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DERIVATIVES OF SUCROSE 3′,4′-EPOXIDE

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ABSTRACT

A facile, one-pot synthesis of α-D-glucopyranosyl 3,4-anhydro-β-D-tagatofuranoside (**1**) from sucrose in good yield is reported. Derivatives of **1** can also be obtained from 4,6:2,1′-di-*O*-isopropylidenesucrose and from 2,3,6,1′,6′-penta-*O*-benzoylsucrose by treatment with triphenylphosphine and diethyl azodicarboxylate. The n.m.r. spectra (^{13}C,^{1}H) and conformation of derivatives of **1** are discussed. A new anhydrosucrose (1′,4′) is reported.

INTRODUCTION

Epoxides (oxiranes) have been widely used as synthetic intermediates in carbohydrate chemistry[1]. Until recently, the most common method of preparation was from a vicinal *trans*-hydroxy,sulfonyloxy group, the synthesis of which may involve complex strategies.

We have reported[2] that treatment of methyl α- and β-D-fructofuranoside with triphenylphosphine (TPP) and diethyl azodicarboxylate (DEAD) in *N*,*N*-dimethylformamide gave high yields of the corresponding methyl 3,4-anhydro-D-tagatofuranosides, and that no protection of the primary hydroxyl-groups was necessary. This is an unusual reaction, since primary hydroxyl-groups react[3] much more rapidly with TPP and DEAD (to form dialkoxytriphenylphosphoranes) than secondary hydroxyl-groups. Presumably, the success of the epoxidation reaction depends on a favourable rate of formation from an antiperiplanar *trans*-1,2-diol system, where one of the hydroxyl groups has been converted into the oxytriphenylphosphonium leaving-group. The primary hydroxyl-groups are effectively protected as dialkoxytriphenylphosphoranes which are hydrolysed during work-up. The mechanism of this reaction has been discussed[3].

It was considered that application of this methodology to sucrose might yield the sucrose epoxide **1** (α-D-glucopyranosyl 3,4-anhydro-β-D-tagatofuranoside), which would be a useful intermediate for the synthesis of sucrose derivatives mod-

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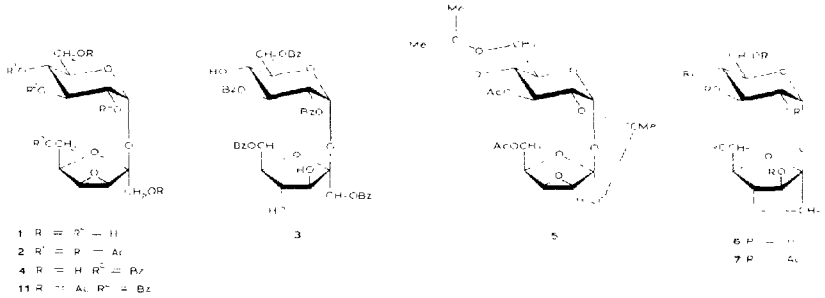
ified in the D-fructosyl moiety. Such modified sucroses were required for studies[4] of the structure–activity relationship of substrates for invertase (β-D-fructofuranosidase). The epoxide **1** was known hitherto only as its hexa-acetate, which was obtained in low yield in six steps from sucrose[5].

RESULTS AND DISCUSSION

Treatment of sucrose in *N*,*N*-dimethylformamide with TPP and DEAD at room temperature for 16 h followed by acetylation gave impure, syrupy hexa-acetate (**2**, ~24%) of **1**, from which the contaminant was difficult to remove by chromatography. In view of the facile conversion[6] of methyl α-D-glucopyranoside into methyl 3,6-anhydro-α-D-glucopyranoside with TPP/DEAD, 3,6-anhydro formation with sucrose was considered to be a possible origin of the impurity. A sucrose derivative with HO-3′ and HO-4′ unsubstituted, but with HO-6 blocked, was therefore sought. Since the Mitsunobu reaction can be used for the selective esterification of primary hydroxyl-groups[7], the epoxidation of sucrose in the presence of a carboxylic acid was investigated. From model studies with sucrose and benzoic acid[8] or thioacetic acid[9], it was anticipated that esterification at positions 6 and 6′ would precede epoxide or 3,6-anhydro ring-formation.



Treatment of sucrose in *N*,*N*-dimethylformamide with acetic acid (2.2 equiv.), TPP (4.5 equiv.), and DEAD (4.5 equiv.) at room temperature for 16 h followed by deacetylation afforded the required **1**, from which the pure hexa-acetate (**2**, 42%) was isolated. The impurity formed previously was not observed. This method is presently the most convenient procedure known for the synthesis of **1**, and is suitable for large-scale preparations.

Other readily available 6-substituted sucrose derivatives, suitable for conversion into **1**, are 2,3,6,1′,6′-penta-*O*-benzoylsucrose[10] (**3**), 4,6:2,1′-di-*O*-isopropylidenesucrose[11], and 6,6′-di-*O*-*tert*-butyldimethylsilylsucrose[12]. The conversion of the pentabenzoate into the 3′,4′-anhydro derivative **4** and into **1** was reported in a preliminary communication[13], and the yield of **4** from **3** has since been

increased to 80% by using the much cheaper reagent di-isopropyl azodicarboxylate (DIAD) (DIAD can be used instead of DEAD in the one-pot procedure together with chloroform, instead of *N*,*N*-dimethylformamide, as solvent). By this procedure, **1** is available from sucrose in three steps, with an overall yield of ~40% comparable to the one-pot procedure.

Treatment of 4,6:2,1′-di-*O*-isopropylidenesucrose with TPP and DEAD in refluxing benzene, followed by acetylation, gave 3,6′-di-*O*-acetyl-3′,4′-anhydro-4,6:2,1′-di-*O*-isopropylidene-"tagatosucrose" (**5**, 60%), which was readily converted into **1**. A one-pot procedure was also developed, using the crude reaction-mixture from acetalation of sucrose (which contained 4,6:2,1′-di-*O*-isopropylidenesucrose and 4,6-*O*-isopropylidenesucrose in the ratio ~2:1). The mixture was treated with TPP/DEAD in pyridine at 70° for 2.5 h, followed by deacetalation to give **1** (30%). The use of pyridine as solvent resulted in a very dark reaction-mixture. Preliminary experiments with 6,6′-di-*O*-*tert*-butyldimethylsilylsucrose and TPP/DEAD indicated a very clean conversion into the corresponding 3′,4′-anhydro derivative, but this method was not pursued as the procedures noted above were considered to be more convenient.

The ^{13}C-n.m.r. data of the derivatives of the sucrose epoxide **1** are given in Table I. The oxirane structure is clearly demonstrated by the upfield shift of the signals for C-3′ and C-4′ by ~20 p.p.m. relative to the corresponding signals for the parent acylated sugar. The signal for C-5′ in these compounds is also shifted upfield by 4–5 p.p.m.; otherwise, the chemical shifts are very similar to those in the parent

TABLE I

^{13}C-N.M.R DATA FOR ANHYDROSUCROSE DERIVATIVES

	1[ad]	**2**[bd]	**2**[cc]	**3**[bd]	**4**[bd]	**5**[ce]	**6**[ae]	**7**[ce]
C-1	93.1	89.7	89.8	90.2	90.3	93.3	93.9	91.3
C-2	70.9	68.9	69.1	71.2	71.0	63.9	72.1	68.8
C-3	72.7	70.3	70.5	73.6	73.7	72.3[j]	73.7[m]	70.5[n]
C-4	69.4	68.2	68.3	69.7	69.8	71.0[j]	70.2	68.3
C-5	72.3	69.8	70.0	71.5	71.3	71.7[j]	71.7	70.1[n]
C-6	60.1[f]	62.3	62.3[g]	64.0[h]	62.7[i]	62.5[k]	61.4[l]	62.2
C-1′	60.5[f]	62.3	62.4[g]	64.3[h]	63.9[i]	69.6[k]	76.7	76.4
C-2′	104.5	102.8	102.9	103.4	103.0	104.4	109.8	108.3
C-3′	56.3	56.4	56.5	78.7	56.4	57.6	78.3	70.7[n]
C-4′	55.3	54.9	55.0	75.9	54.8	56.1	82.2	79.6
C-5′	76.5	75.1	75.3	79.6	74.9	75.6	73.8[m]	77.3
C-6′	63.3	65.6	65.6	65.7	65.8	63.9	61.5[l]	64.9
Other signals						101.4 99.5	O Me C O Me	

[a]In D_2O. [b]In acetone-d_6. [c]In $CDCl_3$. [d]At 22.3 MHz. [e]At 75.5 MHz. [f–n]Numbers with the same letter in a vertical row may be interchanged.

sugars. The chemical shifts of the carbons in the anhydrotagatofuranoside moiety were very similar to those found for methyl 3,4-anhydro-β-D-tagatofuranoside[2]. The chemical shifts of the primary carbons in **1**–**5** were assigned as C-6 < C-1′ < C-6′ by comparison with the data for acetylated 6- and 6′-thiosucrose and 6,6′-dithiosucrose[9]. The values for C-6 and C-1′ in **1**–**3** are similar, and the assignments are not certain.

The ^{1}H-n.m.r. data for the derivatives of sucrose epoxide **1** are given in Tables II and III. The spectra of the acetylated derivatives were recorded for solutions in benzene-d_6, which is a good solvent for ^{1}H-n.m.r. spectroscopy of acetylated sugars[14]. The first-order interpretation of the spectra of **2** and **4** was verified by irradiation techniques and refined by calculation of theoretical spectra with the help of the Bruker spin-simulation program (PANIC). In these calculations, the vicinal and geminal coupling-constants were taken as positive and negative, respectively. The most noticeable feature in the spectrum of **2** is the upfield shift of the signals for H-3′ and H-4′ by ~1.5 p.p.m. relative to those of H-3′,4′ in sucrose octa-acetate. Also, the $J_{3',4'}$ and $J_{4',5'}$ values are much smaller for **2** than for sucrose octa-acetate. Since the furanoside ring in **2** carries an oxirane ring, only two conformations are possible, namely, O-5 *cis* or *trans* to the epoxide oxygen. The preferred puckering mode probably involves the *cis* arrangement, since this would avoid *syn*-1,3 interactions between the glucosyl moiety and the C-5′ substituent. In support of this view, an X-ray analysis[2] of the closely related structure methyl 3,4-anhydro-1,6-di-*O*-*p*-tolylsulfonyl-β-D-tagatofuranoside showed that O-5 was slightly out of the plane and on the β-face. The $J_{3,4}$ (2.9 Hz) and $J_{4,5}$ (1.1 Hz) values[15] in the latter compound were virtually identical to the $J_{3',4'}$ and $J_{4',5'}$ values for **2**. The glucosyl group of **2** is in the $^4C_1$ conformation.

The impurity formed in the reaction of sucrose with TPP/DEAD, and noted above, was initially considered to be 3,6-anhydrosucrose or 3′,6′-anhydrosucrose. However, although the elemental analysis and n.m.r. data indicated a monoanhydrosucrose, the m.p. and n.m.r. data were inconsistent with those for 3,6-anhydrosucrose[16], 3′,6′-anhydrosucrose[17], or 2,1′-anhydrosucrose[18]. A 1′,4′-anhydro structure **6**, not hitherto reported, was therefore tentatively assigned to this by-product. The ^{13}C-n.m.r. spectrum showed the expected set of peaks for the glucose moiety, in addition to one other CH_2OH group (6′). The remaining peaks were consistent with the proposed 1′,4′-anhydrofructofuranoside moiety; in particular, the signal for C-2′ was shifted downfield to 109.8 p.p.m. (*cf.* 108.9 p.p.m. for C-2 of 1,2-*O*-isopropylidene-β-D-fructofuranose[19] triacetate) and that for C-1′ was shifted downfield to 76.7 p.p.m. (*cf.* 76.8 p.p.m. for C-1′ of 3,6:1′,4′:3′,6′-trianhydrosucrose[20].

The ^{1}H-n.m.r. spectra of **6** and its hexa-acetate **7** were also consistent with the presence of a 1′,4′-anhydro ring. In particular, the signals for H-1′a and H-1′b in **7** were well resolved, and appeared as a doublet of doublets with J_{gem} 8.5 Hz (*cf.* $J_{1'a,1'b}$ 8 Hz for 2,4-di-*O*-acetyl-3,6:4,1′:3′,6′-trianhydrosucrose[20]). The J_{gem} value for -CH_2OH or -CH_2OAc groups is usually 11–13 Hz (see Table III). From a study

TABLE II

^{1}H-N M R CHEMICAL SHIFTS (P P M) FOR ANHYDROSUCROSE DERIVATIVES

	1[ac]	**2**[bd]	**4**[bd]	**5**[bc]	**6**[ac]	**7**[bc]
H-1	5.47	6.13	6.52	6 29	5.48	5.98
H-2	3.54	5.03	5.44	3.81	3 64	5 14
H-3	3.77	5.89	6.29	5.82	3 78	5.67
H-4	3.43	5.34	3.89	3.69	3.45	5.38
H-5	3.7–3.9	4.36	4 59	4.26	3 91	4.65
H-6a	3.7–3.9	4.36	4.81	3.77	3.85	4.26
H-6b	3.7–3.9	4.36	4.77	3.75	3 77	4.32
H-1′a	3.73	4.09	4.74	3.80	4 04	3.95
H-1′b	3.70	3.98	4.17	3.03	4.04	3.26
H-3′	3.96	3.34	3.53	3 08	4.53	4.79
H-4′	3.98	3.05	3.01	3.06	4.32	4.01
H-5′	4.17	3.71	3.72	3 55	4.47	4.06
H-6′a	3.83	4.21	4.31	4.33	3.97	4.55
H-6′b	3.82	4.16	4.29	4.32	3.76	4.06
OH			3.39			
OAc		1.65–1.77		1.6,1.8		1 67–1.76
ArH			6.8–8.2			
$(CH_3)_2C$				1.25,1.27		
				1.28,1.36		

[a]In D_2O. [b]In C_6D_6. [c]At 300 MHz. [d]At 270 MHz.

TABLE III

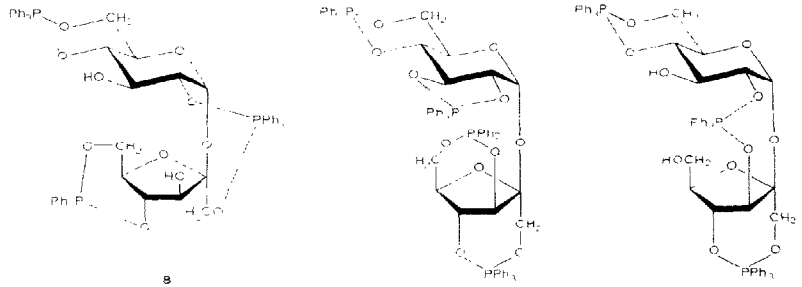
^{1}H-N M R COUPLING CONSTANTS (Hz) FOR ANHYDROSUCROSE DERIVATIVES

J	**2**[bd]	**4**[bd]	**1**[ac]	**5**[bc]	**6**[ac]	**7**[bc]
1,2	3.9	3.8	3.9	3 7	3.8	3.6
2,3	10 4	10.2	9.9	9 4	9.9	10.4
3,4	9.3	9.3	9.2	9 4	9.3	9.3
4,5	10.0	10.0	9.9	9.8	9.8	10.3
5,6a		1.9		5.2	2.3	2.6
5,6b		4.3		5.2	4.8	4.4
6a,6b		−11.7			−12.5	−11.8
1′a,1′b	−11.7	−11.7	−12.5	−12 0		8.5
3′,4′	2.7	2 9	3.0	2.9	2.2	2.2
4′,5′	1.1	0.9	0.7	0.9	~0	~0
5′,6′a	4.7	5.0	6 4	10.5	~o	~0
5′,6′b	4.0	5.0	5.1	10.5	·~0	·~0
6′a,6′b	− 11.5	−11.8	−11.6	−11.8	−13.0	−11.8
4,OH		3.4				
1′b,5′						1 3

[a]In D_2O. [b]In C_6D_6. [c]At 300 MHz. [d]At 270 MHz.

of models, formation of a 1′,4′-anhydro ring results in a reduction of the H-4′,5′ dihedral angle to ~90°, and, as expected, the coupling constant is ~0 Hz. Zero coupling between H-5′ and the H-6′ has been observed for 3,6:1′,2′:3′,6′-tri-anhydrosucrose[18]. One unusual feature of the spectrum of **7** is the small (1.3 Hz) long-range coupling between H-1′b and H-5′. This could be a through-space coupling transmitted *via* the lone-pair p-orbitals on O-5′ and O-1′(O-4′). Several examples of spin–spin coupling across five single-bonds are known[21].

In view of the concurrent formation of the 1′,4′- (**6**) and 3′,4′-anhydrosucrose (**2**), it is surprising that formation of a 1,4-anhydro ring was not observed with methyl β-D-fructofuranoside[2]. Moreover, our rationale for prior blocking of positions 6 and 6′ of sucrose (to prevent the formation of "impurity") was based on a false assumption, and yet blocking positions 6 and 6′ (by acetylation) prevents the formation of the 1′,4′-derivative **6**! An explanation for this apparently anomalous result is based on the formation of dialkoxytriphenylphosphoranes noted above. It is possible that sucrose reacts with TPP and DEAD to form an equilibrium mixture of phosphoranes, including, in particular, the 4,6:2,1′:4′,6′ (**8**), 2,3:4,6:1′,4′:3′,6′ (**9**), and 4,6:2,3′:1′,4′ (**10**) derivatives. There is ^{31}P-n.m.r. evidence for the formation of such cyclic phosphoranes with particular sucrose derivatives[8]. The 2,1′:4′,6′ derivative **8** is ideally set up to form 1′,4′-anhydrosucrose (**6**), whereas the 1′,4′-derivatives **9** and **10** give rise to **1**. The mechanism of cyclic ether formation from dialkoxytriphenylphosphoranes has been discussed elsewhere[3]. Clearly, acetylation of HO-6′ in sucrose blocks the formation of **8** and therefore of **6**. The epoxide **1** can still be formed, however, from such intermediates as **10**.



8 **9** **10**

EXPERIMENTAL

Melting points were determined with a Tottoli apparatus and are uncorrected. ^{1}H-n.m.r. spectra (internal Me_4Si) were recorded at 22.3 or 75.5 MHz with a Bruker HX-90 or CXP-300 spectrometer. Microanalyses were performed by the Chemistry Department, University of Queensland. Column chromatography was

performed on Kieselgel 60 (Merck, 70–230 or 230–400 mesh), and t.l.c. was conducted on silica gel GF_{254} (Merck). Organic solvents were redistilled. *N,N*-Dimethylformamide was dried by distillation from P_2O_5 under reduced pressure, and stored over molecular sieves (4A). Solvents were removed under reduced pressure at <50°. Optical rotations were determined with a Perkin–Elmer 241 polarimeter.

2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl 1,6-di-O-acetyl-3,4-anhydro-β-D-tagatofuranoside (**2**). — To an ice-cold solution of sucrose (2 g, 5.8 mmol) in *N,N*-dimethylformamide (20 mL) were added, with stirring under an atmosphere of nitrogen, glacial acetic acid (0.76 mL, 2.2 equiv.) and triphenylphosphine (6.9 g, 4.5 equiv.). A solution of diethyl azodicarboxylate (4.1 mL, 4.5 equiv.) in *N,N*-dimethylformamide (10 mL) was then added dropwise during 10 min, with stirring of the solution cooled in an ice-bath. The mixture was then stirred overnight (16 h) at room temperature, solvents were removed, and deacetylation was accomplished in the usual way with methanolic ammonia. The mixture was concentrated to an oil that was partitioned between water and ethyl acetate. The aqueous layer was extracted several times with ethyl acetate and with chloroform to remove triphenylphosphine oxide and diethyl hydrazinedicarboxylate, and then concentrated to dryness, and the residue was acetylated. After normal work-up, flash chromatography[22] (ethyl acetate–hexane, 1:1) afforded **2** (1.42 g, 42%), $[\alpha]_D$ +70° (*c* 1, chloroform), which was identical (^{13}C-n.m.r. spectrum) with a sample prepared previously[13].

α-D-Glucopyranosyl 3,4-anhydro-β-D-tagatofuranoside (**1**). — (*a*) Deacetylation of **2** with methanolic ammonia gave **1**, m.p. 179° (from ethanol), $[\alpha]_D$ +78° (*c* 1, water) (Found: C, 44.1; H, 6.5. $C_{12}H_{20}O_{10}$ calc.: C, 44.4; H, 6.2%). For n.m.r. data, see Tables I–III.

(*b*) Finely powdered sucrose (2 g, 5.8 mmol) was stirred with *N,N*-dimethylformamide (60 mL) for 6 h, and 2,2-dimethoxypropane (4 mL) was then added followed by a catalytic amount of toluene-*p*-sulfonic acid (20 mg). After stirring for 15–16 h at room temperature, triethylamine (0.1 mL) was added, and the mixture was concentrated to dryness. The resulting oil was dissolved in pyridine (10 mL), and triphenylphosphine (3.8 g, 2.5 equiv.) was added, followed by diethyl azodicarboxylate (2.3 mL, 2.5 equiv.) with cooling. The mixture was stirred and heated at 70° for 2.5 h, and then concentrated to dryness. A solution of the resulting, dark oil in acetic acid (20 mL) and water (12 mL) at 50° was stirred for 45 min, and then concentrated, and the residue was partitioned between water (50 mL) and chloroform (50 mL). The aqueous layer was washed thoroughly with chloroform and concentrated to dryness. A solution of the resulting, dark oil in ethanol was decolourised with charcoal (1–2 g) and then concentrated, and the residue was chromatographed (methanol–ethyl acetate, 1:4), to give **1** as a foam (0.76 g, 40%), which crystallised (0.6 g) from ethanol or water–2-propanol on seeding.

1′,4′-Anhydrosucrose (**6**). — Treatment of sucrose (1 g) in *N,N*-dimethylformamide (10 mL) with TPP (3 equiv.) and DEAD (3 equiv.), as described above but in the absence of acetic acid, gave a clear oil (0.83 g, 48%) that had the same

R_f value as **2** in t.l.c. However, the ^{13}C-n.m.r. spectrum indicated a mixture of **2** and the 1′,4′-anhydrosucrose derivative **7** in the ratio ~1:1. Repeated chromatography gave **7** that was 90% pure by ^1H-n.m.r. spectroscopy, which revealed 6 AcO groups. Deacetylation of **7** with methanolic ammonia gave **6**, m.p. 168° (from water–2-propanol), $[\alpha]_D$ +123° (*c* 1.2, methanol) (Found: C, 42.1; H, 6.6. $C_{12}H_{20}O_{10} \cdot H_2O$ calc.: C, 42.1; H, 6.5%). For n.m.r. data, see Tables I–III.

2,3,6-Tri-O-benzoyl-α-D-glucopyranosyl 3,4-anhydro-1,6-di-O-benzoyl-β-D-tagatofuranoside (**4**). — Sucrose 2,3,6,1′,6′-pentabenzoate (**3**) was prepared in 50% yield by a slight modification of the literature procedure[10]: prior to chromatography, the organic phase was washed with aqueous 30% potassium fluoride and then filtered through Celite to remove insoluble tributyltin fluoride. This procedure greatly facilitated the subsequent chromatography, without affecting the isolated yield of **3**. Although a yield of 87% of **3** was reported[10], in our hands, the yield was consistently ~50%.

To an ice-cold solution of **3** (4.0 g, 4.6 mmol) and triphenylphosphine (2.41 g, 2.0 equiv.) in dry chloroform (15 mL) was added dropwise during 20 min a solution of di-isopropyl azodicarboxylate (1.9 mL, 2.0 equiv.) in chloroform (10 mL). The solution was allowed to attain room temperature. After 3 h, t.l.c. (ethyl acetate–hexane, 1:1) indicated a clean conversion into **4**. The solution was concentrated and the residue was flash-chromatographed twice (ethyl acetate–hexane, 1:2), to give **4** as a syrup (3.2 g, 80%), $[\alpha]_D$ +51° (*c* 1, chloroform) (Found: C, 66.5; H, 4.9. $C_{47}H_{40}O_{15}$ calc.: C, 66.8; H, 4.8%). For n.m.r.data, see Tables I–III.

Acetylation of **4** gave 4-*O*-acetyl-2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl 3,4-anhydro-1,6-di-*O*-benzoyl-β-D-tagatofuranoside (**11**) as a syrup, $[\alpha]_D$ +66° (*c* 1, chloroform) (Found: C, 66.7; H, 5.1. $C_{49}H_{42}O_{16}$ calc.: C, 66.4; H, 4.8%). ^1H-N.m.r. data (100 MHz, benzene-d_6) δ 2.12 (s, 3 H, OAc), 3.98 (dd, 1 H, $J_{3',4'}$ 2.6, $J_{4',5'}$ 1.1 Hz, H-4′), 4.01 (d, 1 H, H-3′), 4.16–4.67 (m, 8 H, H-5,6a,6b,1′a,1′b,5′,6′a,6′b), 5.57 (dd, 1 H, $J_{3,4}$ 10.1, $J_{4,5}$ 9.1 Hz, H-4), 5.33 (dd, 1 H, $J_{1,2}$ 3.6, $J_{2,3}$ 9.8 Hz, H-2), 5.97 (d, 1 H, H-1), and 6.02 (dd, 1 H, H-3).

3,6′-Di-O-acetyl-3′,4′-anhydro-4,6:2,1′-di-O-isopropylidene-"tagatosucrose" (**5**). — To a solution of 4,6:2,1′-di-*O*-isopropylidenesucrose[11] (260 mg, 0.6 mmol) and triphenylphosphine (314 mg, 2 equiv.) in dry benzene (2 mL) was added diethyl azodicarboxylate (190 μL, 2 equiv.). The solution was boiled under reflux for 1.5 h and then stirred overnight at room temperature. After concentration, the residue was fractionated by flash chromatography (acetone–dichloromethane, 1:20; then acetone–ethyl acetate, 1:20), to give "di-*O*-isopropylidenesucrose epoxide", which, on acetylation, gave **5** (180 mg, 60%) as a foam, $[\alpha]_D$ +56° (*c* 1, chloroform) (Found: C, 53.9; H, 6.4. $C_{22}H_{32}O_{12}$ calc.: C, 54.1; H, 6.6). For n.m.r. data, see Tables I–III.

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