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# PREPARATION AND RING-OPENING REACTIONS OF A 2,3-ANHYDRIDE DERIVED FROM SUCROSE*†

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## ABSTRACT

Selective tosylation of 6,1′,6′-tri-*O*-tritylsucrose afforded the 2-*O*-tosyl derivative and not the 3-*O*-tosyl derivative as previously claimed. Treatment of the 2-tosylate with base afforded mainly (40%) the 2,3-*manno*-epoxide together with the 3,4-*altro*-epoxide which arose by migration of the epoxide ring. Ring-opening of the 2,3-epoxide with a variety of nucleophilic anions took place exclusively at C-3 to give altropyranosyl derivatives, whereas reaction of the epoxide with ammonium thiocyanate afforded the 2,3-*allo*-episulphide. Ring-opening of the 2,3-*manno*-epoxide with lithium iodide in ether gave 37% of the 3-deoxy-3-iodomanno-pyranosyl isomer, which arose by prior rearrangement of the 2,3-epoxide to the 3,4-epoxide.

## INTRODUCTION

Despite the importance of epoxides (oxiranes) as synthetic intermediates in carbohydrate chemistry[1], the synthesis of oxiranes of sucrose raises special synthetic problems because of the multifunctionality of the molecule and the lack of suitably blocked precursors. The first preparation of an epoxide derivative of sucrose was described in 1973 by Ballard *et al.*[2] who studied the exhaustive chlorination of sucrose with sulphuryl chloride, which led to the isolation, *inter alia*, of 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 3′,4′-anhydro-1′,6′-dichloro-1′,6′-dideoxy-β-D-*ribo*-hexulofuranoside 2,3-sulphate in 17% yield. Later, Khan *et al.*[3] described the preparation of both possible 3′,4′-epoxides from some suitably blocked 3′- and 4′-tosylates, and were able to utilise these epoxides for the synthesis of 4′-amino-4′-deoxysucrose derivatives. More recently, Guthrie and his co-workers[4] described the formation of some 3′,4′-anhydrides directly from sucrose, its 2,3,6,1′,6′-pentabenzoate, and its 4,6:2,1′-di-*O*-isopropylidene derivative by the

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use of triphenylphosphine–diethyl azodicarboxylate (TPP–DEAD). Recently[5], we reported the first derivative in which the oxirane ring was located in the pyranosyl ring of the disaccharide and now report a further synthesis of a 2,3- and a 3,4-epoxide derived from sucrose and their ring-opening reactions.

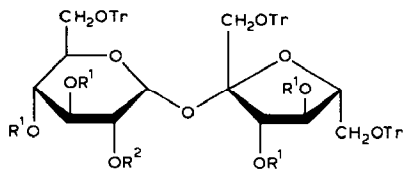
## RESULTS AND DISCUSSION

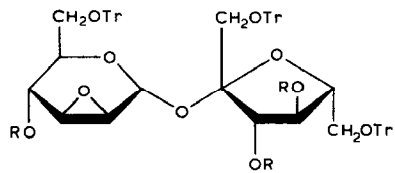
Selective monotosylation of 6,1′,6′-tri-*O*-tritylsucrose[6] (**1**) with 1 mol. equiv. of tosyl chloride was sluggish, and it was necessary to use at least 2 mol. equiv. of the reagent, which afforded the 2-tosylate **2** in 52% yield. The product was unequivocally characterised as the 2-tosylate by its subsequent reactions and by comparison of the $^1$H-n.m.r. spectrum of the derived tetra-acetate **3** with that[7] of 6,1′,6′-tri-*O*-tritylsucrose penta-acetate (**4**). The two spectra were very similar except that the H-2 resonance for **3** showed a marked upfield shift of 0.25 p.p.m. which was consistent with the presence of a tosyloxy group at position 2.

The greater reactivity of HO-2 towards tosylation by the acid chloride was expected, since it is well established that the HO-2 groups of $\alpha$-glucopyranosides normally have a much greater reactivity towards acid chlorides than the other secondary hydroxyl groups[8]. For example, the tetramolar tosylation of sucrose leads to the preferential formation of the 2,6,1′,6′-tetratosylate[9] and the selective monotosylation of 6,1′,6′-tri-*O*-mesitylenesulphonylsucrose gave the 2-tosylate in good yield[9]. In contrast, Jezo[10] claimed that tosylation of **1** at 50° gave the 3-tosylate in high yield. However, the physical data reported by Jezo were similar to those for the 2-tosylate, and repetition of Jezo's experiment gave the 2-tosylate in 33% yield.

When the 2-tosylate **2** was heated under reflux with methanolic 0.4M sodium methoxide for 2 h, it gave a mixture of products of which two were preponderant. These were isolated by chromatography, to give the crystalline 2,3-epoxide **5** in 40% yield and the syrupy 3,4-epoxide **7** in 15% yield.

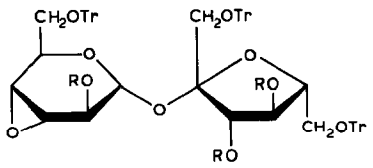
The major epoxide **5** was converted into a triacetate **6**, the $^1$H-n.m.r. spectrum of which showed four resonances below $\delta$ 5. The H-3′ and H-4′ resonances were readily recognised at $\delta$ 5.76 and 5.31 as a doublet and triplet ($J_{3',4'} = J_{4',5'} = 7.5$ Hz), respectively, showing that the fructofuranosyl ring was



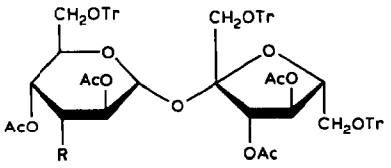




**1** $R^1 = R^2 = H$
**2** $R^1 = H, R^2 = Ts$
**3** $R^1 = Ac, R^2 = Ts$
**4** $R^1 = R^2 = Ac$

**5** R = H
**6** R = Ac



7 R = H
8 R = Ac



9 R = $N_3$
10 R = $SCSNMe_2$
11 R = SAc

unperturbed. The H-1 resonance was located at $\delta$ 5.51 a a singlet and H-4 as a doublet at $\delta$ 5.10 ($J_{4,5}$ 10 Hz). Signals due to H-2 and H-3 appeared as doublets at $\delta$ 3.00 and 3.14 ($J_{2,3}$ 2.5 Hz), respectively. The above data are in complete accord with the structure **6**; in particular, the lack of coupling between the pairs of vicinal protons H-1/H-2 and H-3/H-4 indicated that these were *trans* related, since such a relationship in pyranoid epoxides results in $^3J$ couplings of about zero[11]. The subsequent ring-opening reactions of **6** further supported the structure assigned.

The slower-moving epoxide **7** was acetylated to give **8**, the $^1$H-n.m.r. spectrum of which also showed four resonances to low field of $\delta$ 5. The doublet and triplet due to H-3′ and H-4′ were unperturbed, but the H-1 and H-2 resonances appeared as singlets at $\delta$ 5.73 and 5.11, respectively, and H-3 and H-4 resonated at higher field as an AB quartet centred at $\delta$ ~3.03. As above, the lack of coupling between the pairs of vicinal protons H-2/H-3 and H-4/H-5 indicated that these hydrogens were *trans*-related. These data clearly indicated that the product was the 3,4-anhydro-altropyranoside **7**. The small or non-existent coupling between H-1/H-2 is common in altropyranosides[12].

The formation of both the 2,3- and 3,4-epoxides from the 2-tosylate was expected since it is well established that epoxide rings which are vicinal to a *trans* hydroxyl group undergo base-catalysed rearrangement, affording ultimately a mixture of two epoxides, the ratio of which reflects their relative thermodynamic stabilities, provided that equilibrium is attained[13].

Ring-opening of the 2,3-epoxide was expected to occur by axial attack at C-3, to give 3-substituted altropyranosides, particularly since attack at the position adjacent to the anomeric group would not be favoured for stereoelectronic reasons[1,14]. As predicted, the 2,3-epoxide **5** underwent ring-opening with a variety of nucleophilic anions to give altropyranosides in good yields. Thus, reaction with sodium azide in the presence of ammonium chloride in boiling aqueous ethanol gave a single product which was isolated after *O*-acetylation as the crystalline tetra-acetate **9** in 92% yield. The $^1$H-n.m.r. spectrum of **9** was clearly compatible only with the altropyranoside structure, since the couplings $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ in the pyranoid ring were all small (see Table I), and showed that the ring existed in the predicted $^4C_1$ conformation. *O*-Detritylation and *O*-acetylation gave 3-azido-3-deoxy-$\alpha$-D-altropyranosyl $\beta$-D-fructofuranoside hepta-acetate (**12**) as a syrup in 65% overall yield; the $^1$H-n.m.r. spectrum of **12** was in complete accord with the structure assigned (Table I).

TABLE I

N.M.R. PARAMETERS: FIRST-ORDER CHEMICAL SHIFTS (P.P.M.) AND COUPLING CONSTANTS (Hz)

| *Atom* | **3**[a,b] | **6**[a,b] | **8**[c,d] | **9**[a,b] | **12**[d,e] | **10**[d,c] | **11**[b,c] | **13**[c,d] | **15**[c,d] |
|---|---|---|---|---|---|---|---|---|---|
| H-1 | 5.62d | 5.51s | 5.73s | 5.45s | 5.58s | 5.90d | 5.34d | 5.86d | 5.87d |
| H-2 | 4.59dd | 3.00d | 5.11s | 4.92dd | 5.02dd | 5.57dd | 4.88dd | 3.15t | 5.51dd |
| H-3 | 5.22m | 3.14d | 3.06d | | 3.94t | 5.76t | 4.27t | 3.52dd | 4.68dd |
| H-4 | | 5.10d | 3.01d | 5.29dd | 5.32dd | 6.38dd | 5.62dd | 5.81dd | 5.97t |
| H-5 | 4.25m | | 4.30m | | 4.71dt | 4.39bd | 3.96bd | | 4.37dt |
| H-6a | | | 3.42dd | | | 3.62dd | | | |
| H-6b | | | 3.12dd | | | 3.18dd | 2.92dd | 3.00dd | 3.20dd |
| H-1'a | 3.27d | | 3.75d | | 4.57d | 3.76d | | | |
| H-1'b | 3.10d | | | | 4.41d | 3.69d | | | |
| H-3' | 5.86d | 5.76d | 6.16d | 5.63d | 5.73d | 6.16d | 5.75d | 6.27d | 6.22d |
| H-4' | 5.37t | 5.31t | 6.02t | 5.51t | 5.69t | 5.97t | 5.53t | 5.66t | 5.96t |
| H-5' | 4.25m | | 4.42m | | 4.26m | 4.49m | 4.22m | | 4.40dt |
| H-6'a | | | | | | 3.83dd | | | |
| H-6'b | | | | | | 3.65d | | | |
| $J_{1,2}$ | 3.5 | 0 | 0 | 1 | 1.5 | 1.8 | 2.0 | 5.1 | 1.8 |
| $J_{2,3}$ | 10 | 2.5 | 0 | 4.0 | 3.9 | 4.0 | 3.7 | 6.4 | 2.6 |
| $J_{3,4}$ | | 0 | 4.0 | 4.5 | 3.9 | 4.5 | 4.0 | 3.5 | 11.4 |
| $J_{4,5}$ | | 10 | 1 | 9.0 | 9.8 | 9.6 | 9.6 | 9.7 | 9.0 |
| $J_{5,6a}$ | | | | | 4.0 | 1.9 | | | 2 |
| $J_{5,6b}$ | | | 2 | | 4 | 2.7 | | | 2 |
| $J_{6a,6b}$ | | | | | | 8.3 | | | |
| $J_{1'a,1'b}$ | 11 | | | | 12.0 | 7 | | | |
| $J_{3',4'}$ | 7 | 7.5 | 6.6 | 7.5 | 6.6 | 7.7 | 7.3 | 7.0 | 7.0 |
| $J_{4',5'}$ | 7 | 7.5 | 7.0 | 7.5 | 6.5 | 8.0 | 8.0 | 7.5 | 7.7 |
| $J_{5',6'a}$ | | | 4 | | | 5.5 | | | |
| $J_{5',6'b}$ | | | 4 | | | 3.7 | | | |
| $J_{6'a,6'b}$ | | | 7 | | | 8.5 | | | |

[a]At 90 MHz. [b]In $CDCl_3$. [c]At 250 MHz. [d]In $C_6D_6$. [e]At 360 MHz.

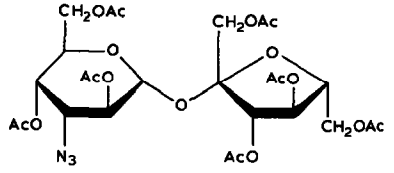
Similarly, treatment of **5** with sodium *N,N*-dimethyldithiocarbamate in aqueous 2-methoxyethanol in the presence of ammonium chloride at 100° for 1.5 h gave the 3-*S*-(*N,N*-dimethylaminothiocarbonyl)-3-thioaltropyranoside which, after *O*-acetylation, was isolated as its tetra-acetate **10** in 91% yield; **10** was identified by its $^1$H-n.m.r. parameters (Table I) which were similar to those of **9**.

The reaction of the 2,3-epoxide **5** with potassium thioacetate and ammonium chloride in aqueous ethanol under reflux for 24 h followed by *O*-acetylation also gave one major product; this was isolated as an amorphous solid in 65% yield by chromatography and characterised as the 3-*S*-acetyl-3-thioaltropyranoside **11** from its $^1$H-n.m.r. spectrum which closely resembled that of **10** (Table I).

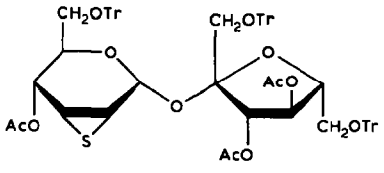
Treatment of **6** with ammonium thiocyanate in 2-methoxyethanol at 100° afforded a complex mixture of products from which the major isomer was obtained in only 23% yield. Since the i.r. spectrum revealed that this product did not contain a thiocyanate group, and in view of the known conversion of some epoxide derivatives into the corresponding episulphides[15] of opposite configuration by this reaction, the compound was probably the 2,3-*allo*-episulphide **13**. This possibility

was confirmed by its $^1$H-n.m.r. spectrum which was clearly consistent with a triacetate derivative in which the fructofuranosyl ring was unperturbed, with normal values for $J_{3',4'}$ and $J_{4',5'}$; however, the H-1 and H-4 resonances appeared as a doublet ($J_{1,2}$ 5.1 Hz) and a double doublet ($J_{3,4}$ 3.5 and $J_{4,5}$ 9.7 Hz) at $\delta$ 5.86 and 5.81, respectively. In the upfield part of the spectrum, the H-2 and H-3 resonances were observed as double doublets at $\delta$ 3.15 and 3.52, respectively, with $J_{2,3}$ = 6.4 Hz. The high-field position of the H-2 and H-3 resonances indicated that they were part of the episulphide (thiirane) ring, and the relatively large coupling constants between the pairs of vicinal protons H-1/H-2 and H-3/H-4 confirmed that they were *cis*-related.

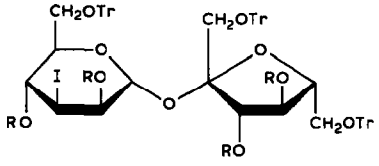
When **5** was treated with a large excess of lithium iodide in ether for 3–4 days, a complex mixture of products was formed, from which the major component was isolated in 37% yield, and shown to be a mono-iodo derivative. The $^1$H-n.m.r. spectrum of the derived tetra-acetate **15** at 250 MHz was largely first-order (Table I) and the assignments could be made readily by matching of coupling constants, but they were clearly not in agreement with the expected 3-deoxy-3-iodoaltropyranoside structure. As before, the H-3′ and H-4′ resonances were readily assigned, and H-1 resonated as a narrow doublet at $\delta$ 5.87 ($J_{1,2}$ 1.8 Hz), and this coupling was also present in a narrow double-doublet at $\delta$ 5.51 ($J_{2,3}$ 2.6 Hz) which was therefore assigned to H-2. The H-3 resonance appeared at higher field ($\delta$ 4.68, $J_{3,4}$ 11.4 Hz), suggesting that the iodo group was located at C-3. The H-4 resonance was present at $\delta$ 5.97 ($J_{4,5}$ ~9 Hz). The large couplings between the pairs of vicinal protons H-3/H-4 and H-4/H-5 indicated that they were axially situated, and the small coupling between H-3 and H-2 indicated that H-2 was equatorial, suggesting that the product was the 3-deoxy-3-iodomannopyranosyl derivative **14**,




12




13




14 R = H

15 R = Ac

which could not arise directly from **5**. It is proposed that the product arises from a series of equilibria in which **5** initially isomerises to **7**. Subsequent ring-opening of **7** with iodide then produces either the 4-iodo-idopyranoside or the 3-iodomanno-pyranoside. Thus, it appears that the *manno* isomer arises because it must be one of the thermodynamically favoured products.

## EXPERIMENTAL

Unless otherwise stated, optical rotations were measured at ambient temperatures (18–20°) in chloroform solution. Column chromatography was performed on Silica Gel G (Merck 7734) with the stated solvent mixture. Light petroleum (b.p. 40–60°) was used throughout. Acetylation was carried out by dissolving the compound in pyridine (5–10 mL/g) and adding acetic anhydride (5–10 mL/g); after standing at room temperature for 1–18 h, the mixture was poured into water and the product was filtered off if crystalline, or extracted into chloroform. The chloroform solution was then washed well with water, dilute hydrochloric acid, and aqueous sodium hydrogencarbonate, dried ($MgSO_4$), and evaporated to dryness.

*2-O-Tosyl-6,1',6'-tri-O-tritylsucrose* (**2**). — To an ice-cold solution of 6,1',6'-tri-*O*-tritylsucrose[6] (**1**; 10 g, 9.36 mmol) in dry pyridine (150 mL) was added dropwise a solution of tosyl chloride (3.5 g, 18.7 mmol) in dry pyridine (30 mL), and the mixture was kept at room temperature for 2 days. T.l.c. (chloroform–acetone, 2:1) then revealed one major product together with several minor components. The mixture was then treated with water and evaporated to dryness, the last traces of pyridine being removed by co-evaporation with toluene. The resulting semi-crystalline mixture was subjected to column chromatography with chloroform–acetone (20:1). Initially, mixtures of minor products were eluted which were not further investigated, and these were followed by **2** which was obtained as a white crystalline solid (5.9 g, 52%), m.p. 134° (from ethanol), $[\alpha]_D$ +33° (*c* 1) (Found: C, 74.25; H, 5.93. $C_{76}H_{70}O_{13}S$ calc.: C, 74.65; H, 5.75%). Jezo[10] reported m.p. 135–136°, $[\alpha]_D$ +25.4°, for this product which he wrongly claimed to be the 3-tosylate.

Conventional acetylation (acetic anhydride–pyridine) afforded the tetra-acetate **3**, m.p. 119° (from ethanol), $[\alpha]_D$ +78° (*c* 1) (Found: C, 72.35; H, 5.65; S, 2.51. $C_{84}H_{78}O_{17}S$ calc.: C, 72.5; H, 5.6; S, 2.3%). Jezo[10] reported m.p. 125–126°, $[\alpha]_D$ +60°, for this product.

*2,3-Anhydro-6-O-trityl-α-D-mannopyranosyl 1,6-di-O-trityl-β-D-fructofuranoside* (**5**) *and 3,4-anhydro-6-O-trityl-α-D-altropyranosyl 1,6-di-O-trityl-β-D-fructofuranoside* (**7**). — A solution of **2** (10 g) in methanolic 0.4M sodium methoxide (100 mL) was heated under reflux for 2 h, after which t.l.c. indicated two prominent and several minor products. The mixture was neutralised by the careful addition of Amberlite IR-120($H^+$) resin, and then evaporated to leave a yellow solid. Column chromatography with ether–light petroleum (1:3) gave several minor components which were not investigated further; the major components (*A* and *B*) were then eluted with a 1:1 solvent mixture.

Fraction *A* afforded **5** (3.5 g, 41%), m.p. 126–128° (from ether–light petroleum), $[\alpha]_D$ +15° (*c* 1) (Found: C, 78.55; H, 6.35. $C_{69}H_{62}O_{10}$ calc.: C, 78.85; H, 5.9%).

Acetylation of **5** afforded **6** (93%), m.p. 189° (from ether–light petroleum), $[\alpha]_D$ +48° (*c* 1) (Found: C, 76.4; H, 5.85. $C_{75}H_{68}O_{13}$ calc.: C, 76.55; H, 5.8%).

Fraction *B* afforded **7** (1.3 g, 15%), m.p. 124–127°, $[\alpha]_D$ −4° (*c* 0.6) (Found: C, 79.0; H, 6.0. $C_{69}H_{62}O_{10}$ calc.: C, 78.85; H, 5.9%).

Acetylation of **7** afforded **8**, m.p. 105–108°, $[\alpha]_D$ +10° (*c* 0.7) (Found: C, 76.19; H, 5.66. $C_{75}H_{68}O_{13}$ calc.: C, 76.53; H, 5.8%).

*2,4-Di-*O*-acetyl-3-azido-3-deoxy-6-*O*-trityl-α-*D*-altropyranosyl 3,4-di-*O*-acetyl-1,6-di-*O*-trityl-β-*D*-fructofuranoside* (**9**). — A solution of **5** (1 g, 0.95 mmol) in aqueous 90% ethanol (11 mL) containing sodium azide (1 g, 15.4 mmol) and ammonium chloride (1 g, 19 mmol) was heated under reflux for 24 h. T.l.c. (ether–acetone, 10:1) then indicated the formation of a slower-moving product. The mixture was evaporated to dryness and the residue was acetylated with acetic anhydride (3 mL) and pyridine (7 mL). Recrystallisation from ether–light petroleum gave **9** (1.1 g, 92%), m.p. 104°, $[\alpha]_D$ +25° (*c* 1) (Found: C, 73.0; H, 5.45; N, 3.5. $C_{77}H_{71}N_3O_{14}$ calc.: C, 73.25; H, 5.65; N, 3.35%).

*2,4,6-Tri-*O*-acetyl-3-azido-3-deoxy-α-*D*-altropyranosyl 1,3,4,6-tetra-*O*-acetyl-β-*D*-fructofuranoside* (**12**). — A solution of **9** (1 g, 0.83 mmol) in a mixture of chloroform (5 mL), acetic acid (5 mL), and hydrobromic acid (1.5 mL, 45% solution in acetic acid) was kept at −5° for 3 min and then poured into ice–water. The chloroform layer was separated and the aqueous layer then extracted with a further portion of chloroform. The combined chloroform extracts were washed well with water and aqueous sodium hydrogencarbonate, dried ($MgSO_4$), and evaporated to a syrup that was then acetylated. The resulting syrup was chromatographed on a short column (ether) to give pure syrupy **12** (0.35 g, 65%), $[\alpha]_D$ +29° (*c* 1) (Found: C, 47.25; H, 5.3; N, 6.05. $C_{26}H_{35}N_3O_{17}$ calc.: C, 47.2; H, 5.3; N, 6.35%).

*2,4-Di-*O*-acetyl-3-*S*-(N,N-dimethylaminothiocarbonyl)-3-thio-6-*O*-trityl-α-*D*-altropyranosyl 3,4-di-*O*-acetyl-1,6-di-*O*-trityl-β-*D*-fructofuranoside* (**10**). — A mixture of **5** (0.5 g), sodium *N,N*-dimethylaminodithiocarbamate (1 g), and ammonium chloride (0.5 g) in 2-methoxyethanol (15 mL) and water (1 mL) was heated at 100° for 1.5 h. T.l.c. (ether) then indicated that one slower-moving product had been formed. The dark-brown reaction mixture was evaporated to dryness and the residue was acetylated to give **10** (0.58 g, 91%), m.p. 127–129°, $[\alpha]_D$ +14° (*c* 1) (Found: C, 71.5; H, 5.82; N, 0.85: S, 4.71. $C_{80}H_{77}NO_{14}S_2$ calc.: C, 71.7; H, 5.75; N, 1.05; S, 4.77%).

*2,4-Di-*O*-acetyl-3-*S*-acetyl-3-thio-6-*O*-trityl-α-*D*-altropyranosyl 3,4-di-*O*-acetyl-1,6-di-*O*-trityl-β-*D*-fructofuranoside* (**11**). — A solution of **5** (0.5 g, 0.5 mmol), potassium thioacetate (1 g), and ammonium chloride (0.5 g) in aqueous 96% ethanol (20 mL) was heated under reflux for 24 h. T.l.c. (ether–light petroleum, 2:1) then revealed one major and several minor products. The mixture was then evaporated to dryness and the residue was acetylated to give a product that was

purified by chromatography [ether–light petroleum (1:1)]. The thioacetate **11** was obtained a a white amorphous solid (0.4 g, 65%), m.p. 113–116°, $[\alpha]_D$ +20° (*c* 0.6) (Found: C, 73.0; H, 6.0; S, 2.6. $C_{79}H_{74}O_{15}S$ calc.: C, 73.3; H, 5.7; S, 2.5%).

*4-O-Acetyl-2,3-epithio-6-O-trityl-α-D-allopyranosyl 3,4-di-O-acetyl-1,6-di-O-trityl-β-D-fructofuranoside* (**13**). — A solution of **6** (2.5 g, 2.1 mmol) and ammonium thiocyanate (7 g) in 2-methoxyethanol (50 mL) was heated at 100° for 12 h and then evaporated to dryness. The residue was extracted with chloroform, and the insoluble inorganic material was removed by filtration. T.l.c. (ether–light petroleum, 1:1) indicated that the product consisted of one faster-moving major component, several minor components, and some unreacted starting-material. Column chromatography (ether–light petroleum, 1:3) of the mixture gave **13** as the first fraction, which was isolated as an amorphous solid (0.6 g, 23%), $[\alpha]_D$ +51° (*c* 0.75) (Found: C, 75.0; H, 6.25; S, 2.3. $C_{75}H_{68}O_{12}S$ calc.: C, 75.5; H, 5.7; S, 2.7%).

Further elution of the column afforded **6** (0.5 g) and a minor component (0.2 g) that was eluted by changing the composition of the solvent to 1:2, but was not further examined.

*3-Deoxy-3-iodo-6-O-trityl-α-D-mannopyranosyl 1,6-di-O-trityl-β-D-fructofuranoside* (**14**). — A solution of the 2,3-epoxide **5** (0.6 g, 0.6 mmol) in ether (50 mL) was heated under reflux with lithium iodide (5 g) for 3.5 days. T.l.c. (ether–light petroleum, 4:1) then revealed a fast-moving major product followed by a trail of several slower-moving, minor components. The mixture was cooled, inorganic material was filtered off, and the ethereal solution was evaporated to dryness to give a yellow solid that was then extracted with chloroform. The extract was filtered, washed well with aqueous 10% sodium thiosulphate, dried ($MgSO_4$), and evaporated to dryness. Column chromatography (ether–light petroleum, 3:2) of the residue gave, first, the 3-iodide **14** as an amorphous solid (0.25 g, 37%), $[\alpha]_D$ −0.6° (*c* 0.8) (Found: C, 69.9; H, 5.6; I, 11.4. $C_{69}H_{63}IO_{10}$ calc.: C, 70.2; H, 5.3; I, 10.8%).

Acetylation of **14** gave **15** as an amorphous solid, $[\alpha]_D$ +22.7° (*c* 0.9) (Found: C, 68.4: H, 5.3; I, 8.2. $C_{77}H_{71}IO_{14}$ calc.: C, 68.65; H, 5.3; I, 9.4%).

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