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2,3′-Anhydrosucrose*

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ABSTRACT

Alkaline hydrolysis of α-D-glucopyranosyl 3,4-anhydro-β-D-*ribo*-hexulofuranoside (**1**) involves participation of HO-2 and leads to 2,3′-anhydrosucrose (**2**). The structure of **2** was assigned on the basis of the n.m.r. and mass spectra of its hexa-acetate **3** and confirmed by the formation from **2** of the 6,6′-di- (**4**) and 6,1′,6′-tri-*O*-trityl (**5**) derivatives, the 4,6-*O*-isopropylidene derivative (**6**), and 2,3′:3,4-dianhydro-*galacto*-sucrose, isolated as the tetra-acetate **7**. The structure of **7** was confirmed by its conversion into the 4′-*O*-tosyl-6,1′,6′-tri-*O*-trityl derivative **14** and by unambiguous synthesis from **6**.

INTRODUCTION

Methanolysis[1,2] of α-D-glucopyranosyl 3,4-anhydro-β-D-*lyxo*-hexulofuranoside involves the participation of HO-1′. Apparently, attack of HO-1′ on C-3′ leads to the 1′,3′-anhydro derivative and attack by HO-2 then gives 2,1′-anhydro-(α-D-glucopyranosyl β-D-*xylo*-hexulofuranoside). For the isomeric oxirane derivative, α-D-glucopyranosyl 3,4-anhydro-β-D-*ribo*-hexulofuranoside (**1**), both HO-6′ and HO-2 could participate in the opening of the oxirane ring. The 4′,6′-anhydro derivative of α-D-glucopyranosyl β-D-*xylo*-hexulofuranoside (or products of its transformation) are expected in the former reaction, and 2,3′-anhydrosucrose (six-membered anhydro ring) in the latter. We approached this problem by studying the hydrolysis of **1**, which should be simpler than methanolysis.

RESULTS AND DISCUSSION

Treatment of **1** (prepared from the hexa-acetate[3,4]) with 0.1M sodium hydroxide for 20 h at 100° gave 2,3′-anhydrosucrose (**2**, 75%). The signals for H-2 and H-3′ in the ^{1}H-n.m.r. spectrum of the hexa-acetate (**3**) of **2** were shifted upfield by 1.05 and 1.17 p.p.m., respectively, in comparison with the data for sucrose octa-acetate[5] and confirmed the anhydro ring to be located at positions 2 and 3′. Further evidence was the cross-peak between H-2 and H-3′ in the delayed-COSY spectrum of **3**. The mass

* Dedicated to Professor Leslie Hough in the year of his 65th birthday.
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spectrum of **3** lacked ions formed by the cleavage of glycosidic linkage[6], but there were ions m/z 503 ($M^+ - CH_2OCOCH_3$) and 383 ($503^+ - 2\ CH_3COOH$). Apparently, **2** is formed by intramolecular attack of HO-2 in **1** on C-3′. The magnitudes of the $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ values for **3** (Table I) are lower than the usual values[7] for sucrose, which indicates some deformation of the pyranose ring. The effect is less pronounced with **2**.

The behaviour of 2,3′-anhydrosucrose (**2**) and sucrose in several well-known reactions was compared.

The reaction of **2** with 3 equiv. of trityl chloride in pyridine was similar to that of sucrose[8], in that it gave the 6,6′-di- (**4**, 53%) and the 6,1′,6′-tri-*O*-trityl derivative (32%, isolated as its tri-acetate **5**); HO-1′ is less reactive than HO-6,6′.

Reaction of **2** with 2.5 equiv. of 2,2-dimethoxypropane in *N*,*N*-dimethylforma-

TABLE I

^{1}H-N.m.r. data

	1[a]	2[a]	3[b]	4[b]	5[b]	6[c]	7[b]	8[b]
	Chemical shifts (δ, p.p.m.)							
H-1[d]	5.468	5.421	5.294	5.118	5.726	5.340	5.002	4.922
H-2	3.629	–	3.823	3.586	3.928	3.689	3.934	3.538
H-3	3.775	4.020	5.270	3.630	5.111	3.559	3.519	3.478
H-4	3.502	3.527	4.886	3.526	5.165	3.910	3.399	3.354
H-5	3.871	–	4.329	3.744	3.953	–	4.539	3.382
H-6A	–	–	4.338	3.357	3.306	–	4.336	3.617
H-6B	–	–	4.177	3.278	2.965	–	4.213	3.569
H-1′A	3.818	–	4.299	3.768	3.525	–	4.234	3.544
H-1′B	3.691	–	4.160	3.710	3.089	–	4.125	3.369
H-3′	4.071	4.186	4.079	4.028	4.215	4.118	4.095	3.810
H-4′	4.133	4.353	5.050	4.298	5.051	4.214	5.083	4.182
H-5′	4.346	3.982	4.193	4.153	3.814	3.844	4.226	4.315
H-6′A	3.787	3.813	4.459	3.415	3.462	–	4.418	3.434
H-6′B	3.753	–	4.362	3.222	3.266	–	4.263	3.215
	Coupling constants (Hz)							
$J_{1,2}$	3.8	3.8	3.1	3.7	4.0	3.6	1.9	4.2
$J_{2,3}$	9.9	8.1	5.2	7.9	6.0	9.3	2.4	7.8
$J_{3,4}$	9.2	8.0	5.1	8.2	6.1	9.0	3.9	9.1
$J_{4,5}$	9.9	9.2	6.9	8.9	9.1	6.9	2.7	5.2
$J_{5,6A}$	4.2	–	7.1	4.0	2.6	–	6.5	2.1
$J_{5,6B}$	2.5	–	3.0	4.0	3.5	–	6.0	2.2
$J_{6A,6B}$	–	–	11.4	10.1	10.4	–	11.6	10.8
$J_{1'A,1'B}$	12.5	–	11.9	11.5	9.8	–	12.0	10.0
$J_{3',4'}$	2.8	3.5	1.1	2.6	1.0	2.7	1.0	2.4
$J_{4',5'}$	<1	4.4	2.0	2.9	2.0	3.4	1.2	2.6
$J_{5',6'A}$	5.7	4.4	7.7	6.1	6.8	6.0	6.5	6.6
$J_{5',6'B}$	7.0	6.4	5.5	6.2	6.2	5.7	5.9	6.0
$J_{6'A,6'B}$	12.0	12.1	11.5	9.5	10.0	–	10.1	9.5

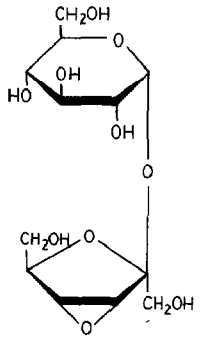
	10[b]	11[b]	12[b]	14[b]	15[b]	16[b]	17[b]	18[b]
	Chemical shifts (δ, p.p.m.)							
H-1[d]	5.275	5.048	5.135	4.876	5.313	5.317	5.036	5.268
H-2	3.760	3.969	3.924	3.944	3.833	3.874	3.628	3.863
H-3	4.687	3.381	3.381	3.443	5.240	5.198	5.304	5.398
H-4	3.571	3.272	3.162	3.269	3.702	3.678	4.735	4.693
H-5	3.541	4.423	3.903	3.784	3.988	4.047	4.298	4.315
H-6A	4.170	4.411	3.387	3.190	3.949	3.861	3.326	4.216
H-6B	4.117	4.311	3.251	3.155	3.670	3.861	3.265	4.170
H-1′A	–	4.234	3.239	3.263	4.311	4.321	4.243	4.284
H-1′B	–	4.137	3.121	2.938	4.156	4.180	4.108	4.132
H-3′	4.090	4.331	4.581	4.519	4.177	4.098	4.007	4.057
H-4′	4.745	5.193	5.342	5.150	5.172	5.104	5.068	5.021
H-5′	4.063	4.219	3.876	3.852	4.128	4.177	4.154	4.127
H-6′A	–	4.304	3.432	3.261	4.381	4.411	4.441	4.340
H-6′B	–	4.186	3.299	3.046	4.381	4.338	4.323	4.288
	Coupling constants (Hz)							
$J_{1,2}$	2.6	3.4	3.3	1.9	3.5	3.7	2.5	3.5
$J_{2,3}$	4.4	4.4	4.6	2.4	6.1	6.1	4.2	5.9
$J_{3,4}$	4.9	4.0	4.0	3.9	9.0	6.5	3.9	5.9
$J_{4,5}$	6.1	0.6	0.6	2.6	10.0	9.1	4.5	8.3
$J_{5,6A}$	5.8	5.0	5.3	7.9	5.5	4.0	6.7	3.3
$J_{5,6B}$	6.1	5.7	6.3	6.2	9.9	4.0	6.0	4.4
$J_{6A,6B}$	11.8	12.9	10.0	8.6	10.4	e	9.6	12.4
$J_{1'A,1'B}$	–	12.0	10.0	10.0	12.0	11.9	11.9	11.9
$J_{3',4'}$	<1	2.9	2.7	0.7	2.0	1.5	0.9	1.2
$J_{4',5'}$	2.8	2.5	2.9	1.7	3.0	2.5	1.7	2.4
$J_{5',6'A}$	–	5.4	7.2	7.7	5.7	5.8	7.4	7.4
$J_{5',6'B}$	–	5.6	4.3	4.8	5.7	7.2	6.2	5.3
$J_{6'A,6'B}$	–	10.8	10.0	9.6	e	11.7	11.5	11.7

[a] D_2O. [b] $CDCl_3$. [c] CD_3OD. [d] See formula **1** for numbering. [e] Not observed because of magnetic non-equivalence.

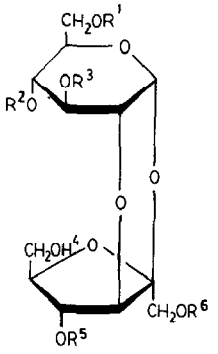
Other data: **3** δ 2.092, 2.094, 2.102, 2.106, 2.113, and 2.115 (6 s, 6 AcO); **4** δ 2.482 (d, HO-4), 2.736 (d, HO-3), 2.870 (t, HO-1′), 7.15–7.46 (m, 30 H, 2 Tr), $J_{3,OH}$ 2.8, $J_{4,OH}$ 3.9, $J_{1',OH}$ 6.2 Hz; **5** δ 1.744, 1.851, and 2.018 (3 s, 3 AcO), 7.06–7.47 (m, 45 H, 3 Tr); **6** δ 1.379 (s, 3 H), 1.503 (s, 3 H); **7** δ 2.094, 2.097, 2.100, and 2.128 (4 s, 4 AcO); **8** δ 7.20–7.50 (m, 30 H, 2 Tr); **10** δ 2.459 (s, 3 H), 7.373 (m, 4 H), 7.77–7.82 (m, 4 H); **11** δ 2.002, 2.100, and 2.103 (3 s, 3 AcO), 7.377 and 7.829 (AA′BB′, 4 H); **12** δ 2.328 (s, 3 H), 7.088 and 7.677 (AA′BB′, 4 H), 7.13–7.46 (m, 45 H, 3 Tr); **14** δ 2.351 (s, 3 H), 7.121 and 7.628 (AA′BB′, 4 H), 7.18–7.43 (m, 45 H, 3 Tr); **15** δ 1.357 (s, 3 H); 1.449 (s, 3 H), 2.079, 2.103, 2.114, and 2.131 (4 s, 4 AcO); **16** δ 2.100, 2.117, 2.122, and 2.157 (4 s, 4 AcO); **17** δ 1.863, 2.032, 2.077, and 2.092 (4 s, 4 AcO), 2.365 (s, 3 H), 7.193 and 7.721 (AA′BB′, 4 H), 7.23–7.32 (m, 15 H, Tr), $J_{3,5}$ 0.9 Hz; **18** δ 2.059, 2.085, 2.089, 2.095, and 2.104 (5 s, 5 AcO), 2.450 (s, 3 H), 7.349 and 7.780 (AA′BB′, 4 H).

mide gave mainly* 2,3′-anhydro-4,6-*O*-isopropylidenesucrose (**6**, 75%), which reflects the fact that a 2,1′-acetal cannot be formed, in contrast to sucrose[9].

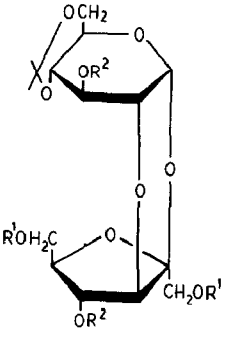
The reaction of **2** with 3 equiv. of diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP) gave a dianhydro derivative, isolated as the tetra-acetate **7**. Two resonances (51.92 and 50.76 p.p.m.) in the ^{13}C-n.m.r. spectrum of **7** appeared in the region (48–58 p.p.m.), typical[10] for epoxides, and exhibited large couplings (185.1 and 181.0 Hz), diagnostic for oxiranes[10], to H-3 and H-4 (3.519 and 3.399 p.p.m.; ^{1}H,^{1}H-COSY data). Therefore, **7** is a 3,4-epoxide, but the $J_{4,5}$ value (2.7 Hz) compared with that



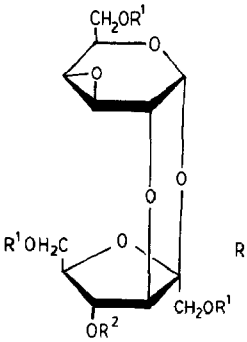
1



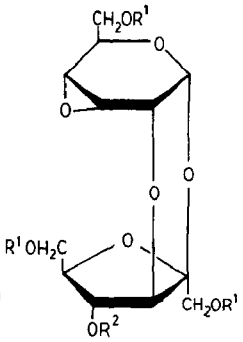
2 $R^1=R^2=R^3=R^4=R^5=R^6=H$
3 $R^1=R^2=R^3=R^4=R^5=R^6=Ac$
4 $R^1=R^4=Tr, R^2=R^3=R^5=R^6=H$
5 $R^1=R^4=R^6=Tr, R^2=R^3=R^5=Ac$
10 $R^3=R^5=Ts, R^1=R^2=R^4=R^6=H$
16 $R^1=R^2=H, R^3=R^4=R^5=R^6=Ac$
17 $R^1=Tr, R^2=Ts, R^3=R^4=R^5=R^6=Ac$
18 $R^2=Ts, R^1=R^3=R^4=R^5=R^6=Ac$



6 $R^1=R^2=H$
8 $R^1=Tr, R^2=H$
9 $R^1=Tr, R^2=Ts$
15 $R^1=R^2=Ac$



7 $R^1=R^2=Ac$
13 $R^1=Tr, R^2=H$
14 $R^1=Tr, R^2=Ts$



11 $R^1=Ac, R^2=Ts$
12 $R^1=Tr, R^2=Ts$

* Minor products with R_F values larger than that of **6** exhibited ^{1}H signals for methoxyl groups and were probably acyclic acetals.

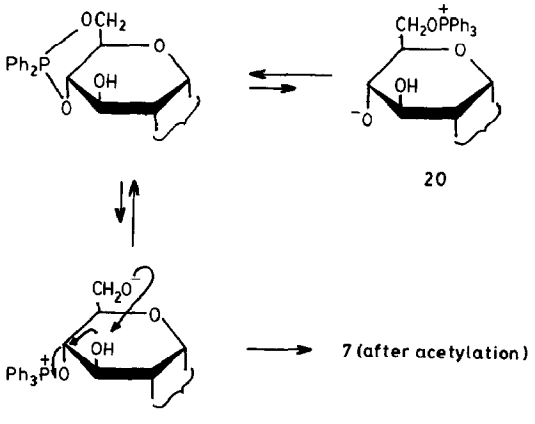
(1 Hz) for the 3,4-epoxide derived from *altro*-sucrose[11]* does not allow assignment of the configuration of the epoxide ring. A hint that favours the *galacto* configuration is provided by a cross-peak between H-4 and H-5 in the ROESY[12] spectrum of **7**.

A solution of this problem was attempted by chemical correlation. The 1',6'-di-*O*-trityl derivative **8** was prepared from the 4,6-acetal **6** and converted into the 3,4'-ditosylate **9**. Hydrolysis of **9** gave 2,3'-anhydro-3,4'-di-*O*-tosylsucrose (**10**) which, upon treatment with sodium methoxide and then acetylation, gave the oxirane **11**, the pyranose moiety of which should have the *allo* configuration. Deacetylation of **11** and tritylation of the product gave 2,3':3,4-dianhydro-4'-*O*-tosyl-6,1',6'-tri-*O*-trityl-*allo*-sucrose (**12**). When **7** was deacetylated and then tritylated, and the resulting 6,1',6'-tri-*O*-trityl derivative **13** was tosylated, the product (**14**) had an $[\alpha]_D$ value and n.m.r. spectra different from those of **12**. Hence, the configuration on the aldose moiety in **7** is *galacto*.

This conclusion was proved by following the reaction sequence. The 4,6-acetal **6** was converted into the tetra-acetate **15** from which the isopropylidene group was removed to give 3,1',4',6'-tetra-*O*-acetyl-2,3'-anhydrosucrose (**16**). Two methods of selective 4-tosylation of **16** were employed. First, **16** was tritylated and then tosylated to give **17**, detritylation and acetylation of which gave 3,6,1',4',6'-penta-*O*-acetyl-2,3'-anhydro-4-*O*-tosylsucrose (**18**). Second, partial acetylation of **16** followed by tosylation, which gave **18**. Reaction of **18** with sodium methoxide and acetylation of the product then gave **7**.

Thus, it is established that **2** has a 2,3'-anhydro ring and that the aldose moiety of **7** has the *galacto* configuration.

The formation of the oxirane **7** in the reaction of **2** with DEAD–TPP is surprising since similar treatment of methyl α-D-glucopyranoside leads to the 3,6-anhydro derivative[13]. However, sucrose itself gives a *lyxo*-furanose 3',4'-epoxide[14] and a 3',6'-anhydro derivative[15], *i.e.*, anhydro derivatives that cannot be formed from **2**. It is possible that **2** reacts with DEAD–TPP to give a six-membered dialkoxyphosphorane[16] of the



* Nomenclature: the terms *allo*-, *altro*-, and *galacto*-sucrose connote α-D-allopyranosyl β-D-fructofuranoside, α-D-altropyranosyl β-D-fructofuranoside, and β-D-fructofuranosyl α-D-galactopyranoside, respectively. The primed numbers for substituents refer to the fructofuranosyl moiety.

trans-decalin type that will be in equilibrium with the phosphonium salts **19** and **20**. Provided that the intramolecular substitution in **19** is faster than that in **20**, then **2** should form an oxirane having the *galacto* configuration.

EXPERIMENTAL

General. — Melting points were determined with a Kofler apparatus and are not corrected. Optical rotations ($c \sim 1$) were measured in 20-cm cuvettes at 20°. T.l.c. was performed on silica gel (Merck) with detection with 1% cerium(IV) sulfate in aqueous 10% sulfuric acid. Column chromatography was performed on silica gel (100–160 μm, Lachema, Brno). Solvents were removed at $<50°$ (bath)/15 mmHg. Reactions were monitored by t.l.c. "Usual work-up" connotes decomposition with water, dilution with chloroform, washing with aqueous 10% sulfuric acid, aqueous 5% sodium hydrogen carbonate, and water, drying ($MgSO_4$), and removal of the solvents.

The ^1H- and ^{13}C-n.m.r. spectra (400 and 100 MHz, respectively) were obtained with a Varian VXR-400 FT spectrometer at 25°. The assignments given in Tables I and II were based on $^1H,^1H$-COSY, delayed $^1H,^1H$-COSY, ^1H, ^{13}C-COSY, and ^1H *J*-resolved spectra. E.i.-mass spectra (70 eV) were obtained with a Finnigan MAT-90 mass spectrometer with an accelerating voltage of 5 kV, an ion-source temperature of 250°, and the direct inlet at 170°.

2,3'-Anhydrosucrose (**2**) *and its 3,4,6,1',4',6'-hexa-acetate* (**3**). — A solution of **1** {880 mg, 2.72 mmol; m.p. 191–192°, $[\alpha]_D$ +83° (water)} in 0.1M sodium hydroxide (16 mL) was heated for 20 h at 100°, then passed through a column of Amberlite IRC-50 (H^+) resin (30 mL) and concentrated to dryness. Crystallization of the residue from aqueous 95% ethanol gave **2** (449 mg, 51%), m.p. 201–203°, $[\alpha]_D$ +72° (water). Chromatography [silica gel (30 g), chloroform–ethanol–ammonia–water (10:15:1.5:1.5)] of the material in the mother liquor gave more (210 mg) **2** (total yield, 74.9%).

Anal. Calc. for $C_{12}H_{20}O_{10}$: C, 44.44; H, 6.22. Found: C, 44.14; H, 6.12.

Acetylation of **2** (100 mg, 308 mmol) with acetic anhydride (2 mL) and pyridine (4 mL) produced **3** in a quantitative yield. Chromatography (ether–light petroleum, 4:1) gave **3** as a syrup, $[\alpha]_D$ +43° (chloroform). Mass spectrum: *m/z* 503 (2.6%), 383 (44), 331 (5.5), 229 (12), 215 (35), 110 (77), 108 (31), 43 (100).

Anal. Calc. for $C_{24}H_{32}O_{16}$: C, 50.00; H, 5.60. Found: C, 49.77; H, 5.61.

Tritylation of **2**. — A mixture of **2** (309 mg, 0.954 mmol), pyridine (10 mL), and trityl chloride (800 mg, 3 equiv.) was stored for 78 h at room temperature, then decomposed with water, and worked-up as usual. T.l.c. (benzene–ethanol, 100:5) of the residue (1.2 g) revealed compounds with R_F 0.7 and 0.3, triphenylmethanol, and several minor components with low R_F. Column chromatography [silica gel (50 g), benzene–ethanol (100:1→100:3)] gave an amorphous compound (325 mg), R_F 0.7, and a compound (408 mg) with R_F 0.3. Acetylation of the former with pyridine (4 mL) and acetic anhydride (1 mL) afforded 3,4,4'-tri-*O*-acetyl-2,3'-anhydro-6,1',6'-tri-*O*-tritylsucrose (**5**; 362 mg, 32.2%) as an amorphous precipitate from ethanol, m.p. 125–128°, $[\alpha]_D$ +37° (chloroform).

TABLE II

^{13}C-N.m.r. chemical shifts

Atom	**1**[a]	**2**[a]	**3**[b]	**4**[b]	**5**[b]	**6**[c]	**7**[b]	**8**[b]
C-1[d]	93.46	93.76	88.95	91.28	90.89	93.24	87.73	91.79
C-2	71.80	75.44	69.60	73.31	70.87	76.64	66.02	74.29
C-3	73.56	75.47	71.18	73.50	72.36	74.28	51.92	72.12
C-4	69.94	70.98	66.65	69.97	67.81	73.23	50.76	71.90
C-5	73.52	76.97	71.06	72.51	70.18	66.48	68.51	64.60
C-6	60.96	62.98	64.70	63.13	61.49	64.10	62.09	61.70
C-1′	61.05	64.93	61.33	63.90	66.49	63.35	64.66	65.08
C-2′	107.26	108.37	103.73	106.85	106.08	101.01	102.61	99.59
C-3′	58.51	79.92	75.73	78.14	77.19	79.15	75.91	78.05
C-4′	59.03	77.78	77.75	76.68	78.85	77.30	77.96	77.11
C-5′	81.79	87.06	81.16	85.55	83.04	87.27	81.16	85.92
C-6′	62.14	64.47	64.03	64.62	65.11	64.78	64.24	64.71

	11[b]	**12**[b]	**14**[b]	**15**[b]	**16**[b]	**17**[b]	**18**[b]
C-1[d]	87.95	89.35	87.68	90.99	90.20	87.92	89.40
C-2	64.25	64.64	66.31	73.04	70.94	68.58	70.30
C-3	49.17	49.16	52.47	72.71	75.18	70.26	71.19
C-4	52.59	52.64	51.53	70.61	68.55	72.12	72.73
C-5	69.10	70.06	68.92	65.08	74.11	73.80	70.04
C-6	63.56	63.74	61.60	62.08	61.82	61.29	63.80
C-1′	63.84	65.02	65.00	64.45	64.55	64.75	64.66
C-2′	102.10	102.95	103.35	104.19	104.18	102.96	104.07
C-3′	75.74	76.60	77.20	75.55	76.29	76.23	75.71
C-4′	82.53	84.17	83.93	77.27	77.63	77.92	77.55
C-5′	80.40	81.22	81.27	80.97	80.99	81.44	81.18
C-6′	63.77	63.81	62.83	64.05	63.99	63.84	61.43

[a] D_2O. [b] $CDCl_3$. [c] CD_3OD. [d] See formula **1** for numbering.

Other signals: **3** δ 20.62 (q), 20.68 (q), 20.69 (q), 20.72 (q, 3 C), 169.22 (s), 169.45 (s), 169.66 (s), 169.91 (s), 170.51 (s), 170.55 (s); **4** δ 86.76 (s), 87.06 (s), 127.07 (d, 3 C), 127.21 (d, 3 C), 127.87 (d, 6 C), 127.96 (d, 6 C), 128.59 (d, 6 C), 128.73 (d, 6 C), 143.41 (s, 3 C), 143.75 (s, 3 C); **5** δ 20.67 (q), 20.72 (q), 20.89 (q), 126.87 (d, 3 C), 126.97 (d, 3 C), 127.22 (d, 3 C), 127.68 (d, 6 C), 127.79 (d, 6 C), 127.93 (d, 6 C), 128.70 (d, 6 C), 128.74 (d, 6 C), 127.93 (d, 6 C), 128.70 (d, 6 C), 128.74 (d, 6 C), 128.79 (d, 6 C), 143.30 (s, 3 C), 143.67 (s, 3 C), 143.93 (s, 3 C), 169.26 (s), 169.27 (s), 169.34 (s); **6** δ 19.55 (q), 29.63 (q), 107.63 (s); **7** δ 20.79 (q, 2 C), 20.83 (q, 2 C), 169.64 (s), 170.04 (s), 170.63 (s), 170.68 (s); **8** δ 18.96 (q), 28.92 (q), 86.64 (s), 88.48 (s), 107.61 (s), 127.04 (d, 3 C), 127.41 (d, 3 C), 127.83 (d, 6 C), 128.04 (d, 6 C), 128.75 (d, 12 C), 142.79 (s, 3 C), 143.83 (s, 3 C); **11** δ 20.71 (q), 20.76 (q), 20.78 (q), 21.69 (q), 128.10 (d, 2 C), 130.01 (d, 2 C), 132.82 (s), 145.50 (s), 170.02 (s), 170.36 (s, 2 C); **12** δ 21.63 (q), 87.01 (s, 2 C), 87.13 (s), 126.77 (d, 3 C), 127.02 (d, 3 C), 127.23 (d, 3 C), 127.60 (d, 6 C), 127.86 (d, 6 C), 127.93 (d, 6 C), 128.01 (d, 2 C), 128.57 (d, 6 C), 128.68 (d, 6 C), 128.86 (d, 6 C), 129.73 (d, 2 C), 132.52 (s), 143.38 (s, 3 C), 143.59 (s, 3 C), 144.00 (s, 3 C), 144.65 (s, 3 C); **14** δ 21.66 (q), 86.71 (s), 86.74 (s), 86.97 (s), 127.00 (d, 6 C), 127.05 (d, 3 C), 127.72 (d, 6 C), 127.80 (d, 6 C), 127.89 (d, 6 C), 127.96 (d, 2 C), 128.62 (d, 6 C), 128.66 (d, 6 C), 128.73 (d, 6 C), 129.87 (d, 2 C), 133.22 (s), 143.54 (s), 143.68 (s, 3 C), 143.79 (s, 3 C), 144.95 (s, 3 C); **15** δ 18.91 (q), 20.70 (q), 20.77 (q), 20.90 (q), 20.98 (q), 28.79 (q), 99.69 (s), 169.51 (s), 169.93 (s), 170.03 (s), 170.69 (s); **16** δ 20.72 (q), 20.76 (q), 20.84 (q), 20.94 (q), 169.56 (s), 170.05 (s), 171.03 (s), 171.25 (s); **17** δ 20.62 (q), 20.77 (q, 2 C), 20.84 (q), 21.65 (q), 87.06 (s), 127.16 (d, 3 C), 127.82 (d, 6 C), 128.06 (d, 2 C), 128.71 (d, 6 C), 129.82 (d, 2 C), 133.32 (s), 143.39 (s, 3 C), 144.90 (s); **18** δ 20.70 (q, 2 C), 20.74 (q), 20.77 (q), 20.79 (q), 21.66 (q), 127.89 (d, 2 C), 129.92 (d, 2 C), 133.05 (s), 145.48 (s), 169.36 (s), 169.42 (s), 169.90 (s), 170.42 (s), 170.48 (s).

Anal. Calc. for $C_{75}H_{68}O_{13}$: C, 76.51; H, 5.82. Found: C, 76.62; H, 5.99.

The compound with R_F 0.3 was 2,3′-anhydro-6,6′-di-*O*-tritylsucrose (**4**, 52.9%), which crystallized from ethanol with one molecule of solvent; m.p. 117–120°, and 212–214°, $[\alpha]_D$ +19.5° (chloroform).

Anal. Calc. for. $C_{50}H_{48}O_{10}\cdot C_2H_5OH$: C, 73.05; H, 6.36. Found: C, 73.31; H, 6.42.

2,3′-Anhydro-4,6-O-*isopropylidenesucrose* (**6**). — 2,2-Dimethoxypropane (0.5 mL, 2.5 equiv.) and freshly melted *p*-toluenesulfonic acid (25 mg) were added at 60° with stirring to a solution of **2** (518 mg, 1.6 mmol) in *N,N*-dimethylformamide (6 mL). The mixture was stirred for 90 min, sodium hydrogen carbonate (100 mg) was added, and, after 15 min, the solvent was removed at 15 Pa. The residue was extracted with ethanol, the extract was concentrated, and the residue was subjected to column chromatography on silica gel (35 g). Faster-moving compounds were eluted with benzene–ethanol (100:5). Elution with benzene–ethanol (10:1) then afforded **6** (414 mg, 71.1%), $[\alpha]_D$ +49° (ethanol).

Anal. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.64. Found: C, 49.34; H, 6.81.

On storage, **6** crystallized as a hydrate, m.p. 110–114° (from ethyl acetate), having the same n.m.r. spectra as **6**.

Anal. Calc. for $C_{15}H_{24}O_{10}\cdot H_2O$: C, 47.12; H, 6.85. Found: C, 46.84; H, 6.71.

6,1′,4′,6′-Tetra-O-*acetyl-2,3′:3,4-dianhydro*-galacto-*sucrose* (**7**). — (*a*) Triphenylphosphine (910 mg, 3 equiv.) was added with stirring to a solution of **2** (375 mg, 1.16 mmol) in *N,N*-dimethylformamide (10 mL) at 0°. Diethyl azodicarboxylate (610 mg, 3 equiv.) was added after 10 min, the mixture was allowed to attain room temperature, and, after 24 h, the *N,N*-dimethylformamide was evaporated at 15 Pa. A solution of the residue in water (20 mL) was extracted with ethyl acetate (3 × 20 mL) and dichloromethane (3 × 20 mL), then concentrated to dryness, and pyridine (6 mL) and acetic anhydride (2.5 mL) were added to the residue. After 16 h, the mixture was decomposed with water and concentrated to dryness, and toluene was repeatedly evaporated from the residue. Chromatography [silica gel (50 g), ether–light petroleum (4:1)] of the residue gave **7** (221 mg, 40.3%), $[\alpha]_D$ −28° (chloroform).

Anal. Calc. for $C_{20}H_{26}O_{13}$: C, 50.63; H, 5.52. Found: C, 50.51; H, 5.82.

(*b*) Methanolic M sodium methoxide (2 mL) was added to a solution of **18** (71 mg, 0.103 mmol) in methanol (2 mL). After 10 min, the solution was neutralized with carbon dioxide and concentrated to dryness. The residue was acetylated conventionally with pyridine (4 mL) and acetic anhydride (1 mL) for 48 h. Column chromatography [silica gel (15 g), ether–light petroleum (4:1)] of the product gave **7** (41 mg, 84%).

2,3′-Anhydro-4,6-O-*isopropylidene-1′,6′-di*-O-*tritylsucrose* (**8**). — A mixture of **6** (409 mg, 1.12 mmol), pyridine (10 mL), and trityl chloride (2.5 g, 8 equiv.) was left for 4 days at room temperature, then decomposed, and worked-up as usual. Column chromatography of the product on silica gel (40 g) gave triphenylmethanol (eluted with benzene). Elution with benzene–ethanol (100:1) then gave syrupy **8** (840 mg, 88.4%), $[\alpha]_D$ +37° (chloroform).

Anal. Calc. for $C_{53}H_{52}O_{10}$: C, 74.98; H, 6.17. Found: C, 74.83; H, 6.45.

2,3′-Anhydro-4,6-O-*isopropylidene-3,4′-di*-O-*tosyl-1′,6′-di*-O-*tritylsucrose* (**9**). —

A mixture of **8** (836 mg, 0.98 mmol), pyridine (10 mL), and tosyl chloride (1.9 g, 10 equiv.) was stored at room temperature for 80 h, then worked-up as usual. Column chromatography [silica gel (50 g), benzene–chloroform (1:1)] of the product gave a faster-moving component (85 mg), then **9** (866 mg, 76.4%) that precipitated from ethanol as an amorphous powder, $[\alpha]_D$ −11° (chloroform).

Anal. Calc. for $C_{67}H_{64}O_{14}S_2$: C, 69.53; H, 5.57; S, 5.54. Found: C, 69.77; H, 5.83; S, 5.30.

2,3'-Anhydro-3,4'-di-O-*tosylsucrose* (**10**). — A solution of **9** (675 mg, 0.584 mmol) in acetone (14 mL), acetic acid (14 mL), and water (6 mL) was heated for 4 h at 65°, then concentrated to dryness. Chromatography [silica gel (40 g), benzene–ethanol (100:5→100:7)] of the residue afforded a mixture (181 mg) of faster-moving compounds, then **10** (240 mg, 65%). Repeated hydrolysis of the faster-moving compounds [acetone (4 mL), acetic acid (4 mL), water (2 mL)], followed by chromatography, produced more (86 mg) **10** (total yield, 88%). Compound **10** was amorphous, $[\alpha]_D$ +31° (ethanol). ^{13}C-N.m.r. data (100 MHz, $CDCl_3$): δ 21.72 (q, 2 C), 60.54 (t), 61.53 (t), 63.77 (t), 66.16 (d), 70.17 (d), 76.57 (d), 77.42 (d), 80.19 (d), 82.65 (d), 83.23 (d), 88.02 (d), 103.93 (s), 127.93 (d, 2 C), 127.98 (d, 2 C), 130.15 (d, 2 C), 130.24 (d, 2 C), 132.54 (s), 132.82 (s), 145.74 (s), 145.87 (s).

Anal. Calc. for $C_{26}H_{32}O_{14}S_2$: C, 46.36; H, 5.10; S, 10.14. Found: C, 49.37; H, 5.40.

6,1',6'-Tri-O-*acetyl-2,3':3,4-dianhydro-4'*-O-*tosyl*-allo-*sucrose* (**11**). — Methanolic M sodium methoxide (6 mL) was added to a solution of **10** (182 mg, 0.288 mmol) in methanol (6 mL). The mixture was stored for 50 min at room temperature, neutralized with carbon dioxide, and concentrated to dryness, and the residue was acetylated conventionally with pyridine (4 mL) and acetic anhydride (2 mL). Column chromatography [silica gel (30 g), benzene–ethanol (100:1)] of the product gave **11** (135 mg, 80%), m.p. 144–146° (from ethanol), $[\alpha]_D$ −21° (chloroform).

Anal. Calc. for $C_{25}H_{30}O_{14}S$: C, 51.19; H, 5.15; S, 5.47. Found: C, 51.39: H, 5.05; S, 5.57.

2,3':3,4-Dianhydro-4'-O-*tosyl-6,1',6'-tri*-O-*trityl*-allo-*sucrose* (**12**). — Methanolic M sodium methoxide (2 drops) was added to a solution of **11** (52 mg, 0.09 mmol) in methanol (10 mL). After 2 h, when deacetylation was complete (t.l.c.), the solution was neutralized with carbon dioxide, then concentrated. Pyridine (4 mL) and trityl chloride (300 mg, 12 equiv.) were added to the residue, and the mixture was stored for 7 days at room temperature, then worked-up as usual. Column chromatography [silica gel (15 g)] of the product gave triphenylmethanol [eluted with light petroleum–ethyl acetate (95:5)], then **12** (59 mg, 55%) [eluted with benzene], $[\alpha]_D$ −2° (chloroform).

Anal. Calc. for $C_{76}H_{66}O_{11}S$: C, 76.87; H, 5.60; S, 2.70. Found: C, 76.70; H, 5.97; S, 2.87.

2,3':3,4-Dianhydro-6,1',6'-tri-O-*trityl*-galacto-*sucrose* (**13**). — Methanolic M sodium methoxide (2 drops) was added to a solution of **7** (221 mg, 0.466 mmol) in methanol (10 mL). The mixture was stored overnight, then neutralized with carbon dioxide, and concentrated to dryness. Pyridine (8 mL) and trityl chloride (1.3 g, 10 equiv.) were added to the residue, and the mixture was stored for 72 h at room temperature and then

worked-up as usual. Column chromatography [silica gel (40 g), benzene] of the residue gave amorphous **13** (196 mg, 40.7%), $[\alpha]_D$ −13.5° (chloroform).

Anal. Calc. for $C_{69}H_{60}O_9$: C, 80.21; H, 5.85. Found: C, 80.34; H, 5.82.

*2,3':3,4-Dianhydro-4'-*O*-tosyl-6,1',6'-tri-*O*-trityl*-galacto-*sucrose* (**14**). — Tosyl chloride (260 mg, 10 equiv.) was added to a solution of **13** (140 mg, 0.136 mmol) in pyridine (6 mL). The reaction mixture was left for 5 days at room temperature, then worked-up as usual. Column chromatography [silica gel (30 g), benzene] of the product gave amorphous **14** (151 mg, 94%), $[\alpha]_D$ −33° (chloroform).

Anal. Calc. for $C_{76}H_{66}O_{11}S$: C, 76.87; H, 5.60; S, 2.70. Found: C, 76.63; H, 5.84; S, 3.01.

*3,1',4',6',-Tetra-*O*-acetyl-2,3'-anhydro-4,6-*O*-isopropylidenesucrose* (**15**). — Compound **6** (342 mg, 0.94 mmol) was acetylated conventionally with pyridine (4 mL) and acetic anhydride (2 mL). Column chromatography [silica gel (40 g), benzene–ethanol (100:1)] of the product afforded **15** (435 mg, 87%), $[\alpha]_D$ +32° (chloroform).

Anal. Calc. for $C_{23}H_{32}O_{14}$: C, 51.87; H, 6.06. Found: C, 51.86; H, 5.84.

*3,1',4',6'-Tetra-*O*-acetyl-2,3'-anhydrosucrose* (**16**). — A solution of **15** (256 mg, 0.48 mmol) in aqueous 60% acetic acid (10 mL) was heated for 30 min at 50°, then concentrated to dryness. Column chromatography [silica gel (25 g), benzene–ethanol (100:5)] of the residue provided **16** (163 mg, 69%), $[\alpha]_D$ +39° (chloroform).

Anal. Calc. for $C_{20}H_{28}O_{14}$: C, 48.78; H, 5.73. Found: C, 48.88; H, 5.77.

*3,1',4',6'-Tetra-*O*-acetyl-2,3'-anhydro-4-*O*-tosyl-6-*O*-tritylsucrose* (**17**). — A mixture of **16** (156 mg, 0.317 mmol), pyridine (5 mL), and trityl chloride (300 mg, 3.5 equiv.) was left for 72 h at room temperature. More trityl chloride (100 mg) was added, the mixture was kept for 48 h at 40°, then worked-up as usual. Column chromatography [silica gel (20 g), benzene–ethanol (100:1)] of the product yielded triphenylmethanol (220 mg) and a product, contaminated with several minor components, which was treated conventionally with pyridine (4 mL) and tosyl chloride (430 mg). Column chromatography [silica gel (20 g), benzene–ethanol (100:1)] of the product yielded crude **17** (200 mg) together with 3–4 minor components. Recrystallization from ethanol gave **17** (131 mg, 46.5%), m.p. 164–167°, $[\alpha]_D$ +19° (chloroform).

Anal. Calc. for $C_{46}H_{48}O_{16}S$: C, 62.15; H, 5.44; S, 3.61. Found: C, 62.33; H, 5.59.

*3,6,1',4',6'-Penta-*O*-acetyl-2,3'-anhydro-4-*O*-tosylsucrose* (**18**). — (*a*) Pyridine–acetic anhydride (9:1; 0.745 mL, 1.2 equiv.) was added at 0° to a solution of **16** (284 mg, 0.577 mmol) in pyridine (6 mL). The mixture was stored for 16 h at room temperature, decomposed with water, and concentrated to dryness, and toluene was evaporated from the residue. Column chromatography [silica gel (40 g), benzene–ethanol (100:5)] of the residue gave the hexa-acetate **3** (55 mg, 16.5%), a mixture (116 mg) of major and minor compounds (R_F ~0.3), and **16** (74 mg, 26%). The mixture (95 mg) was dissolved in pyridine (4 mL), tosyl chloride (340 mg, 10 equiv.) was added, and, after 48 h, the mixture was worked-up as usual. Column chromatography [silica gel (10 g), benzene–ethanol (100:1)] of the product yielded **18** (101 mg), $[\alpha]_D$ +46° (chloroform).

Anal. Calc. for $C_{29}H_{36}O_{17}S$: C, 50.58; H, 5.27; S, 4.66. Found: C, 50.88; H, 5.45; S, 4.67.

(*b*) A solution of **17** (118 mg, 0.133 mmol) in acetone (2 mL), acetic acid (2 mL), and water (1 mL) was heated for 7 h at 60°, then concentrated to dryness. Pyridine (4 mL) and acetic anhydride (1 mL) were added to the residue, the mixture was stored overnight, then decomposed with water, and concentrated to dryness, and toluene was evaporated from the residue. Column chromatography [silica gel (15 g), light petroleum–ethyl acetate (95:5)] gave triphenylmethanol, and elution with benzene–ethanol (100:2) gave **18** (73 mg, 80%).

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