzoylsucrose (**9**), each of which was synthesised by an unambiguous route.

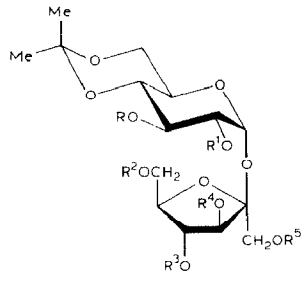
The *tert*-butyldiphenylsilyl group[7] has been used to block primary hydroxyl groups in sugar derivatives[8]. Treatment[7] of 2,1':4,6-di-*O*-isopropylidenesucrose with *tert*-butylchlorodiphenylsilane (1.4 mol. equiv.) gave the 4',6'-di-*O*-*tert*-butyldiphenylsilyl derivative **23** (23%) and the expected product **6** (32%). The structures of **23** and **6** followed from the ^{1}H-n.m.r. (Table V) and mass spectra (Table VI) of the acetylated derivatives **24** and **25**, respectively. Thus, the diacetate **24** gave low-field signals at δ 4.99 (t, $J_{3,4}$ 9.6 Hz) and 5.01 (d, $J_{3',4'}$ 6.8 Hz) belonging to H-3 and H-3', respectively. Similarly the triacetate **25** gave low-field signals for H-3,3',4'. The mass spectrum of **24** showed fragment ions at *m/z* 681 and 607 confirming the presence of two silyl groups on the fructofuranosyl moiety. Compound **25** gave corresponding ions at *m/z* 485 and 411. A better yield (66%) of crystalline **6**,



1 $R^1 = R^2 = R^3 = R^4 = R^5 = H, R = R^6 = R^7 = Bz$
5 $R^1 = R^3 = R^5 = H, R^2 = R^4 = Ac, R = R^6 = R^7 = Bz$
7 $R = R^1 = R^2 = R^3 = R^5 = R^6 = R^7 = H, R^4 = {}^tBuPh_2Si$
8 $R^1 = R^2 = R^4 = R^5 = R^6 = H, R = R^3 = R^7 = Bz$
9 $R = R^1 = R^2 = R^3 = R^5 = H, R^4 = R^6 = R^7 = Bz$
10 $R = R^1 = R^2 = R^5 = R^6 = H, R^3 = R^4 = R^7 = Bz$
12 $R^1 = R^2 = R^3 = R^5 = R^7 = H, R = R^4 = R^6 = Bz$
18 $R = R^1 = R^2 = R^5 = R^7 = H, R^2 = R^4 = Ac, R^6 = Bz$
19 $R = R^1 = R^2 = R^3 = R^4 = R^5 = R^7 = Ac, R^6 = Bz$
20 $R^1 = R^3 = H, R^2 = R^4 = Ac, R = R^5 = R^6 = R^7 = Bz$
21 $R^1 = R^2 = R^3 = R^4 = Ac, R = R^5 = R^6 = R^7 = Bz$
22 $R^1 = R^2 = R^3 = R^4 = R^5 = Ac, R = R^6 = R^7 = Bz$
33 $R = R^1 = R^2 = R^3 = R^5 = R^7 = H, R^6 = Bz, R^4 = {}^tBuPh_2Si$
34 $R = R^1 = R^2 = R^3 = R^5 = R^7 = Ac, R^6 = Bz, R^4 = {}^tBuPh_2Si$
35 $R^1 = R^2 = R^3 = R^5 = H, R = R^6 = R^7 = Bz, R^4 = {}^tBuPh_2Si$
36 $R^1 = R^2 = R^3 = R^5 = Ac, R = R^6 = R^7 = Bz, R^4 = {}^tBuPh_2Si$
37 $R^1 = R^2 = R^5 = R^6 = H, R = R^3 = R^7 = Bz, R^4 = {}^tBuPh_2Si$
38 $R^1 = R^2 = R^5 = R^6 = Ac, R = R^3 = R^7 = Bz, R^4 = {}^tBuPh_2Si$
39 $R^1 = R^2 = R^4 = R^5 = R^6 = Ac, R = R^3 = R^7 = Bz$
43 $R = R^1 = R^2 = R^3 = R^5 = Ac, R^4 = R^6 = R^7 = Bz$
44 $R^1 = R^2 = R^3 = R^5 = R^7 = Ac, R = R^4 = R^6 = Bz$
46 $R = R^1 = R^2 = R^5 = R^6 = Ac, R^3 = R^4 = R^7 = Bz$
47 $R^1 = R^2 = R^4 = R^5 = R^6 = R = H, R^3 = R^4 = Bz$
48 $R^1 = R^2 = R^5 = R^6 = R^7 = Ac, R = R^3 = R^4 = Bz$
49 $R^1 = R^2 = R^3 = R^5 = R^6 = H, R = R^4 = R^7 = Bz$
50 $R^1 = R^2 = R^3 = R^5 = R^6 = Ac, R = R^4 = R^7 = Bz$



2 $R = R^1 = R^2 = R^3 = Ac$
3 $R^2 = R^3 = H, R = R^1 = Ac$
4 $R^2 = H, R = R^1 = Ac, R^3 = Bz$
6 $R = R^2 = R^3 = H, R^1 = {}^tBuPh_2Si$
13 $R^3 = H, R = R^1 = R^2 = Ac$
14 $R^2 = H, R = R^1 = R^3 = Ac$
15 $R^1 = R^2 = R^3 = H, R = Ac$
16 $R = R^1 = Ac, R^2 = R^3 = Bz$
17 $R = R^1 = R^2 = Ac, R^3 = Bz$
23 $R = R^1 = H, R^1 = R^2 = {}^tBuPh_2Si$
24 $R = R^3 = Ac, R^1 = R^2 = {}^tBuPh_2Si$
25 $R = R^2 = R^3 = Ac, R^1 = {}^tBuPh_2Si$
26 $R = R^2 = H, R^3 = Bz, R^1 = {}^tBuPh_2Si$
27 $R = H, R^2 = R^3 = Bz, R^1 = {}^tBuPh_2Si$
28 $R = R^2 = R^3 = Bz, R^1 = {}^tBuPh_2Si$
29 $R^2 = H, R = R^3 = Bz, R^1 = {}^tBuPh_2Si$
30 $R = R^2 = Ac, R^3 = Bz, R^1 = {}^tBuPh_2Si$
31 $R = Ac, R^2 = R^3 = Bz, R^1 = {}^tBuPh_2Si$
32 $R^2 = Ac, R = R^3 = Bz, R^1 = {}^tBuPh_2Si$



11 $R = R^1 = R^2 = R^3 = R^4 = R^5 = H$
40 $R = R^1 = R^3 = H, R^2 = R^4 = R^5 = Bz$
41 $R = R^1 = R^3 = Ac, R^2 = R^4 = R^5 = Bz$
45 $R = R^3 = R^4 = H, R^1 = R^2 = R^5 = Bz$

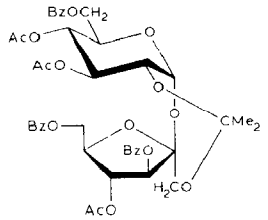


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TABLE II

^{1}H-N M R DATA FOR COMPOUNDS **1, 5, 8, 9, 10, 18, 20, 33, 35,** AND **37**

Compound[a]	*Chemical shifts (δ) (first-order couplings, Hz, in parentheses)*								
	H-1 ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-3'* ($J_{3',4'}$)	*H-4'* ($J_{4',5'}$)	*H-2–6 H-1',H-4'–6' OH*	*Aryl*	*OAc*	*^{t}Bu*
1[b]	5.55d (3.1)			5.80d (8.5)		3.20–4.90m	7.20–8.20m		
5	5.64d (3.4)	(9.8)	5.16t (9.8)	5.48d (7.0)		3.35–4.80m	7.10–8.20m	2.06 2.13	
8[b]	5.84d (3.6)	5.00dd (10.1)				3.40–4.85m	7.25–8.20m		
9[c]	5.53d (3.5)			5.81d (7.8)	4.62t (7.8)	3.10–5.00m	7.25–8.25m		
10[b]	5.85d (3.8)	4.88dd (10.0)				3.20–5.00m	7.20–8.20m		
18[b]	5.43d (3.5)	3.62dd (10.0)	5.29t (10.0)	5.65d (8.0)		3.40–4.55m	7.35–8.25m	2.07 2.11	
20	5.66d (3.7)	(9.9)	5.07t (9.9)	6.04d (6.0)	5.87dd (5.5)	3.40–4.85m	7.10–8.15m	2.07 2.10	
33[b]	5.33d (3.5)			5.55d (6.5)	4.39t (6.5)	3.20–4.30m	7.30–8.15m		1.04
35	5.54d (3.5)			5.54d (7.5)		3.20–4.75m	7.15–8.10m		1.01
37	5.63d (3.5)	4.97dd (10.0)				3.40–4.55m	7.10–8.10m		0.98

[a]In $CDCl_3$ unless otherwise stated. [b]In CD_3OD. [c]In $CD_3OD/CDCl_3$.

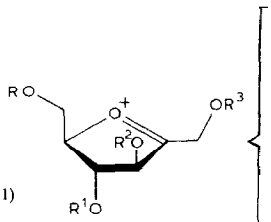
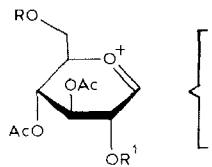
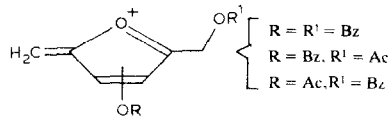
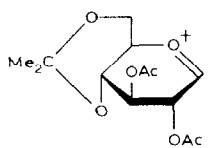
obtained directly without column chromatography, was achieved if the silylation method of Khan and co-workers[4] was employed.

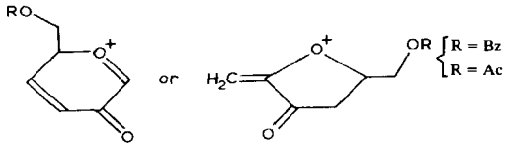
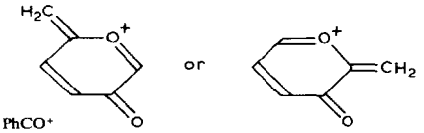
Monobenzoylation of **6** gave (t.l.c.) a mixture of two fast-moving (**28** and **29**) and two-slow moving components (**26** and **27**). The slowest-moving component (**26**) was the major product. Column chromatography of the mixture gave the dibenzoate **27** and the benzoate **26** (55%), which crystallised and, in subsequent reactions, could be crystallised directly from the product mixture. Further column chromatography gave the tribenzoate **28** and the dibenzoate **29**. The structures of these benzoates were assigned on the basis of their ^{1}H-n.m.r. spectra and the mass spectra of acetylated derivatives. Thus, each benzoate gave a low-field signal characteristic of H-3' (d). The dibenzoate **27** also gave a signal at δ 6.04 (dd, $J_{3',4'}$ 4.8, $J_{4',5'}$ 4.0 Hz) for H-4' and **29** gave a signal at δ 5.60 (t, $J_{3,4}$ 9.3 Hz) for H-3. The mass spectra of **28** and the acetylated derivative **31** showed fragment ions at *m/z* 609 and 535 confirming the presence of two benzoyl groups on the fructofuranosyl moiety. Therefore **31** is the 3',4'-dibenzoate. The mass spectra of the acetylated derivatives **30** and **32** showed fragment ions at *m/z* 547 and 473 indicating the presence of only one benzoate group on the fructofuranosyl moiety. Compounds **28**

TABLE III

MASS-SPECTRAL DATA FOR COMPOUNDS **19, 21, 22, 34, 36, 38, 39, 41, 43,** AND **46**

m/z of principal fragments (% of base peak)

19	**21**	**22**	**34**	**36**	**38**	**39**	**41**	**43**	**46**
				651(0 6)					 R = ^{t}Bu(Ph)$_2$Si,R^1 = Ac,R^2 = R^3 = Bz R = ^{t}Bu(Ph)$_2$Si,R^1 = Ac,R^3 = Bz,R^3 = Ac R = ^{t}Bu(Ph)$_2$Si,R^1 = Ac,R^2 = Ac,R^3 = Bz R = R^2 = R^3 = Bz,R^1 = Ac R^1 = R^2 = R^3 = Bz,R = Ac R = R^1 = Ac,R^2 = R^3 = Bz R = R^1 = R^3 = Ac,R^2 = Bz R = R^1 = R^2 = Ac,R^3 = Bz
			589(0 9)						
					589(2 2)				
							517(5 9)		
	517(23 7)							517(1 9)	
		455(4 2)							455(12 1)
393(17 8)									
						393(9 0)			
					455(11 2)	455(13 4)			 R = R^1 = Bz R = Bz,R^1 = Ac R = R^1 = Ac
	393(45 5)	393(11 2)		393(21 1)					393(17 3)
331(24 6)			331(17 9)					331(5 4)	
	335(14 9)	335(3 0)		335(4 1)			335(4 8)	335(2 3)	 R = R^1 = Bz R = Bz, R^1 = Ac R = Ac,R^1 = Bz
273(21 2)		273(1 6)	273(6.0)					273(0 8)	
					273(1 7)	273(14 0)			273(6 9)
							287(5 2)		

	231(38 9)	231(8.7)		231(25.2)	231(7 0)	231(13 1)	231(1.4)	231(1.0)	231(5.3)	
169(42.2)	169(4 2)	169(3 0)	169(45.3)	169(7 4)	169(4 0)	169(3.6)	169(6.1)	169(10.4)	169(9 4)	
			241(19.0)	241(16.1)	241(8.2)					$(Ph)_2Si{=}O^+CH_2CHO$
			199(16.2)	199(14.6)	199(8.0)					$(Ph)_2Si{=}O^+H$
										
109(30.0)	109(9.8)	109(5.4)	109(32.8)	109(16.3)	109(4 6)	109(8 4)	109(6 2)	109(9 0)	109(9.2)	
105(80 0)	105(100)	105(100)	105(100)	105(100)	105(100)	105(100)	105(100)	105(45.0)	105(100)	$PhCO^+$
43(100)	43(81.0)	43(81 0)	43(91 7)	43(78 7)	43(34 7)	43(93.8)	43(59.4)	43(100)	43(24 4)	$MeCO^+$

and **32** showed a fragment ion at *m/z* 307 indicating the presence of a benzoate group on the glucopyranosyl ring. Thus, **30** is confirmed to be the 3′-monobenzoate and **32** the 3,3′-dibenzoate.

Attempted hydrolysis of the acetal groups from **26** with trifluoroacetic acid resulted in decomposition and loss of the silyl protecting-group. However, hydrolysis with aqueous 60% acetic acid at 50° gave crystalline **33** in excellent yield, the structure of which was confirmed by ^{1}H-n.m.r. data (Table II), especially the signal at δ 5.55 (d, H-3′). This assignment was supported by the mass spectra of the acetylated derivative **34**, which showed a fragment ion at *m/z* 589 corresponding to the fructofuranosyl moiety substituted by a benzoyl and a silyl group. Dibenzoylation of **33** gave a complex mixture (t.l.c.). Fractionation of the mixture gave the 6,1′,3′-tribenzoate **35** (15%), and also the 2,6,1′,3′-tetrabenzoate and the 6,3′-dibenzoate which were not fully characterised. The reason for the low yield of **35** is not understood since it was reasonable to expect the two primary hydroxyl groups at positions 6 and 1′ to be selectively benzoylated.

The preparation, in good yield, of crystalline 6′-*O*-*tert*-butyldiphenylsilylsucrose (**7**) has been described[4]. Tribenzoylation of **7** gave a syrupy mixture of several products (t.l.c.); the major component corresponded to **35**, which was isolated (22%) by column chromatography together with 10% of the 2,6,1′-tribenzoate **37**. The ^{1}H-n.m.r. spectrum of **37** showed a characteristic low-field signal at δ 4.97 (dd, $J_{1,2}$ 3.5, $J_{2,3}$ 10.0 Hz) for H-2. The mass spectrum of the acetate (**38**) of **37** contained fragment ions at *m/z* 589 and 455. The former confirmed the presence of a benzoate group on the fructofuranosyl ring and the latter the presence of two benzoate groups on the glucopyranosyl ring. Removal of the *tert*-butyldiphenylsilyl group from **35** and **37** with tetrabutylammonium fluoride[7] gave **1** and **8**, respectively. The ^{1}H-n.m.r. spectrum of the tribenzoate **8** again showed a characteristic low-field signal at δ 5.00 (dd) which confirmed that the secondary position benzoylated was 2.

2,1′,6′-Tri-*O*-benzoylsucrose (**10**) was synthesised from 4,6-*O*-isopropylidenesucrose hexa-acetate[9], deacetylation of which followed by tribenzoylation gave a complex mixture (t.l.c.) containing two components each with a mobility slightly greater than that of **3**. These components were isolated by column chromatography.

The ^{1}H-n.m.r. spectrum of the faster-moving component indicated that it was a mixture of tribenzoates in the ratio 4:1. The major isomer gave a low-field signal at δ 5.62 (d, $J_{3',4'}$ 6.8 Hz) indicating that it was esterified at position 3′. The remaining two benzoate groups were on the primary hydroxyl groups and therefore the compound was the 1′,3′,6′-tribenzoate **40**. The minor isomer also gave a low-field signal at δ 5.07 (d, $J_{3',4'}$ 6.2 Hz), characteristic of substitution at position 3′; the other benzoate groups were located at the primary positions. The signal for the anomeric proton was at very low field (δ 6.20), compared with the corresponding signal (δ 5.61) for the major isomer, and was characteristic of the anomeric proton of a 2,1′:4,6-diacetal. Acetylation of the mixture gave a product which contained

TABLE IV

^{1}H-N M R DATA FOR COMPOUNDS **19, 21, 22, 34, 36, 38, 39, 43,** AND **46**

Compound[a]	*Chemical shifts (δ) (first-order couplings, Hz, in parentheses)*											
	H-1 ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5}$)	*H-3'* ($J_{3',4'}$)	*H-4'* ($J_{4',5'}$)	*H-6,1',6'*	*Aryl*	*OAc*			*^{t}Bu*
19	5.67d	4.93dd	5.40dd	5.02t	5.72d	5.57dd	3.85–4.55m	7.35–8.20m	1.97	1.97	1.97	
	(3.6)	(10.0)	(9.5)	(9.5)	(6.8)	(6.0)			2.07	2.12	2.12	
									2.12			
21	5.80d	4.97dd	5.53t	5.19t	5.97d	5.79t	4.15–4.80m	7.10–8.20m	1.85	1.97	1.97	
	(3.5)	(9.8)	(9.8)	(9.8)	(6.0)	(6.0)			2.08			
22	5.75d	4.95dd	5.48t	5.17t	5.79d	5.58t	4.15–4.75m	7.20–8.20m	1.85	1.95	1.97	
	(3.5)	(9.8)	(9.8)	(9.8)	(5.6)	(5.6)			2.08	2.08		
34[b]	5.67d	5.06dd	5.67dd	5.18t	5.97d	5.84t	3.90–4.60m	7.00–8.35m	1.68	1.68	1.72	1.16
	(3.6)	(10.0)	(9.5)	(9.5)	(6.5)	(6.5)			1.76	1.76	1.80	
36	5.61d	4.91dd	5.45t	5.13t	5.77d	5.65t	3.75–4.60m	7.10–8.20m	1.89	1.90	1.95	1.03
	(3.6)	(9.8)	(9.8)	(9.8)	(6.5)	(6.5)			2.01			
38	5.93d	5.11dd	5.72dd	5.29t	5.56d	5.52t	3.70–4.65m	7.15–8.20m	1.93	1.98	1.98	1.04
	(3.6)	(10.0)	(9.8)	(9.8)	(5.6)	(5.6)			2.10			
39[b]	6.13d	5.35dd	6.09dd	5.58t	5.74d	5.50t	3.90–4.95m	6.90–8.35m	1.66	1.66	1.80	
	(3.8)	(10.2)	(9.5)	(9.5)	(5.4)	(5.4)			1.91	1.92		
43	5.75d	4.95dd	5.45dd	5.03dd	5.87d	4.68t	3.90–4.80m	7.10–8.20m	1.90	1.93	1.96	
	(3.5)	(10.0)	(9.2)	(10.0)	(6.0)	(6.0)			2.07	2.07		
46	5.95d	5.08dd	5.73t	5.17t	5.57d	5.45t	4.10–4.75m	7.10–8.20m	1.94	1.98	2.03	
	(3.6)	(9.8)	(9.8)	(9.8)	(4.9)	(4.9)			2.10	2.13		

[a]In $CDCl_3$ unless otherwise stated. [b]In C_6D_6/CD_3OD.

TABLE V

^{1}H-N M R DATA FOR COMPOUNDS **6** AND **23–32**

Compound[a]	*Chemical shifts (δ) (first-order couplings, Hz, in parentheses)*											
	H-1 ($J_{1,2}$)	*H-3* ($J_{2,3}$) ($J_{3,4}$)	*H-3'* ($J_{3',4'}$)	*H-4'* ($J_{4',5'}$)	*H-2–6 H-1',H-3'–6' OH*	*OH*	*Aryl*	*OAc*		CMe_2		*^{t}Bu*
6	5.96d (3.3)				3.10–4.30m	2.48s	7.20–7.80m			1.39 1.47	1.43 1.48	1.04
23	5.88d (2.9)				2 80–4.35m	2.43s 2.04d (10.0)	7.10–7.80m			1.37 1.42	1.42 1.47	0.95 1.04
24	5.86d (3.6)	4.99t (9.6) (9.6)	5.01d (6.8)		2.90–4.45m		7.15–7.75m	1.78	2.00	1.37 1.37	1.37 1.37	0.97 0.98
25	5.92d (3.7)	5.17t (9.2) (9.2)	5.09d (6.2)	5.60dd (4.8)	3.30–4.40m		7.20–7.75m	2.03 2.21	2.05	1.24 1.40	1.40 1.44	1.03
26	5.93d (3.0)		5.11d (6.4)	4.56ddd (5.2)	3.30–4.35m	3.02d ($J_{HO,4'}$ = 2.8) 2.47s	7.25–8.20m			1.32 1.44	1.42 1.48	1.06
27	5.94d (2.4)		5.42d (4.8)	6.04dd (4.0)	3.25–4.60m	2.37s	7.20–8.20m			1.35 1.45	1.35 1.45	0.99
28	6 02d (3.5)	5.35t (9.4) (9.4)	5.45d (5.0)	6.04t (5.0)	3.25–4.60m		7 10–8.30m			1.17 1.38	1.27 1.40	0.98
29	6.06d (3.6)	5.60t (9.3) (9.3)	4.97d (6.2)	4.50t (6.2)	3.25–4.40m		7.20–8.35m			1.16 1.42	1 21 1.42	1.06
30	5.93d (3.4)	5.11t (9.2) (9.2)	5.27d (5.0)	5.77t (5.0)	3.10–4.40m		7.10–8.25m	1.98	2.06	1.24 1.30	1.25 1.38	1.03
31	5.98d (3.2)	5.09t (9.3) (9.3)	5.43d (5.2)	6.02dd (4.6)	3.25–4.60m		7.10–8.25m	1.99		1.26 1.38	1.30 1.42	0.98
32	5.99d (3.5)	5.37t (9.5) (9.5)	5.29d (5.4)	5.80dd (4.4)	3.30–4.50m		7.20–8.30m	2.07		1.16 1.39	1.29 1.39	1.05

[a]In $CDCl_3$.

two components (t.l.c.), and the major product **41** was isolated by preparative t.l.c. The mass spectrum of **41** (Table III) confirmed the presence of three benzoate groups on the fructofuranosyl ring with fragment ions at *m/z* 517 (ketofuranosyl cation) and 287 (hexopyranosyl cation). The minor component was also isolated and identified as the 6,3′,6′-tribenzoate **42** on the basis of the ^{13}C-n.m.r. data. The ^{13}C chemical shifts of the signals of the acetal carbon and methyl groups of isopropylidene acetals reflect[10,11] the size of the acetal ring. Thus, for a six-membered ring, the signal for the acetal carbon is in the range δ 97.1–99.5 and for the methyl carbons, δ 18.2–19.3 and δ 28.6–29.2. In agreement with these findings, **41** showed values of δ 99.7, 19.1, and 28.9. The chemical shift data for the various substituted 2,1′:4,6-diacetals (Tables VII and VIII) showed that the signal at δ 101.1–102.6 could be attributed to the acetal carbon of the eight-membered ring and the signals at δ 23.7–24.4 and 25.3–25.7 to the methyl groups. The ^{13}C-n.m.r. spectrum of **42** had signals at δ 101.6, 24.0, and 25.6, indicating the presence of the eight-membered 2,1′-acetal. Evidently, the mono-isopropylidenation of sucrose gave some of the 2,1′-acetal along with the 4,6-acetal. Hydrolysis of the mixture with trifluoroacetic acid gave two products (t.l.c.), and preparative t.l.c. gave the major component, 1′,3′,6′-tri-*O*-benzoylsucrose (**9**). The ^{1}H-n.m.r. spectrum of **9** showed the expected low-field signal for H-3′ at δ 5.81 (d) and the mass spectrum of the acetylated derivative **43** confirmed the presence of three benzoate groups on the fructofuranosyl ring. The minor component was identified as the known[6] 6,3′,6′-tribenzoate **12**, and thus **42** was 6,3′,6′-tri-*O*-benzoyl-2,1′-*O*-isopropylidenesucrose triacetate.

The slower-moving component was shown by ^{1}H-n.m.r. spectroscopy to have one secondary and two primary positions benzoylated and to be 2,1′,6′-tri-*O*-benzoyl-4,6-*O*-isopropylidenesucrose (**45**). Removal of the isopropylidene group from **45** gave the 2,1′,6′-tribenzoate **10**.

Tribenzoylation of **7** gave the 6,1′,3′-tribenzoate **35** and the 2,6,1′-tribenzoate **37** as the major products. No other tribenzoates were isolated. A component having a mobility (t.l.c.) faster than that of **35** was isolated and assigned the 2,6,1′,3′-tetrabenzoate structure on the basis of its ^{1}H-n.m.r. spectrum. Similarly, a component of mobility slower than that of **37** was isolated and assigned the 6,3′-dibenzoate structure. The above results indicate that the relative reactivity of the secondary hydroxyl groups of **7** towards benzoylation is in the order HO-3′ > HO-2 ⩾ HO-3,4,4′. This order of reactivity was also evident during the benzoylation of **11**, with the isolation of the 1′,3′,6′-tribenzoate **40** and the 2,1′,6′-tribenzoate **45**. These results confirm the order of reactivity described in the partial benzoylation of sucrose[5].

The ^{13}C-n.m.r. data are given in Tables VII–X. Substitution at position 6′ in the diacetal derivatives resulted in a significant shift (3.0–6.1 p.p.m.) to low field of the signal for C-4′. The presence of the diacetal structure resulted in a shift to high field of the signal for C-5, where it appeared in a characteristic group of four signals corresponding to three primary carbons and the secondary carbon. A comparison

TABLE VI

MASS-SPECTRAL DATA FOR COMPOUNDS **16, 17, 24, 25, 28,** AND **30–32**

m/z *of principal fragments (% of base peak)*							
16	**17**	**24**	**25**	**28**	**30**	**31**	**32**
699(0.7)	637(2.0)						[M−Me]+
		681(0.7)					R = ^{t}Bu(Ph)$_2$Si, R^1 = Ac R = R^1 = Bz R = Ac, R^1 = Bz R = R^1 = Ac
				609(0.6)		609(0.3)	
					547(0.4)		547(1.4)
			485(1.1)				
		607(2.5)					R = ^{t}Bu(Ph)$_2$Si, R^1 = Ac R = R^1 = Bz R = Ac, R^1 = Bz R = R^1 = Ac
				535(16.8)		535(5.0)	
					473(5.4)		473(30.9)
			411(10.1)				
397(0.7)							R = R^1 = Bz R = Ac, R^1 = Bz
	335(1.6)						
				307(26.2)			307(41.4)
245(8.2)	245(14.4)	245(9.6)	245(10.6)		245(5.2)	245(3.7)	R = Bz R = Ac

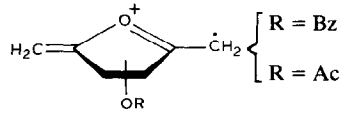
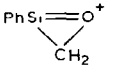
214(24.6)	214(3.6)							
152(0.3)	152(47.2)							
		241(76.2)	241(35.8)	241(7.9)	241(13.2)	241(3.9)	241(52.5)	$(Ph)_2Si{=}O^+CH_2CHO$
		199(56.9)	199(19.6)	199(8.8)	199(10.3)	199(5.4)	199(40.6)	$(Ph)_2Si{=}\overset{+}{O}H$
		135(76.0)	135(11.4)	135(7.2)	135(11.9)	135(4.9)	135(23.4)	
105(100)	105(100)	105(8.8)	105(2.1)	105(100)	105(100)	105(100)	105(100)	$PhCO^+$
43(31.8)	43(74.4)	43(100)	43(100)	43(25.6)	43(50.0)	43(25.8)	43(93.0)	$MeCO^+$

TABLE VII

^{13}C-N M R CHEMICAL SHIFTS (p.p.m.) FOR COMPOUNDS[a] **2–4, 13–17, 41, 42,** AND **45**

Atom	[b]	**2**	**3**	**4**	**13**	**14**	**15**	**16**	**17**	**41**	**42**	**45**
C-2′	103.2	104.7	104.1	104.9	104.6	104.8	103.5	105.2	105.0	104.2	105.3	103.5
C-1	91.3	91.6	91.3	91.3	91.5	91.9	91.4	91.9	91.7	90.8	91.1	90.7
C-5′	82.5	79.8	79.9	81.7	81.1	79.4	83.1	80.5	80.2	78.7	80.3	79.4
C-3′	78.8	77.3	79.7	82.5	80.6	78.4	79.5	77.8	77.7	77.0	78.1	78.3
C-4′	73.8	77.1	78.1	76.8	76.1	79.9	73.8	78.4	77.6	75.4	77.7	76.0
C-4	73.5[c]	71.9[c]	71.9[c]	72.1[c]	72.2[c]	72.2[c]	71.5	72.0[c]	71.9[c]	71.8[c]	71.8[c]	74.0
C-2	73.1[c]	71.5[c]	71.7[c]	71.5[c]	71.9[c]	72.0[c]	71.5	71.6[c]	71.5[c]	71.0[c]	71.6[c]	73.4
C-3	68.9	70.6	71.1	70.6	71.1	71.3	70.9	70.9	70.8	69.5	70.9[e]	69.0
C-5	64.1	64.5	64.0	64.4	64.5	64.4	64.1	64.8	64.8	64.8	68.3[e]	64.3
C-1′	66.6	66.0	65.9	65.7	66.3	66.1	66.3	66.3	66.0	64.8[d]	66.1	65.1[d]
C-6′	62.2	65.1	65.9	65.7	66.0	66.1	62.0	64.4	64.4	64.1[d]	64.7	64.3[d]
C-6	61.5	62.1	62.3	62.2	62.6	62.5	61.5	62.1	62.1	61.9	62.7	62.0
Acetal	102.6	101.5	101.5	101.5	101.7	102.0	101.8	101.5	101.5		101.6	
carbons	100.2	99.7	99.9	99.6	100.1	100.1	100.0	99.5	99.5	99.7		100.2
Acetal	29.0	29.1	29.1	29.0	29.5	29.5	29.7	29.1	29.0	28.9		28.9
methyl	25.3	25.4	25.4	25.5	25.7	25.7	25.3	25.6	25.5		25.6	
carbons	24.3	23.8	24.1	23.9	24.3	24.4	24.2	23.9	23.9		24.0	
	19.2	19.1	19.1	19.0	19.4	19.4	19.1	19.1	19.1	19.1		19.1

[a]In $CDCl_3$. [b]2,1′:4,6-Di-*O*-isopropylidenesucrose for purposes of comparison. [c,d,e]Assignments may be reversed.

TABLE VIII

^{13}C-N.M.R. CHEMICAL SHIFTS (p.p.m.) FOR COMPOUNDS[a] **6** AND **23–32**

Atom	**6**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**
C-2′	103.4	103.7	103.6	104.4	104.2	104.9	104.9	104.6	104.7	104.9	105.0
C-1	91.0	90.7	90.7	91.3	91.0	91.4	91.7	91.2	91.5	91.6	91.8
C-5′	81.7	84.3	83.9	81.3	83.2	82.3	82.4	84.0	81.8	82.3	82.0
C-3′	79.4	79.4	75.6	77.6	81.0	78.7	78.4	82.2	78.2	78.3	78.4
C-4′	79.4	78.8	78.4	77.8	77.6	78.7	78.4	77.6	78.0	78.3	78.0
C-4[b]	73.8	73.8	71.8	72.0	73.9	73.9	72.1	72.2	71.8	71.8	72.0
C-2[b]	73.4	73.0	71.5	71.6	73.1	72.9	71.6	71.7	71.4	71.4	71.3
C-3	69.8	70.2	70.8	70.6	70.4	70.1	71.6	71.5	70.7	70.7	71.3
C-5	63.7	63.3	63.4	64.2	63.7	63.8	64.1	64.1	64.0	64.1	64.1
C-1′	66.6	66.1	66.2	66.0	66.3	66.6	66.3	66.1	66.0	66.2	66.2
C-6′	65.9	65.8	65.9	65.2	65.9	64.8	64.9	65.9	65.0	65.0	65.0
C-6	62.2	62.0	62.0	62.0	62.3	62.1	62.1	62.3	62.0	62.0	62.1
Acetal	101.9	101.6	101.1	101.3	101.6	101.6	101.3	101.4	101.3	101.3	101.3
carbons	100.0	99.6	99.4	99.6	99.7	99.5	99.4	99.6	99.4	99.4	99.5
Acetal	29.1	29.2	29.3	29.1	29.2	29.1	29.0	29.0	29.0	28.9	29.0
methyl	25.4	25.4	25.5	25.4	25.5	25.6	25.5	25.4	25.6	25.6	25.5
carbons	24.2	24.3	24.0	23.8	24.1	24.1	23.8	23.9	23.8	23.7	23.8
	19.2	19.2	19.1	19.1	19.2	19.2	19.1	19.0	19.0	19.1	19.1

[a]In $CDCl_3$. [b]Assignments may be reversed.

TABLE IX

^{13}C-N M R CHEMICAL SHIFTS (p.p.m.) FOR COMPOUNDS **1, 5, 8, 9, 10, 12, 18, 20, 33, 35, 37, 47,** AND **49**

Atom	*Sucrose*[a,b]	**1**[c]	**5**[c]	**8**[d]	**9**[e]	**10**[d]	**12**[e]	**18**[d]	**20**[c]	**33**[d]	**35**[c]	**37**[c]	**47**[d]	**49**[d]
C-2′	104.5	103.0	103.2	104.4	103.2	104.6	104.7	105.0	104.3	105.5	102.9	103.1	106.3	104.8
C-1	93.0	93.5	92.7	91.4	93.0	91.1	92.2	93.5	93.4	93.3	91.9	89.7	90.6	94.3
C-5′	82.1	82.6	80.7	84.1	80.6	80.7	80.9	81.2	79.5	85.0	82.8	81.3	80.7	80.9
C-3′	77.3	80.4	81.4	79.3	79.2	79.1	80.2	80.3	76.0	80.7	81.2	78.4	77.1	79.2
C-4′	74.8	73.8	74.2	75.6	74.3	76.1	77.9	75.5	77.6	75.6	74.1	75.6	76.3	76.5
C-3	73.4	72.1	76.0	72.3	74.1	74.5	74.9	77.1	75.8	75.1	74.0	71.0	72.1	74.8
C-5	73.2	71.8	71.6	72.3	73.6	72.7	74.1	74.6	71.8	74.1	71.7	71.6	72.1	73.2
C-2	71.8	71.2	70.5	74.9	72.0	75.0	72.1	71.4	70.6	73.2	71.0	72.8	74.9	72.3
C-4	70.0	70.3	69.0	72.1	71.0	71.9	71.4	69.4	68.6	71.2	70.0	70.8	72.1	72.1
C-6′	63.1	65.2	65.5	65.5	66.7	66.6	65.7	66.9	64.8	66.7	66.4	64.5	66.6	67.0
C-1′	62.2	63.7	64.0	65.2	65.6	65.8	64.9	64.7	63.7	65.3	64.4	64.5	65.4	65.7
C-6	61.0	60.8	63.7	63.7	62.4	62.6	64.6	62.2	63.3	62.4	63.8	64.1	63.5	64.7

[a]Data from the literature[13] for purposes of comparison. [b]In D_2O. [c]In $CDCl_3$. [d]In CD_3OD. [e]In $CDCl_3/CD_3OD$.

TABLE X

^{13}C-N.M R CHEMICAL SHIFTS (p.p.m.) FOR COMPOUNDS **19, 21, 22, 34, 36, 38, 39, 43, 44, 45, 46, 48,** AND **50**

Atom	*Sucrose octa-acetate*[b]	**19**	**21**	**22**	**34**	**36**	**38**	**39**	**43**	**44**	**46**	**48**	**50**
C-2′	104.2	103.7	104.6	104.4	103.4	104.0	104.0	104.4	104.2	104.3	104.6	104.6	105.3
C-1	90.1	89.9	90.5	90.4	89.6	90.0	90.3	90.6	90.3	90.3	90.7	90.5	90.7
C-5′	79.3	78.7	79.1	79.0	81.3	81.5	81.3	79.1	79.1	79.1	79.6	79.5	80.3
C-3′	75.9	76.4	77.3	77.3	76.8	77.5	76.7	76.3	77.1	77.0	76.5	76.3	76.7
C-4′	75.2	74.8	76.1	75.3	75.0	75.2	75.2	75.2	75.6	75.7	76.1	75.9	76.5
C-2	70.4	69.9	70.2	70.2	69.9	70.2	71.0	71.1	70.0	70.2	71.1	71.3	70.5
C-3	69.8	69.9	70.0	70.0	69.9	70.0	70.1	69.8	70.0	70.0	69.8	69.8	69.8
C-5	68.6	68.6	68.8	68.8	68.3	68.5	68.7	68.9	68.8	68.7	69.0	68.9	68.9
C-4	68.4	68.4	68.7	68.6	68.3	68.5	68.5	68.6	68.4	68.7	68.3	68.5	68.6
C-6′	63.7	64.0	64.6	64.5	64.5	64.6	63.9	63.7	64.4	64.2	64.2	64.0	64.1
C-1′	63.0	63.7	63.4	63.3	64.0	64.2	63.5	63.1	64.4	64.0	63.6	63.1	62.9
C-6	61.9	61.8	62.1	62.1	61.8	61.9	62.1	62.2	61.9	62.2	61.9	62.3	62.2

[a]In $CDCl_3$. [b]Data from the literature[13] for purposes of comparison.

of the ^{13}C-n.m.r. spectra of **42** and **41** shows that this shift to high field is a result of the presence of the 4,6-acetal rather than the 2,1′-acetal.

EXPERIMENTAL

General methods. — For details of the general procedures, see the preceding paper[6]. Preparative t.l.c. was performed on silica gel GF (Analtech). T.l.c. was performed with *A*, ether–light petroleum (4:1); *B*, dichloromethane–ethyl acetate–ethanol (6:3:1); and ethyl acetate–light petroleum, *C* 4:1, *D* 2:3, and *E* 3:2. The ^{1}H- and ^{13}C-n.m.r. spectra (internal Me_4Si) were recorded with a Jeol FX90Q spectrometer at 89.55 and 22.50 MHz, respectively, and are recorded in Tables I, II, IV, V, and VII–X. The mass spectra are documented in Tables III and VI.

3,6′-Di-O-acetyl-2,1′:4,6-di-O-isopropylidenesucrose[2] (**3**). — A solution of 2,1′:4,6-di-*O*-isopropylidenesucrose tetra-acetate[1–3] (**2**, 2 g) in methanol (100 mL) was treated with methanolic 0.1M sodium methoxide (0.25 mL) and the reaction was monitored by t.l.c. (solvent *B*). After ~1.5 h, t.l.c. revealed a major product (**3**) and **2, 13, 14,** and **15**, as minor products. The reaction was terminated by the addition of solid carbon dioxide, and the product was adsorbed onto a column of silica gel and eluted with solvent *C* to give **3** as a syrup (1.13 g, 66%), $[\alpha]_D^{25}$ +49° (*c* 2, chloroform); lit.[2] $[\alpha]_D$ +49.5° (chloroform). Also eluted from the column was **15** (0.33 g, 21%), $[\alpha]_D^{25}$ +32.5° (*c* 2, chloroform); lit.[2] $[\alpha]_D$ +28° (chloroform). The earlier fractions from the column, containing **2, 13,** and **14**, were combined. Column chromatography (solvent *D*) then gave **2** (75 mg, 3.7%); **13** (49 mg, 2.7%), $[\alpha]_D^{25}$ +31° (*c* 2.1, chloroform); and **14** (36 mg, 2.0%), $[\alpha]_D^{25}$ +23° (*c* 2.1, chloroform).

3,6′-Di-O-acetyl-3′-O-benzoyl-2,1′:4,6-di-O-isopropylidenesucrose (**4**). — A solution of **3** (1.13 g) in anhydrous pyridine (10 mL) was treated with benzoyl chloride (0.28 mL, 1.1 mol. equiv.) at 0°. The mixture was kept at room temperature for 18 h, then treated with water (a few drops), and concentrated to dryness. The syrupy product showed two components in t.l.c. (solvent *E*). Column chromatography (light petroleum–ethyl acetate, 3.5:1.5) gave **16** (0.255 g, 16%) and then **4** (1.102 g, 81%).

Recrystallisation of **16** from ether–light petroleum gave **16**, m.p. 178–180°, $[\alpha]_D^{25}$ −24° (*c* 2, chloroform); ν_{max}^{KBr} 1735 cm^{-1} (C=O).

Anal. Calc. for $C_{36}H_{42}O_{15}$: C, 60.50; H, 5.88. Found: C, 60.98; H, 6.18.

Recrystallisation of **4** from ether–light petroleum gave **4**, m.p. 89–91°, $[\alpha]_D^{25}$ +48.5° (*c* 2, chloroform); ν_{max}^{KBr} 3510 (OH), 1730, 1750 cm^{-1} (C=O).

Anal. Calc. for $C_{29}H_{38}O_{14}$: C, 57.05; H, 6.23. Found: C, 57.25; H, 6.52.

The triacetate (**17**) of **4** was isolated as a foam, $[\alpha]_D^{25}$ +17° (*c* 4.7, chloroform); ν_{max}^{KBr} 1755 cm^{-1} (C=O).

3,6′-Di-O-acetyl-3′-O-benzoylsucrose (**18**). — The diacetal **4** (1.15 g) was treated[12] with 9:1 trifluoroacetic acid–water (15 mL). Recrystallisation of the product from acetone gave **18** (0.68 g, 67%), m.p. 67–70°, $[\alpha]_D^{25}$ +33.5° (*c* 2, methanol); ν_{max}^{KBr} 3410 (OH), 1725 cm^{-1} (C=O).

Anal. Calc. for $C_{23}H_{30}O_{14}$: C, 52.08; H, 5.66. Found: C, 52.19; H, 5.72.

The hepta-acetate (**19**) of **18** was isolated as a foam, $[\alpha]_D^{25}$ +42° (*c* 3.6, chloroform); ν_{max}^{KBr} 1750 cm^{-1} (C=O).

3,6'-Di-O-acetyl-6,1',3'-tri-O-benzoylsucrose (**5**). — A solution of **18** (0.5 g) in anhydrous pyridine (10 mL) was treated with benzoyl chloride (0.24 mL, 2.2 mol. equiv.) at 0°. The mixture was kept at room temperature for 18 h, then treated with water (a few drops), and concentrated to dryness. T.l.c. (solvent *B*) of the syrupy product revealed a major fast-moving component and several minor components. Column chromatography of the mixture with ethyl acetate–light petroleum (1:1) gave **20** (0.1 g, 13%) and then **5** (0.33 g, 47%).

Compound **20** was isolated as a foam, $[\alpha]_D^{25}$ +11.5° (*c* 3.9, chloroform); ν_{max}^{KBr} 3480 (OH), 1727 cm^{-1} (C=O).

Anal. Calc. for $C_{44}H_{42}O_{17}$: C, 62.71; H, 4.99. Found: C, 62.73; H, 4.45.

The tetra-acetate (**21**) of **20** was isolated as a foam, $[\alpha]_D^{25}$ +31° (*c* 4.1, chloroform); ν_{max}^{KBr} 1730, 1756 cm^{-1} (C=O).

Compound **5** was isolated as a foam, $[\alpha]_D^{25}$ +58.5° (*c* 2, chloroform); ν_{max}^{KBr} 3480 (OH), 1727 cm^{-1} (C=O).

Anal. Calc. for $C_{37}H_{38}O_{16}$: C, 60.16; H, 5.15. Found: C, 60.16; H, 4.84.

6,1',3'-Tri-O-benzoylsucrose (**1**). — A solution of **5** (0.33 g) in methanol–water (1:1, 40 mL) was treated with trifluoroacetic acid (10 mL) and the mixture was boiled under reflux for 2 h. T.l.c. (solvent *B*) then revealed **1** and several minor components. The mixture was concentrated to dryness and the residue was subjected to column chromatography, using dichloromethane–ethyl acetate–ethanol (60:36:4), to give **1** (0.13 g, 43%) as a foam, $[\alpha]_D^{25}$ +32° (*c* 2, chloroform); ν_{max}^{KBr} 3450 (OH), 1725 cm^{-1} (C=O).

Anal. Calc. for $C_{33}H_{34}O_{14}$: C, 60.55; H, 5.20. Found: C, 60.60; H, 5.15.

The penta-acetate (**22**) of **1** was isolated as a foam, $[\alpha]_D^{25}$ +57° (*c* 4.2, chloroform); ν_{max}^{KBr} 1730, 1755 cm^{-1} (C=O).

6'-O-tert-Butyldiphenylsilyl-2,1':4,6-di-O-isopropylidenesucrose (**6**). — (*a*) Essentially the procedure of Corey and Venkateswarlu[7] was followed. A solution of 2,1':4,6-di-*O*-isopropylidenesucrose[6] (0.4 g) in anhydrous *N,N*-dimethylformamide (1 mL) was treated with *tert*-butylchlorodiphenylsilane (0.35 mL, 1.4 mol. equiv.) and imidazole (0.16 g, 2.5 mol. equiv.) at room temperature for 18 h, poured into ice–water, and extracted with dichloromethane, and the extract was dried ($MgSO_4$) and concentrated to dryness. The syrupy product contained (t.l.c., solvent *B*) two major fast-moving components and a slower-moving minor component (starting material). Column chromatography (solvent *E*) of the mixture gave **23** (0.197 g, 23%) and then **6** (0.202 g, 32%).

Compound **23** was an amorphous solid, $[\alpha]_D^{25}$ −11° (*c* 1.4, chloroform); ν_{max}^{KBr} 3480 cm^{-1} (OH).

Anal. Calc. for $C_{50}H_{66}O_{11}Si_2$: C, 66.80; H, 7.35. Found: C, 66.13; H, 7.60.

The diacetate (**24**) of **23** had m.p. 201–203° (from ether–light petroleum), $[\alpha]_D^{25}$ −27° (*c* 5.9, chloroform); ν_{max}^{KBr} 1750 cm^{-1} (C=O).

Recrystallisation of **6** from ethyl acetate–light petroleum gave material having m.p. 196–197°, $[\alpha]_D^{25}$ +25° (*c* 2, chloroform); ν_{max}^{KBr} 3420 cm^{-1} (OH).

Anal. Calc. for $C_{34}H_{48}O_{11}Si$: C, 61.82; H, 7.27. Found: C, 61.37; H, 7.64.

The triacetate (**25**) of **6** was an amorphous solid, $[\alpha]_D^{25}$ +13° (*c* 5.1, chloroform); ν_{max}^{KBr} 1750 cm^{-1} (C=O).

(*b*). The method of Khan and co-workers[4] was followed. A solution of 2,1′:4,6-di-*O*-isopropylidenesucrose (1.06 g) in anhydrous pyridine (15 mL) was stirred with 4-dimethylaminopyridine (40 mg) and *tert*-butylchlorodiphenylsilane (0.87 mL, 1.4 mol. equiv.) at room temperature for 4 h. The mixture was then poured into ice–water, and the precipitate was collected and recrystallised from ethyl acetate to give **6** (1.1 g, 66%).

3′-O-Benzoyl-6′-O-tert-butyldiphenylsilyl-2,1′:4,6-di-O-isopropylidene-sucrose (**26**). — A solution of **6** (1.6 g) in anhydrous pyridine (10 mL) was treated with benzoyl chloride (0.31 mL, 1.1 mol. equiv.) at 0° as described above for **3**. T.l.c. (solvent *D*) of the product revealed four major components with mobilities faster than that of **6**. Column chromatography (solvent *D*) of this mixture gave a fraction containing the two fastest-moving components, **27** (0.123 g, 5.9%) and **26** (1.02 g, 55%). Further column chromatography (light petroleum–ether, 2:1) of the first fraction gave **28** (0.515 g, 6.4%) and **29** (0.28 g, 13%).

Compound **26** had m.p. 103–105° (from ethyl acetate–light petroleum), $[\alpha]_D^{25}$ −11.5° (*c* 2, chloroform); ν_{max}^{KBr} 3360 (OH), 1722 cm^{-1} (C=O).

Anal. Calc. for $C_{41}H_{52}O_{12}Si$: C, 64.40; H, 6.81. Found: C, 64.71; H, 7.01.

The diacetate (**30**) of **26** was an amorphous solid, $[\alpha]_D^{25}$ +20° (*c* 3.1, chloroform); ν_{max}^{KBr} 1732, 1758 cm^{-1} (C=O).

Compound **27** was an amorphous solid, $[\alpha]_D^{25}$ −59° (*c* 2, chloroform); ν_{max}^{KBr} 3490 (OH), 1730 cm^{-1} (C=O).

Anal. Calc. for $C_{48}H_{56}O_{13}Si$: C, 66.36; H, 6.45. Found: C, 66.44; H, 6.55.

The acetate (**31**) of **27** was an amorphous solid, $[\alpha]_D^{25}$ −12° (*c* 0.9, chloroform); ν_{max}^{KBr} 1731, 1759 cm^{-1} (C=O).

Compound **28** had m.p. 95–97° (from aqueous ethanol), $[\alpha]_D^{25}$ +3° (*c* 2, chloroform); ν_{max}^{KBr} 1730 cm^{-1} (C=O).

Anal. Calc. for $C_{55}H_{60}O_{14}Si$: C, 67.90; H, 6.17. Found: C, 67.39; H, 6.10.

Compound **29** was an amorphous solid, $[\alpha]_D^{25}$ +52° (*c* 3.2, chloroform); ν_{max}^{KBr} 3510 (OH), 1730 cm^{-1} (C=O).

Anal. Calc. for $C_{48}H_{56}O_{13}Si$: C, 66.36; H, 6.45. Found: C, 66.75; H, 6.68.

The acetate (**32**) of **29** was an amorphous solid, $[\alpha]_D^{25}$ −40° (*c* 3.2, chloroform); ν_{max}^{KBr} 1734 cm^{-1} (C=O).

In subsequent reactions, it was possible to crystallise **26** (50%) directly.

3′-O-Benzoyl-6′-O-tert-butyldiphenylsilylsucrose (**33**). — Compound **26** (0.5 g) was heated at 50° with aqueous 60% acetic acid (20 mL). After 1 h, t.l.c. (solvent *B*) showed that no **26** remained and there was a single slow-moving product. The mixture was concentrated to dryness. Column chromatography (acetone–light petroleum, 3:2) of the residue gave **33** (0.359 g, 80%), which, after recrystallisation

from ethyl acetate–light petroleum, had m.p. 137–138°, $[\alpha]_D^{25}$ +13° (*c* 2, chloroform); ν_{max}^{KBr} 3430 (OH), 1740 cm^{-1} (C=O).

Anal. Calc. for $C_{35}H_{44}O_{12}Si$: C, 61.40; H, 6.43. Found: C, 61.42; H, 6.49.

The hexa-acetate (**34**) of **33** was an amorphous solid, $[\alpha]_D^{25}$ +32° (*c* 2.6, chloroform); ν_{max}^{KBr} 1750 cm^{-1} (C=O).

6,1',3'-Tri-O-*benzoyl-6'*-O-tert-*butyldiphenylsilylsucrose* (**35**). — To a solution of **33** (0.512 g) in anhydrous pyridine (20 mL) at −40° was added, dropwise, a solution of benzoyl chloride (0.185 mL, 2.2 mol. equiv.) in anhydrous pyridine (10 mL). The mixture was kept at room temperature for 18 h. T.l.c. then revealed that some **33** remained, so that more benzoyl chloride (0.06 mL, 0.7 mol) was added and the mixture kept at room temperature for a further 6 h. T.l.c. (solvent *B*) then showed that very little **33** remained. The mixture was treated with water (a few drops) and concentrated to dryness, and the residue was subjected to column chromatography (solvent *E*). Fractions 24–34, which contained (t.l.c.) a component with a mobility slightly greater than that of **6**, were concentrated to give **35** (97 mg, 15%). Fractions 1–11, which contained six major components (solvent *D*) having mobilities faster than that of **35**, were concentrated to give the bulk of the product (0.6 g).

In an earlier reaction, 2,6,1',3'-tetra-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilylsucrose and 6,3'-di-*O*-benzoyl-6'-*O*-*tert*-butyldiphenylsilylsucrose were also isolated from the column in low yield and identified on the basis of their ^{1}H-n.m.r. spectra.

Compound **35** was an amorphous solid, $[\alpha]_D^{25}$ −11.5° (*c* 2, chloroform); ν_{max}^{KBr} 3360 (OH), 1722 cm^{-1} (C=O).

Anal. Calc. for $C_{49}H_{52}O_{14}Si$: C, 65.92; H, 5.83. Found: C, 65.90; H, 6.09.

The tetra-acetate (**36**) of **35** was an amorphous solid, $[\alpha]_D^{25}$ +58° (*c* 6.7, chloroform); ν_{max}^{KBr} 1730, 1760 cm^{-1} (C=O).

Tribenzoylation of 6'-O-tert-*butyldiphenylsilylsucrose*[4] (**7**). — To a solution of **7** (4.16 g) in anhydrous pyridine (100 mL) at −40° was added dropwise, during 1 h at −40°, a solution of benzoyl chloride (2.5 mL, 3 mol. equiv.) in anhydrous pyridine (50 mL). The mixture was then kept at room temperature for 18 h when t.l.c. (solvent *B*) revealed several components, the major corresponding to **35**. The mixture was treated with water (a few drops) and concentrated to dryness, and the product was subjected to column chromatography (solvent *E*, 25-mL fractions). Fractions 4–11 (1.85 g) contained the higher benzoates, 14–22 contained **35** (0.96 g, 15%), and 33–42 contained **37** (0.35 g, 5.5%); 23–32 (0.72 g) contained a mixture of **35** and **37**, further column chromatography of which gave **35** (0.42 g, 6.6%).

Compound **37** was an amorphous solid, $[\alpha]_D^{25}$ +20.5° (*c* 2, chloroform); ν_{max}^{KBr} 3450 (OH), 1727 cm^{-1} (C=O).

Anal. Calc. for $C_{49}H_{52}O_{14}Si$: C, 65.92; H, 5.83. Found: C, 65.95; H, 5.63.

The tetra-acetate (**38**) of **37** was an amorphous solid, $[\alpha]_D^{25}$ +68° (*c* 2.7, chloroform); ν_{max}^{KBr} 1730, 1755 cm^{-1} (C=O).

2,6,1'-Tri-O-*benzoylsucrose* (**8**). — M Tetrabutylammonium fluoride in

tetrahydrofuran (3 mL, 2 mol. equiv.) was added to a solution of **37** (1.34 g) in tetrahydrofuran (100 mL) at 0°. The mixture was stirred at room temperature for 4 h when t.l.c. (solvent *B*) revealed **37** and one product. More tetrabutylammonium fluoride (1.5 mL) was added and the mixture was stirred for a further 18 h. T.l.c. then showed that no **37** remained. The mixture was concentrated to dryness and the residue partitioned between dichloromethane and water. The dichloromethane layer was washed with water, dried, and concentrated to dryness. T.l.c. (solvent *B*) revealed one major component and column chromatography (solvent *B*) gave **8** (0.74 g, 76%) as an amorphous solid, $[\alpha]_D^{25}$ +44.5° (*c* 2, chloroform); ν_{max}^{KBr} 3450 (OH), 1722 cm^{-1} (C=O).

Anal. Calc. for $C_{33}H_{34}O_{14}$: C, 60.55; H, 5.20. Found: C, 60.13; H, 5.05.

The penta-acetate (**39**) of **8** was an amorphous solid, $[\alpha]_D^{25}$ +71° (*c* 1.8, chloroform); ν_{max}^{KBr} 1729, 1753 cm^{-1} (C=O).

6,1',3'-Tri-O-benzoylsucrose (**1**). — Treatment of **35** in tetrahydrofuran with tetrabutylammonium fluoride (2 mol. equiv.) at 0° for 1 h gave (t.l.c., solvent *B*) a single major product (**1**) which was isolated (74%) as described above.

Tribenzoylation of 4,6-O-isopropylidenesucrose[9] (**11**). — A solution of **11** (1.23 g) in anhydrous pyridine (25 mL) was treated with a solution of benzoyl chloride (1.15 mL, 3.1 mol. equiv.) in anhydrous pyridine (10 mL) dropwise at −40°. The mixture was then allowed to attain room temperature, stirred overnight at room temperature, treated with a few drops of water, and concentrated to dryness. T.l.c. (solvent *B*) of the residue revealed several components, including two major components with a mobility slightly greater than that of **3**, and the mixture was subjected to column chromatography (solvent *A*). Fractions 64–89 (0.18 g) contained the faster-moving of the two major components. Elution with solvent *C* then gave more (0.17 g) of the faster-moving component and also the slower-moving component **45** (0.27 g, 11%).

The faster-moving component gave a single spot in t.l.c. (solvent *B*), but was shown by ^{1}H-n.m.r. spectroscopy to be a mixture of a major and a minor compound. Conventional acetylation of this mixture (28 mg) gave a syrupy product which contained two components (t.l.c.; ether–light petroleum, 2:1). Preparative t.l.c., using the same solvent, gave the faster-moving major component (**41**, 26 mg) as a syrup, $[\alpha]_D^{25}$ +40° (*c* 2.6, chloroform); and the minor component (**42**, 6 mg), $[\alpha]_D^{25}$ +39° (*c* 0.6, chloroform). C.i.-m.s. gave *m/z* 840 ($M + NH_4^+$) for **42**.

The faster-moving mixture of two components (51 mg) described above was treated with 9:1 trifluoroacetic acid–water (1 mL). The product contained two components (t.l.c., solvent *B*), the major being the slower moving. Preparative t.l.c. (solvent *B*) of the mixture gave 1',3',6'-tri-*O*-benzoylsucrose (**9**, 25 mg) as an amorphous solid, $[\alpha]_D^{25}$ +21° (*c* 2.9, methanol).

Anal. Calc. for $C_{33}H_{34}O_{14}$: C, 60.55; H, 5.20. Found: C, 59.82; H, 5.33.

The penta-acetate (**43**) of **9** was an amorphous solid, $[\alpha]_D^{25}$ +40° (*c* 2.2, chloroform).

Also isolated by preparative t.l.c. was the minor component **12** (6 mg), $[\alpha]_D^{25}$ +15° (*c* 0.6, chloroform); lit.[6] $[\alpha]_D$ +18.0° (chloroform).

The penta-acetate (**44**) of **12** was isolated as a glass, $[\alpha]_D^{25}$ +42° (*c* 0.6, chloroform); lit.[6] $[\alpha]_D$ +45.5° (chloroform).

2,1',6'-Tri-O-benzoylsucrose (**10**). — Compound **45** (0.12 g) was treated with 9:1 trifluoroacetic acid–water (3 mL) in the normal manner, to give **10** (0.08 g, 73%) as an amorphous solid, $[\alpha]_D^{25}$ +33° (*c* 0.8, methanol).

Anal. Calc. for $C_{33}H_{34}O_{14}$: C, 60.55; H, 5.20. Found: C, 60.21; H, 5.30.

The penta-acetate (**46**) of **10** was an amorphous solid, $[\alpha]_D^{25}$ +62° (*c* 2.1, chloroform).

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REFERENCES

1 R. KHAN AND K. S. MUFTI, *Carbohydr. Res.*, 43 (1975) 247–253.
2 R. KHAN, M. R. JENNER, AND H. LINDSETH, *Carbohydr. Res.*, 65 (1978) 99–108.
3 E. FANTON, J. GELAS, D. HORTON, H. KARL, R. KHAN, C.-K. LEE, AND G. PATEL, *J. Org. Chem.*, 46 (1981) 4057–4060.
4 H. KARL, C. K. LEE, AND R. KHAN, *Carbohydr. Res.*, 101 (1982) 31–38.
5 D. M. CLODE, D. MCHALE, J. B. SHERIDAN, G. G. BIRCH, AND E. B. RATHBONE, *Carbohydr. Res.*, 139 (1985) 141–146.
6 D. M. CLODE, W. A. LAURIE, D. MCHALE, AND J. B. SHERIDAN, *Carbohydr. Res.*, 139 (1985) 147–160.
7 E. J. COREY AND A. VENKATESWARLU, *J. Am. Chem. Soc.*, 94 (1972) 6190–6191.
8 S. HANESSIAN AND P. LAVALLÉE, *Can. J. Chem.*, 53 (1975) 2975–2977.
9 R. KHAN, K. S. MUFTI, AND M. R. JENNER, *Carbohydr. Res.*, 65 (1978) 109–113.
10 J. G. BUCHANAN, M. E. CHACON-FUERTES, A. R. EDGAR, S. J. MOORHOUSE, D. I. RAWSON, AND R. H. WIGHTMAN, *Tetrahedron Lett.*, 21 (1980) 1793–1796.
11 G. ASLANI-SHOTORBANI, J. G. BUCHANAN, A. R. EDGAR, D. HENDERSON, AND P. SHAHIDI, *Tetrahedron Lett.*, 21 (1980) 1791–1792.
12 J. E. CHRISTENSEN AND L. GOODMAN, *Carbohydr. Res.*, 7 (1968) 510–512.
13 L. HOUGH AND E. O'BRIEN, *Carbohydr. Res.*, 92 (1981) 314–317.