Carbohydrate Research, 174 (1988) 145–160
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

BRIDGED DERIVATIVES OF SUCROSE: THE SYNTHESIS OF 6,6′-DITHIOSUCROSE, 6,6′-EPIDITHIOSUCROSE, AND 6,6′-EPITHIOSUCROSE*†

LESLIE HOUGH, LEE V. SINCHAREONKUL, ANTHONY C. RICHARDSON‡,
Department of Chemistry, King's College London (KQC), Kensington Campus, Campden Hill Road, London W8 7AH (Great Britain)

FARIDA AKHTAR, AND MICHAEL G. B. DREW
Department of Chemistry, The University, Whiteknights, Reading RG6 2AD (Great Britain)

(Received June 23rd, 1987; accepted for publication, August 24th, 1987)

ABSTRACT

Selective iodination and bromination of sucrose at C-6 and C-6′ has been accomplished by reactions with iodine–triphenylphosphine–imidazole and carbon tetrabromide–triphenylphosphine–pyridine, respectively. Substitution of the bromo groups in 6,6′-dibromo-6,6′-dideoxysucrose hexa-acetate by CNS^-, AcS^-, and $Me_2NCS_2^-$ took place without complications, but when $EtOCS_2K$ was used, a complex reaction sequence took place leading to 6,6′-epithiosucrose hexa-acetate. Similarly, reaction of the dibromo derivative with K_2CS_3 afforded mainly the 6,6′-episulphide together with 6,6′-epidithiosucrose hexa-acetate, which was also formed from the dibromide by sequential treatment with thiourea and sodium metabisulphite. Oxidation of the episulphide with sodium metaperiodate afforded solely the (*R*)-sulphoxide, and oxidation with hydrogen peroxide afforded the sulphone. The episulphide, the episulphide *S,S*-dioxide, and the epidisulphide all showed conformational instability of the ring containing the sulphur atom(s), as indicated by the n.m.r. spectra, but the episulphide *S*-oxide did not show this behaviour.

INTRODUCTION

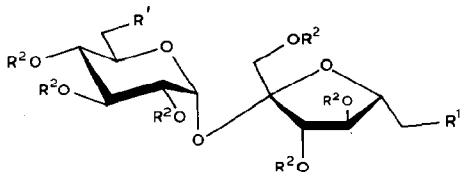
In view of the enormous enhancement of sweetness of sucrose by the introduction of chlorine substituents into the molecule[1], we are engaged in the synthesis of sucrose analogues containing various functionalities. Of particular interest is the thiol group and we now describe some work directed towards the synthesis of derivatives of 6,6′-dithiosucrose.

*Dedicated to Professor Hans Paulsen.
†Sucrochemistry, Part 40. For Part 39, see R. Khan and G. Patel, *Carbohydr. Res.*, 162 (1987) 298–302.
‡Author for correspondence.

0008-6215/88/$ 03.50

RESULTS AND DISCUSSION

The synthesis of the unknown 6,6′-dithiosucrose was investigated first; this requires, as a prerequisite, the introduction of efficient leaving-groups at these positions, and 6,6′-dideoxy-6,6′-di-iodosucrose and the corresponding dibromide were considered to be ideal precursors. These compounds could be prepared directly from sucrose in reasonable yields by halogenation methods utilising triphenylphosphine. The reaction[2] of sucrose with triphenylphosphine, iodine, and imidazole in the ratios 1:3:3:9 in toluene afforded the di-iodide, isolated as its crystalline hexa-acetate **1** in only 40% yield (**1** had been reported[3] previously only as a syrup). Fortunately, the reaction of sucrose with triphenylphosphine and carbon tetrabromide in pyridine[4] gave 91% of the syrupy dibromide **2**, which gave a crystalline hexa-acetate **3**. The structures of these dihalosucroses were readily established from their ^{13}C-n.m.r. parameters, in which both C-6 and C-6′ were shielded (~59 p.p.m. for the di-iodide, ~30 p.p.m. for the dibromide) compared with sucrose octa-acetate.



1 $R^1 = I, R^2 = Ac$
2 $R^1 = Br, R^2 = H$
3 $R^1 = Br, R^2 = Ac$
4 $R^1 = SCSNMe_2, R^2 = H$
5 $R^1 = SCSNMe_2, R^2 = Ac$
6 $R^1 = SCSNMe_2, R^2 = Bz$
7 $R^1 = SAc, R^2 = Ac$
8 $R^1 = SCN, R^2 = Ac$
9 $R^1 = H, R^2 = Ac$

Reaction of the hexa-acetate **3** with either potassium thioacetate or sodium thiocyanate in hot *N,N*-dimethylformamide gave the corresponding derivatives (**7** and **8**, respectively) of 6,6′-dithiosucrose, which were crystalline and readily characterised from their ^{1}H-n.m.r. spectra. The dibromide **2** reacted similarly with sodium *N,N*-dimethylaminodithiocarbamate to give the amorphous 6,6′-dithiocarbamate **4**, which was characterised as its crystalline hexa-acetate (**5**) and its hexa-benzoate (**6**). However, **3** reacted with thiourea to give the bis-thiouronium salt, which was then decomposed, without isolation, by sodium metabisulphite to give less-polar material. Although the product appeared to be pure after isolation by chromatography, it was shown to be a mixture after *O*-deacetylation. Chromatography of the mixture and then re-acetylation gave the faster-moving

major component as a crystalline hexa-acetate in 19% overall yield. The ^{1}H-n.m.r. spectrum indicated the presence of six *O*-acetyl groups, but the resonances due to the ring protons, particularly H-6a,6b,6'a,6'b, were broad and ill-defined. The product was shown to be the epidisulphide **10**, from its elemental analysis and mass spectrum [*m/z* 624 (M^+)], and the u.v. absorptions at λ_{max} 253 (ε 291) and 215 (ε 888) were consistent with a strainless disulphide bridge[5] between C-6 and C-6'. The epidisulphide **10** had arisen from the 6,6'-dithiol by aerial oxidation, a facile phenomenon, observed with other sugar dithiols[6]. The broadening of the ring-proton resonances in the n.m.r. spectrum was interpreted as reflecting conformational instability of the trioxadithiaundecane ring system. Molecular models indicated that the ring could be puckered in two ways with S-6/S-6' being up/down or down/up, and that interconversion would involve considerable deformation (**10a** and **10b**, respectively, Fig. 1). The $^3J_{H,H}$ values of the glucopyranoside ring were close to normal, indicating no appreciable deformation of the $^4C_1$ conformation, but the small values (1.5 Hz) observed for $J_{3',4'}$ and $J_{4',5'}$ indicated that the fructofuranoside ring had been deformed. When the ^{1}H-n.m.r. spectrum of **10** was recorded at elevated temperatures, a sharpening of the resonances occurred until, at 75°, the spectrum had coalesced into a time-averaged spectrum of the two conformers. Surprisingly, the ^{13}C-n.m.r. resonances did not show any appreciable broadening at ambient temperatures.

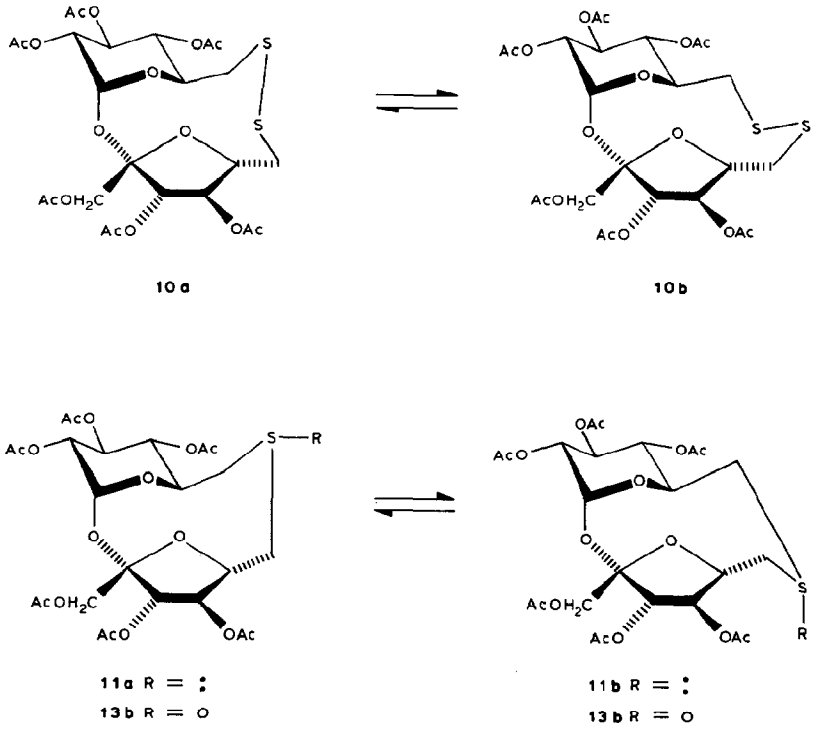


Fig. 1. Conformations of 6,6'-epidithio- (**10**) and 6,6'-epithio-sucrose (**11**) in solution.

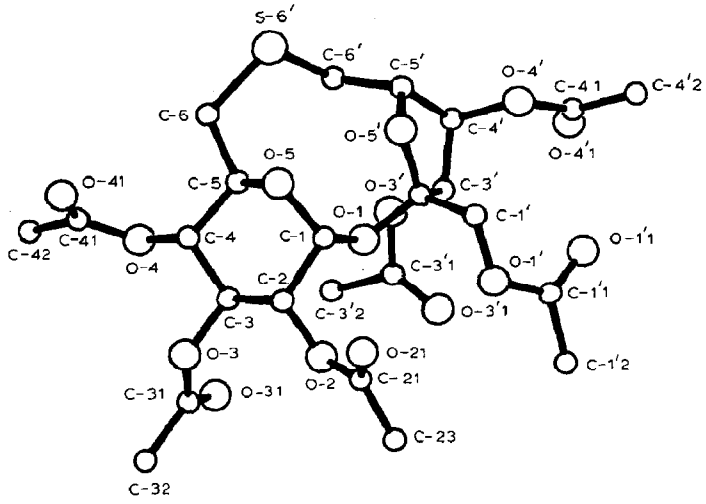
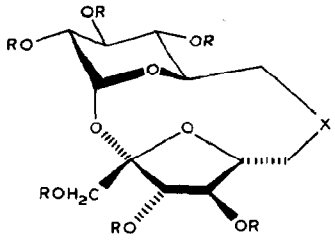
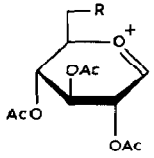


Fig. 2. The crystal structure of 6,6′-epithiosucrose (**11**), showing the atomic numbering scheme. For simplicity, the hydrogen atoms have been omitted.



10 X = —S—S—, R = Ac
11 X = —S—, R = Ac
12 X = S, R = H
13 X = SO, R = Ac
14 X = SO_2, R = Ac



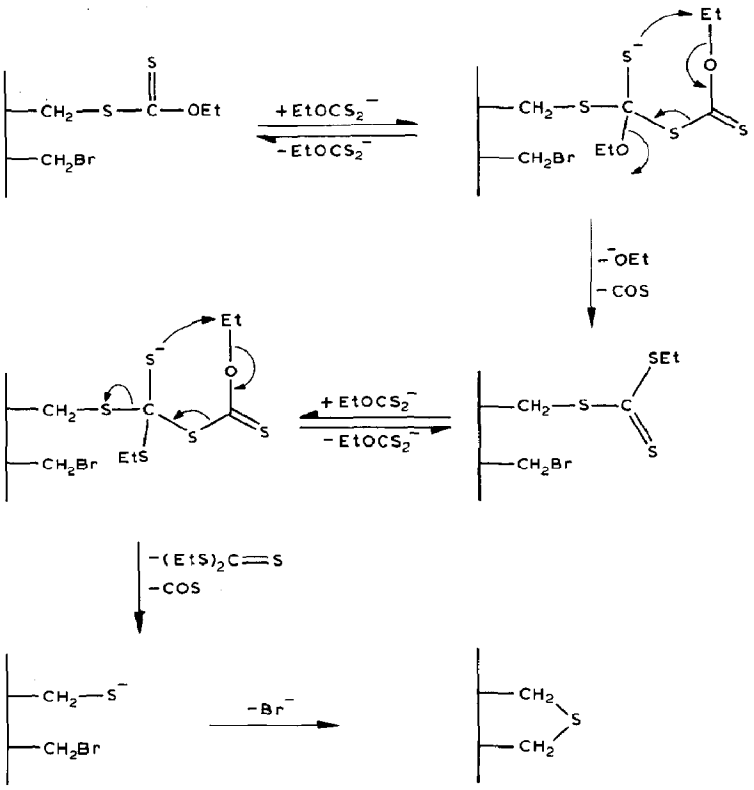
15 R = Br
16 R = SCSOEt
17 R = SCS_2Et
18 R = SH

When the hexa-acetate **3** was treated with potassium *O*-ethyl dithiocarbonate in *N,N*-dimethylformamide, it gave a mixture of products from which the major component was isolated in 46% yield. The product was not the anticipated di-*S*-ethoxythiocarbonyl derivative of 6,6′-dithiosucrose hexa-acetate, since elemental analysis indicated the presence of only one sulphur atom, whereas the ^{1}H-n.m.r. spectrum revealed the expected six acetyl groups and confirmed the absence of any *O*-ethyl groups. As before, considerable line-broadening was observed in the ^{1}H-n.m.r. spectrum with the resonances of H-6 and H-6′ being particularly affected; at elevated temperatures, the resonances sharpened considerably and coalesced at 70°. The compound was therefore identified as 6,6′-epithiosucrose hexa-acetate

(**11**), and this was confirmed by an X-ray structure determination (see below) (Fig. 2). As with **10**, the broadening of the n.m.r. resonances of **11** appeared to be due to conformational instability of the trioxathiadecane ring, for which there is a slow interconversion of the two conformers **11a** and **11b** (Fig. 1), since considerable sharpening of the resonances occurred at elevated temperatures.

The mechanism of formation of the epithiosucrose is obscure since it was unlikely to arise after displacement of both of the bromo substituents by the $EtOCS_2$ anion. The reaction mixture was examined for the presence of a mono-bromo intermediate. Under the reaction conditions employed (*N,N*-dimethylformamide at 100°), short-lived intermediates were observed which were difficult to isolate. However, the overall reaction in acetone was much slower and the intermediates accumulated in reasonable amounts. Thus, after 2.5 h, 41% of the epithiosucrose **11** was isolated together with ~30% of a seemingly homogeneous intermediate (component *A*). However, extensive chromatography of component *A* revealed that it contained at least three components, which could not be isolated. Mass spectrometry of component *A* afforded an insight into the components present. The major pathway for sucrose derivatives is A1-cleavage of the glycosidic bonds, giving the glycosyl carbonium ions, and that from the pyranoside then loses, sequentially, acetic acid, ketene, and acetic acid. Thus, fragment ions were noted at *m/z* 351/353 (1:1), 393, and 409 due to the glycosyl carbonium ions **15–17**, suggesting that mono-ethoxythiocarbonyl (EtOCS–) and mono-ethylthiothiocarbonyl (EtSCS–) derivatives were present. The former ions were much the more intense, suggesting that the ethoxythiocarbonyl derivatives were the major components. Additionally, the glycosyl carbonium ion corresponding to **18** was also present, at *m/z* 305, but this may have arisen from either **16** or **17** by loss of C_2H_4 (McLafferty rearrangement), followed by loss of COS or CS_2, respectively. Fragments corresponding to the sequential loss of HOAc, CH_2O, and HOAc from each of these glycosyl carbonium ions were observed. These results suggested that the first-formed ethoxythiocarbonyl derivative was converted into the ethylthiothiocarbonyl derivative, a known reaction[7], and thence into the thioalkoxide salt (Scheme 1), which could then displace the remaining bromo substituent to give the 6,6′-epithiosucrose hexa-acetate (**11**).

In an effort to characterise component *A* more fully, it was treated with sodium azide in *N,N*-dimethylformamide, but the anticipated azide was not formed and ~58% of the 6,6′-epidithiosucrose hexa-acetate (**10**) was isolated. When component *A* was reacted similarly with lithium chloride, 32% of **10** was formed together with 13% of **11**. The reasons for this behaviour are not clear, but the epidisulphide probably arises by initial attack at the CH_2Br by the thiocarbonyl sulphur, mediated by nucleophilic attack at the C=S by azide, to give the orthoacyl azide [$-CH_2-S-C(OEt)N_3-S-CH_2-$], which would hydrolyse to the dithiol, from which the disulphide arises. The episulphide **11** possibly arises by slow hydrolysis of the S–CS bond, followed by nucleophilic replacement of the bromo group by the liberated thiol.



Scheme 1. Mechanism for the formation of episulphide **11** from dibromide **3**.

Reaction of **3** with potassium trithiocarbonate afforded the episulphide **11** in 24% yield together with 7% of **10**. Presumably, the episulphide arises by displacement of the bromide, to give a species R–S–CS_2K which disproportionates into R–SK and CS_2, followed by displacement of the second bromide by thioalkoxide. The disulphide **10** presumably arose from the species R–S–CS_2K, by direct displacement of the other bromide to give the cyclic 6,6′-trithiocarbonate, which, presumably, underwent ring-opening by attack with excess of trithiocarbonate.

Oxidation of the episulphide **11** with sodium periodate afforded 86% of a single sulphoxide **13**. In contrast to that of **11**, the ^{1}H-n.m.r. spectrum of **13** showed no line-broadening, indicating that there was no conformational instability. Consequently, it was assumed that the *S*-oxygen must occupy a pseudo-equatorial position and that the conformational change would be sterically hindered. The $J_{5,6a}$ (12.1 Hz), $J_{5,6b}$ (3.6 Hz), $J_{5',6'a}$ (13.4 Hz), and $J_{5,6'b}$ values (3.6 Hz) indicated that H-5 and H-5′ must be antiperiplanar to H-6a and H-6′a, respectively. This arrange-

ment occurs only in the conformer **13a** in which the sulphur is "up", which is that found in the crystal structure of the episulphide **11**. In the other conformation, the dihedral angles $\theta_{5',6'a}$ and $\theta_{5',6'b}$ would be ~90° and 30°, respectively, and would lead therefore to much lower J values. Hence, the sulphoxide is identified as the (*R*)-isomer **13**.

Oxidation of either the sulphoxide **13** or the episulphide **11** with acetic acid–hydrogen peroxide afforded the disulphone **14** in good yield, the n.m.r. spectrum of which again indicated that the sulphur-containing ring was conformationally unstable since there was considerable broadening of the signals at ambient temperatures.

Desulphuration of most of the 6,6′-dithio derivatives with Raney nickel gave the hexa-acetate **9** of 6,6′-dideoxysucrose in high yield.

X-Ray crystal structure of **11**. — The molecular conformation of **11** is illustrated in Fig. 2 together with the atomic numbering scheme. The pyranose ring has the usual $^4C_1$ chair conformation. The observed torsion angles vary between 48.9° and 72.6°, rather larger than the range (54.8–56.6°) in sucrose[8]. The fructofuranoside ring exists in a $^4T_5$ conformation with C-4′ and C-5′ displaced by 0.35 and −0.17Å, respectively, from the plane containing C-2′, C-3′, and the ring oxygen. The displacement of C-4′ is *endo* and that of C-5′ is *exo* with respect to C-6′. Thus, the conformation of the fructose ring is different to that in sucrose and other simple sucrose derivatives, but is similar to that found in potassium sucrose octasulphate heptahydrate[9]. Neither of the two linkages between the two monosaccharide moieties seems to be unusually strained, as indicated by the torsional angles (Table III). The torsion angles for the glycosidic linkage are different from those of sucrose[8], but similar to those observed for 1-kestose[10]. The conformation of the trioxathiacyclodecane ring does not resemble any of the preferred conformations of cyclodecane[11], but this is hardly surprising because of the restraints of the two monosaccharide rings. Moreover, the ring conformations are particularly dependent upon H···H contacts, and, in the trioxathiacyclodecane ring, there are eight fewer hydrogen atoms. The only unusual torsion angle (6.6°) is that for C-6–S-6–C-6′–H-6′b. It can be concluded that the formation of the 6,6′-epithio linkage in sucrose occurs without undue strain in the molecule, and, presumably, the epidithiosucrose likewise must be without undue strain.

Attempts to bridge the 6,6′-positions in lactose, with the formation of a dioxathiacyclononane ring, were unsuccessful[12].

EXPERIMENTAL

General. — Optical rotations were determined for solutions in chloroform (18–22°) unless otherwise stated. Light petroleum (b.p. 40–60°) was used throughout. Chromatography was performed on Silica Gel G (Merck 7734), and was sometimes conducted on a dry packed column[13].

*2,3,4-Tri-*O*-acetyl-6-deoxy-6-iodo-α-*D*-glucopyranosyl 1,3,4-tri-*O*-acetyl-6-*

deoxy-6-iodo-β-D-*fructofuranoside* (**1**). — Triphenylphosphine (15.7 g, 60 mmol), iodine (15.3 g, 60 mmol), and imidazole (12.3 g, 180 mmol) were added to a suspension of finely powdered sucrose (6.84 g, 20 mmol) in toluene. The mixture was then stirred vigorously for 6 h at 80°, when t.l.c. (ethyl acetate–ethanol–water, 7:3:1) revealed a major product, several minor components, and some sucrose. The mixture was then extracted thrice with water (50, 25, and 25 mL), and the combined aqueous extracts were concentrated to dryness. A solution of the residue in pyridine (40 mL) was treated with acetic anhydride (25 mL) at room temperature for 16 h and then worked-up in the usual manner. Column chromatography (ether–light petroleum, 1:1) of the product gave **1** (6.5 g, 40%), m.p. 97–99° (from ethanol), $[\alpha]_D$ +38° (Found: C, 35.1; H, 4.0; I, 31.3. $C_{34}H_{32}I_2O_{15}$ calc.: C, 35.4; H, 3.9; I, 31.2%). ^{1}H-N.m.r. data (C_6D_6, 90 MHz): δ 5.57 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.96 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 5.69 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 5.10 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.43 (d, 1 H, $J_{1'a,1'b}$ 12.5 Hz, H-1'a), 4.22 (d, 1 H, H-1'b), 5.56 (d, 1 H, $J_{3',4'}$ 5.0 Hz, H-3'), 5.40 (t, 1 H, $J_{4',5'}$ 5.0 Hz, H-4').

*2,3,4-Tri-*O*-acetyl-6-bromo-6-deoxy-α*-D-*glucopyranosyl 1,3,4-tri-*O*-acetyl-6-bromo-6-deoxy-β*-D-*fructofuranoside* (**3**). — Sucrose (10 g, 30 mmol) was dissolved in pyridine (200 mL) by heating for 30 min at ~60°. The solution was then cooled in an ice-bath, and triphenylphosphine (47 g, 180 mmol) was added, followed by a solution of carbon tetrabromide (30 g, 90 mmol) in pyridine (80 mL) dropwise during 30 min, whilst the temperature was maintained at 0°. The mixture was then heated for 2 h at 70°, when t.l.c. (ethyl acetate–ethanol–water, 9:1:1) revealed one major product. The mixture was cooled, treated with methanol (100 mL), and concentrated. Column chromatography of the residue by elution with chloroform to remove the non-carbohydrate material and subsequently with ethyl acetate–ethanol–water (45:5:3) afforded syrupy 6,6'-dibromo-6,6'-dideoxysucrose (**2**; 12.4 g, 91%), $[\alpha]_D$ +37° (*c* 1, methanol).

Conventional acetylation of **2** afforded **3** in quantitative yield; m.p. 127–128°, $[\alpha]_D$ +51° (Found: C, 39.9; H, 4.5; Br, 22.4. $C_{24}H_{32}Br_2O_{15}$ calc.: C, 40.0; H, 4.5; Br, 22.2%). ^{1}H-N.m.r. data (C_6D_6, 90 MHz): δ 5.78 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.97 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 5.72 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 5.22 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.44 (d, 1 H, $J_{1'a,1'b}$ 12.5 Hz, H-1'a), 4.23 (d, 1 H, H-1'b), 5.60 (d, 1 H, $J_{3',4'}$ 5.0 Hz, H-3'), 5.46 (t, 1 H, $J_{4',5'}$ 5.0 Hz, H-4').

*6,6'-Di-*S-*(*N,N*-dimethylaminothiocarbonyl)-6,6'-dithiosucrose* (**4**). — A mixture of **2** (12 g), sodium *N,N*-dimethyldithiocarbamate (8 g), and dry *N,N*-dimethylformamide (200 mL) was kept for 36 h at 95–100°, when t.l.c. (ethyl acetate–ethanol–water, 8:2:1) showed the reaction was complete, with formation of one major product. The mixture was concentrated to dryness and the brown residue was eluted from a short column of silica gel with methanol to give **4** as a pale-yellow amorphous solid (10 g, 71%), $[\alpha]_D$ +67° (methanol).

Conventional acetylation of **4** afforded the hexa-acetate **5**, m.p. 68–70° (from ethanol), $[\alpha]_D$ +73° (Found: C, 45.0; H, 5.7; N, 3.7; S, 15.8. $C_{30}H_{44}N_2O_{15}S_4$ calc.: C, 45.0; H, 5.5; N, 3.5; S, 16.0%). ^{1}H-N.m.r. data (C_6D_6, 90 MHz): δ 5.78 (d, 1

H, $J_{1,2}$ 3.3 Hz, H-1), 5.09 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 5.84 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 5.26 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 5.82 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3'), 5.72 (t, 1 H, $J_{4',5'}$ 6.0 Hz, H-4'), 2.60, 2.93, 2.98, 3.17 (4 s, 12 H, 2 NMe_2), 2.15, 2.12, 2.11, 1.76, 1.72, 1.67 (6 s, 6 Ac).

Conventional benzoylation of **4** afforded hexabenzoate **6**, m.p. 97–98° (from ethanol), $[\alpha]_D$ +21° (Found: C, 61.5; H, 4.7; N, 2.2. $C_{60}H_{56}N_2O_{15}S_4$ calc.: C, 61.4; H, 4.8; N, 2.4%).

*2,3,4-Tri-*O*-acetyl-6-*S*-acetyl-6-thio-α-*D*-glucopyranosyl 1,3,4-tri-*O*-acetyl-6-*S*-acetyl-6-thio-β-*D*-fructofuranoside* (**7**). — A solution of **3** (4 g) and potassium thioacetate (4 g) in acetone was heated under reflux for 12 h, then cooled, and concentrated to dryness. The residue was extracted with a little chloroform, and the extract was filtered and concentrated to dryness. Column chromatography (chloroform) of the residue gave **7** (2.95 g, 75%), m.p. 39–41° (from methanol), $[\alpha]_D$ +45° (Found: C, 47.6; H, 5.5; S, 8.9. $C_{28}H_{38}O_{17}S_2$ calc.: C, 47.3; H, 5.4; S, 9.0%). ^{1}H-N.m.r. data (C_6D_6, 250 MHz): δ 5.74 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.05 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 5.82 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 5.26 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 3.42 (dd, 1 H, $J_{6a,5}$ 1.9, $J_{6a,6b}$ 15 Hz, H-6a), 3.23 (dd, 1 H, $J_{5,6b}$ 6.3 Hz, H-6b), 4.35 (d, 1 H, $J_{1'a,1'b}$ 12.5 Hz, H-1'a), 4.28 (d, 1 H, H-1'b), 5.69 (d, 1 H, $J_{3',4'}$ 5.6 Hz, H-3'), 5.58 (t, 1 H, $J_{4',5'}$ 5.6 Hz, H-4'), 4.54 (m, 1 H, H-5'), 3.48 (dd, 1 H, $J_{5',6'a}$ 7.5, $J_{6'a,6'b}$ 13.8 Hz, H-6'a), 3.38 (dd, $J_{5',6'b}$ 7.5 Hz, H-6'b), 1.69, 1.73 (2 s, 2 SAc), 2.07, 2.06, 1.89, 1.89, 1.86, 1.74 (6 s, 6 OAc).

*2,3,4-Tri-*O*-acetyl-6-deoxy-6-thiocyanato-α-*D*-glucopyranosyl 1,3,4-tri-*O*-acetyl-6-deoxy-6-thiocyanato-β-*D*-fructofuranoside* (**8**). — A solution of **3** (5 g) and potassium thiocyanate (5 g) in dry *N,N*-dimethylformamide (50 mL) was kept for 22 h at 95–100°, then cooled, and partitioned between water and ether. The aqueous layer was washed well with ether, and the combined ether extracts were dried ($MgSO_4$) and concentrated to dryness. Column chromatography (chloroform) of the residue gave **8** as an amorphous solid which could not be recrystallised but had m.p. 53–55°, $[\alpha]_D$ +72°; lit.[14] m.p. 169–171°, $[\alpha]_D$ +71° (Found: C, 46.0; H, 4.9; N, 4.2; S, 9.5. $C_{26}H_{32}N_2O_{15}S_2$ calc.: C, 46.2; H, 4.7; N, 4.1; S, 9.5%). ^{1}H-N.m.r. data (C_6D_6, 250 MHz): δ 5.82 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.00 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 5.72 (t, 1 H, $J_{3,4}$ 9.7 Hz, H-3), 5.00 (t, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 4.46 (m, 1 H, H-5), 2.98 (dd, 1 H, $J_{6a,5}$ 3.1, $J_{6a,6b}$ 14.2 Hz, H-6a), 2.62 (dd, 1 H, $J_{5,6b}$ 6.8 Hz, H-6b), 4.40 (m, 2 H, H-1'a,1'b), 5.66 (d, 1 H, $J_{3',4'}$ 5.3 Hz, H-3'), 5.36 (t, 1 H, $J_{4',5'}$ 5.1 Hz, H-4'), 4.18 (m, 1 H, H-5'), 3.16 (dd, 1 H, $J_{5',6'a}$ 7.5, $J_{6'a,6'b}$ 15 Hz, H-6'a), 3.00 (dd, $J_{5',6'b}$ 6.0 Hz, H-6'b), 1.97, 1.96, 1.83, 1.77, 1.74, 1.74 (6 s, 6 OAc).

6,6'-Epidithiosucrose hexa-acetate (**10**). — A solution of **3** (10 g, 13.9 mmol) and thiourea (5 g, 66 mmol) in dry *N,N*-dimethylformamide (150 mL) was kept for 20 h at 95–100°, when t.l.c. (ether) indicated that all of **3** had been converted into a very polar product. Sodium metabisulphite (5 g) was then added to the mixture and the heating was continued for a further 5 h, when t.l.c. indicated the formation of a major faster-moving component together with several minor products. The

mixture was then poured into ice–water and extracted with ether (2 × 50 mL). The combined extracts were washed well with water, dried ($MgSO_4$), and concentrated to dryness. Column chromatography (ether–light petroleum, 3:2) gave the major component [as indicated by t.l.c. (ether–light petroleum, 2:1)] as a white amorphous solid (2.1 g) which was subjected to Zemplén deacetylation. T.l.c. (ethyl acetate–ethanol–water, 10:3:1) revealed two products, of which the faster-moving was the major. The mixture was then neutralised with Amberlite IR-120 (H^+) resin and concentrated to dryness, and the residue was acetylated conventionally. Column chromatography (ether–light petroleum, 2:1) of the product gave **10** (1.6 g, 19%), m.p. 175–176° (from ethanol), $[\alpha]_D$ +30°; λ_{max} 253 (ε 382), 215 nm (ε 867) (Found: C, 46.1; H, 5.2; S, 10.3. $C_{24}H_{32}O_{15}S_2$ calc.: C, 46.2; H, 5.1; S, 10.3%). N.m.r. data: ^1H (C_6D_6, 250 MHz, 70°), δ 5.83 (d, 1 H, $J_{1,2}$ 4.1 Hz, H-1), 4.97 (dd, 1 H, $J_{2,3}$ 9.3 Hz, H-2), 5.60 (t, 1 H, $J_{3,4}$ 9.8 Hz, H-3), 4.96 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 4.48 (m, 1 H, H-5), 2.86 (dd, 1 H, $J_{5,6}$ 1.5, $J_{6a,6b}$ 13.9 Hz, H-6a), 2.52 (dd, 1 H, $J_{5,6b}$ 12 Hz, H-6b), 4.44 (d, 1 H, $J_{1'a,1'b}$ 12 Hz, H-1'a), 4.27 (d, 1 H, H-1'b), 5.63 (m, 2 H, H-3',4'), 2.02, 1.85, 1.77, 1.76, 1.73, 1.66 (6 s, 6 Ac); ^{13}C ($CDCl_3$, 15 MHz), δ 105.4 (C-2'), 90.6 (C-1), 83.6 (C-5'), 79.1 (C-3'), 78.4 (C-4'), 71.5 (C-3), 71.5 (C-5), 71.1 (C-2), 70.2 (C-4), 61.9 (C-1'), 34.9 (C-6'), 40.9 (C-6).

Hexa-O-acetyl-6,6'-epithiosucrose (**11**). — A solution of **3** (5 g, 6.9 mmol) and potassium *O*-ethyl dithiocarbonate (3.3 g, 20.8 mmol) in dry *N,N*-dimethylformamide (50 mL) was kept for 4 h at 95–100°, when t.l.c. (ether) indicated reaction to be optimal. The dark-brown mixture was poured into ice–water and extracted with ether, and the extract was washed well with water, dried ($MgSO_4$), and concentrated. T.l.c. (ether) indicated the residue to contain one slower-moving major product, several minor faster-moving components, and a little **3**. Column chromatography (ether–light petroleum, 2:1) gave, initially, a mixture of minor components which was not investigated further, and then **11** (1.9 g, 46%), m.p. 134–135° (from ethanol), $[\alpha]_D$ +60°; λ_{max} 275 (ε 13.8), 210 (ε 518) (Found: C, 48.5; H, 5.5; S, 5.5. $C_{24}H_{32}O_{15}S$ calc.: C, 48.6; H, 5.4; S, 5.4%). ^1H-N.m.r. data (C_6D_6, 250 MHz, 70°): δ 5.84 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1), 4.89 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 5.66 (t, 1 H, $J_{3,4}$ 9.7 Hz, H-3), 4.94 (t, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 4.62 (bt, 1 H, $J_{5,6a}$ ~10 Hz, H-5), 2.60 (bm, 2 H, $H_{6b,6'b}$), 4.64 (d, 1 H, $J_{1'a,1'b}$ 12.5 Hz, H-1'a), 4.26 (d, 1 H, H-1'b), 5.45 (d, 1 H, $J_{3',4'}$ 1.9 Hz, H-3'), 5.03 (bm, 1 H, H-4'), 4.23 (b, 1 H, H-5'), 2.95 (bd, 1 H, H-6'a), 2.10, 1.85, 1.86, 1.73, 1.69, 1.67 (6 s, 6 Ac).

6,6'-Epithiosucrose (**12**). — A solution of **11** (1 g) in methanol was treated with a few drops of methanolic M sodium methoxide, stored for 24 h at room temperature, then neutralised with Amberlite IR-120 (H^+) resin, and concentrated. Column chromatography of the residue (ethyl acetate–ethanol–water, 45:5:3) gave episulphide **12** as a white amorphous solid (0.5 g, 88%), $[\alpha]_D$ +47° (methanol), which analysed as a dihydrate (λ_{max} 1640 cm^{-1}) (Found: C, 37.9; H, 5.9; S, 8.1. $C_{12}H_{20}O_9 \cdot 2\,H_2O$ calc.: C, 38.3; H, 6.4; S, 8.5%). ^{13}C-N.m.r. data (CD_3COCD_3, 15 MHz): δ 106.3 (C-2'), 93.4 (C-1), 81.9 (C-5'), 78.6 (C-3'), 78.5 (C-4'), 76.9 (C-3), 75.0 (C-5), 74.4 (C-2), 73.8 (C-4), 61.2 (C-1'), 34.9 (C-6'), 33.1 (C-6).

Reaction of **3**. — *(a) With potassium trithiocarbonate.* A solution of **3** (5 g, 6.94 mmol) in *N,N*-dimethylformamide (50 mL) was mixed with potassium trithiocarbonate (3.9 g, 21 mmol) and kept for 2 h at 95–100°. T.l.c. (ether) then revealed two products. The mixture was cooled, poured into ice–water, and extracted into ether (2 × 50 mL). The combined extracts were dried ($MgSO_4$) and concentrated. Column chromatography (ether–ethyl acetate, 2:1) of the residue gave, first, the 6,6′-epidisulphide **10** (0.3 g, 7%), m.p. 173–175° (from ethanol), $[\alpha]_D$ −23°.

The final fraction contained the 6,6′-episulphide **11** (1.0 g, 24%), m.p. 133–135° (from ethanol), $[\alpha]_D$ +57°.

(b) With potassium O*-ethyl dithiocarbonate.* A solution of **3** (7.5 g, 10.4 mmol) and potassium *O*-ethyl dithiocarbonate (5.5 g, 34.3 mmol) in dry acetone (150 mL) was heated under reflux and the reaction was monitored by t.l.c. (ether–ethyl acetate, 5:1), which revealed the slow transformation of **3** into a slightly faster-moving product (component *A*) which became prominent after ~1 h, although substantial amounts of **3** remained. At this stage, component *A* appeared to be slowly converted into the slower-moving episulphide. After ~2.5 h, when component *A* appeared to be at its maximum concentration, the mixture was cooled, filtered, and concentrated to dryness. Column chromatography (ether–ethyl acetate, 2:1) of the residue gave, first, component *A* (2.7 g), which was shown by t.l.c. and h.p.l.c. to be a mixture of at least three components of similar mobility. Attempted preparative separations failed to give pure products.

The second fraction contained **11** (2.5 g, 41%).

Reactions of component A. — *(a) With sodium azide.* A solution of component *A* (2 g) and sodium azide (3 g) in *N,N*-dimethylformamide (50 mL) was kept for 2 h at 95–100°, when t.l.c. revealed that all of component *A* had reacted to give a single major product. The mixture was then processed as before and column chromatography (ether–light petroleum, 1:1) of the product gave **10** (0.9 g), m.p. 173–174° (from 96% ethanol), identical with that isolated previously.

(b) With lithium chloride. To a stirred solution of component *A* (1 g) in *N,N*-dimethylformamide (30 mL) was added lithium chloride (1.5 g) and a catalytic amount of iodine. The mixture was kept for 3 h at 95–100°, when t.l.c. (ether) revealed two major products and several faster-moving minor components. The mixture was then processed as before and column chromatography (ether–light petroleum, 1:1) of the product gave fractions containing mixtures of minor components, which were not further investigated; **10** (0.25 g), m.p. 173–175°; and finally **11** (0.1 g), m.p. 132–134° (from ethanol).

6,6′-Epithiosucrose hexa-acetate S*-oxide* (**13**). — To a stirred ice-cold solution of the episulphide **12** (3.4 g, 5.74 mmol) in methanol (50 mL) was added, dropwise during 15 min, a solution of sodium metaperiodate (1.5 g, 6.9 mmol) in distilled water (15 mL). The mixture was maintained for 24 h at 0°, when t.l.c. (chloroform) indicated the conversion of **3** into a slower-moving major product together with traces of several faster-moving components. The mixture was poured into distilled

water (100 mL) and the product extracted into chloroform in the usual way. Dry-packed column chromatography (chloroform–acetone, 10:1→8:1) of the product gave **13** as an amorphous solid, m.p. 113–116°, $[\alpha]_D$ +96°, ν_{max} 1060 cm^{-1} (C–SO–C), λ_{max} 278 (ε 53), 223 (ε 1056) (Found: C, 47.0; H, 5.1; S, 4.9. $C_{24}H_{32}O_{16}S$ calc.: C, 47.4; H, 5.3; S, 5.3%). N.m.r. data: ^1H (C_6D_6, 250 MHz), δ 5.67 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.79 (dd, 1 H, $J_{2,3}$ 9.0 Hz, H-2), 5.48 (t, 1 H, $J_{3,4}$ 9.9 Hz, H-3), 4.84 (t, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 4.48 (m, 1 H, H-5), 3.40 (t, 1 H, $J_{5,6a}$ 12.1 Hz, $J_{6a,6b}$ 12.5 Hz, H-6a), 2.75 (dd, 1 H, $J_{5,6b}$ 3.6 Hz, H-6b), 4.45 (d, 1 H, $J_{1'a,1'b}$ 12.5 Hz, H-1′a), 3.92 (d, 1 H, H-1′b), 5.46 (s, 1 H, $J_{3',4'}$ <1 Hz, H-3′), 4.71 (s, 1 H, $J_{4',5'}$ <1 Hz, H-4′), 4.39 (dd, 1 H, H-5′), 3.84 (t, 1 H, $J_{5',6'a}$ 13.4, $J_{6'a,6'b}$ 14.0 Hz, H-6′a), 2.44 (dd, $J_{5',6'b}$ 3.6 Hz, H-6′b), 2.01, 1.87, 1.86, 1.73, 1.69, 1.67 (6 s, 18 H, 6 Ac); ^{13}C ($CDCl_3$, 15 MHz), δ 107.2 (C-2′), 90.5 (C-1), 81.8 (C-5′), 80.0 (C-3′), 77.7 (C-4′), 71.5 (C-3), 70.7 (C-5), 70.4 (C-2), 64.4 (C-4), 56.7 (C-1′), 61.8 (C-6′), 55.2 (C-6).

6,6′-Epithiosucrose hexa-acetate S,S-*dioxide* (**14**). — The sulphoxide **13** (3 g) was added to a mixture of glacial acetic acid (15 mL) and 30% hydrogen peroxide (7 mL). The mixture was stirred for 24 h at room temperature, when t.l.c. (chloroform–acetone, 1:1) revealed that **13** had been transformed into a faster-moving product. The mixture was concentrated to dryness and column chromatography (chloroform–acetone, 100:1) of the residue gave **14** (2.1 g, 69%), m.p. 217–219° (from ethanol), $[\alpha]_D$ +27°; ν_{max} 1143 and 1320 cm^{-1} (sulphone); λ_{max} 210 nm (ε 331) (Found: C, 46.5; H, 5.3; S, 4.9. $C_{24}H_{32}O_{17}S$ calc.: C, 46.2; H, 5.1; S, 5.1%). ^1H-N.m.r. data ($CDCl_3$, 250 MHz): δ 5.56 (bd, 1 H, H-1), 5.00 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 8.5 Hz, H-2), 5.40 (t, 1 H, $J_{3,4}$ 9.1 Hz, H-3), 4.84 (t, 1 H, $J_{4,5}$ 9.1 Hz, H-4), 4.55 (m, 1 H, H-5), 5.40 (m, 2 H, H-3′,4′).

When the reaction was conducted with **11**, 68% of **14** was obtained.

6,6′-Dideoxysucrose hexa-acetate (**9**). — A mixture of **11** (1 g) and Raney nickel (10 g, wet) in ethanol was heated under reflux for 4 h, when t.l.c. (ether) indicated that the reaction was complete. The catalyst was collected and washed well with ethanol, and the combined filtrate and washings were concentrated to dryness. Column chromatography (ether–light petroleum, 1:1) of the residue gave **9** (0.9 g, 95%), $[\alpha]_D$ +64° (Found: C, 51.6; H, 6.3. $C_{24}H_{34}O_{15}$ calc.: C, 51.3; H, 6.1%). N.m.r. data: ^1H (C_6D_6, 90 MHz): δ 5.77 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.08 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 5.80 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 5.05 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.42 (m, 1 H, H-5 or H-5′), 1.23 (d, 3 H, $J_{5,6}$ 7 Hz, H-6 or H-6′), 4.37 (d, 1 H, $J_{1'a,1'b}$ 12.5 Hz, H-1′a), 4.31 (d, 1 H, H-1′b), 5.68 (d, 1 H, $J_{3',4'}$ 6.0 Hz, H-3′), 5.38 (t, 1 H, $J_{4',5'}$ 6.0 Hz, H-4′), 1.35 (d, 3 H, $J_{5',6'}$ 7 Hz, H-6′ or H-6), 1.88, 1.88, 1.77, 1.74, 1.68, 1.65 (6 s, 6 Ac); ^{13}C ($CDCl_3$, 15 MHz), δ 103.3 (C-2′), 89.5 (C-1), 78.8 (C-5′), 77.3 (C-3′), 76.1 (C-4′), 73.7 (C-3), 70.8 (C-5), 69.9 (C-2), 66.1 (C-4), 63.7 (C-1′), 19.0 (C-6′), 17.1 (C-6).

Desulphuration of the 6,6′-dithiosucrose derivatives **5**, **7**, **8**, and **10** afforded **9** in yields of 70, 65, 60, and 90%, respectively.

*Crystallography**. — A crystal of **11** of approximate size 0.7 × 0.7 × 0.4 mm was set to rotate about the *a* axis on a Stoe Stadi2 diffractometer and data were

collected *via* a variable width scan. Background counts were for 20 s and a scan rate of 0.0166°/s was applied to a width of (2 + sin/tan). A total of 2604 independent reflections were measured with a $2\theta_{max}$ of 50°, of which 1730 with $I > 3\sigma(I)$ were used in subsequent refinement.

Initial attempts to solve the structure *via* the statistical method failed. However, the position of the sulphur atom was located from a sharpened Patterson map and those of the oxygen and carbon atoms were obtained from successive Fourier maps. The S, O, and C atoms were refined anisotropically. The H atoms were

TABLE I

ATOMIC CO-ORDINATES (× 10^4) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	*Atom*	x	y	z
S-6	3857(2)	5000(0)	5513(2)	C-5′	5088(9)	5686(14)	4107(7)
C-1	3126(8)	2158(13)	3161(7)	C-6′	4033(9)	6178(15)	4551(7)
O-1	3273(5)	3447(9)	2691(4)	H-3′	4586(8)	5814(13)	1938(7)
C-2	1896(8)	1459(14)	2668(7)	H-3′2	594(10)	6153(24)	1142(13)
O-2	1763(6)	1419(10)	1719(5)	H-3′2	884(10)	7659(24)	1641(13)
C-21	2387(12)	375(18)	1363(10)	H-3′2	804(10)	6222(24)	2198(13)
O-21	3060(10)	−467(13)	1844(8)	H-4′	4893(7)	7530(16)	3291(6)
C-22	2100(14)	400(26)	361(11)	H-4′2	8497(10)	7759(21)	2225(10)
C-3	818(7)	2362(13)	2868(7)	H-4′2	7960(10)	6174(21)	2040(10)
O-3	−291(5)	1532(10)	2514(5)	H-4′2	8575(10)	6641(21)	3024(10)
C-31	−1053(11)	2099(20)	1777(10)	H-5′	5772(9)	5794(14)	4595(7)
O-31	−968(9)	3315(15)	1507(8)	H-6′1	4195(9)	7165(15)	4766(7)
C-32	−2112(13)	1061(20)	1426(11)	H-6′2	3296(9)	6159(15)	4105(7)
C-4	935(8)	2659(14)	3859(7)	H(1)	3809(8)	1524(13)	3169(7)
O-4	−130(5)	3529(9)	3971(4)	H(2)	1895(8)	470(14)	2889(7)
C-41	−663(9)	3154(17)	4660(8)	H(22A)	2747(14)	−187(26)	225(11)
O-41	−285(8)	2252(13)	5213(7)	H(22B)	2222(14)	1408(26)	215(11)
C-42	−1834(9)	4041(19)	4633(9)	H(22C)	1342(14)	61(26)	13(11)
O-5	3061(5)	2424(9)	4090(4)	H(3)	803(7)	3308(13)	2586(7)
C-5	2137(8)	3480(13)	4175(7)	H(32A)	−2748(13)	1567(20)	1023(11)
C-6	2365(8)	4084(16)	5145(7)	H(32B)	−2355(13)	891(20)	1992(11)
C-1′	5346(8)	3137(14)	2421(7)	H(32C)	−1956(13)	138(20)	1164(11)
O-1′	4853(6)	2854(10)	1482(5)	H(4)	958(8)	1778(14)	4212(7)
C-1′1	5252(11)	3697(17)	855(8)	H(42A)	−2080(9)	3913(19)	5201(9)
O-1′1	5984(9)	4701(13)	1069(5)	H(42B)	−2363(9)	3492(19)	4175(9)
C-1′2	4709(14)	3304(23)	−88(9)	H(42C)	−1874(9)	5064(19)	4475(9)
O-2′	5006(5)	4190(10)	3797(4)	H(5)	2131(8)	4347(13)	3813(7)
C-2′	4485(7)	4102(15)	2856(6)	H(61)	1748(8)	4796(16)	5183(7)
C-3′	4370(8)	5708(13)	2518(7)	H(62)	2307(8)	3284(16)	5548(7)
O-3′	3105(5)	6230(9)	2442(5)	H(1′1)	5480(8)	2218(14)	2737(7)
C-3′1	2345(11)	6142(16)	1616(10)	H(1′2)	6103(8)	3644(14)	2468(7)
O-3′1	2699(10)	5729(15)	950(7)	H(1′2)	4948(14)	3901(23)	−546(9)
C-3′2	1044(10)	6622(24)	1673(13)	H(1′2)	3861(14)	3439(23)	−101(9)
C-4′	5140(7)	6525(16)	3264(6)	H(1′2)	4864(14)	2290(23)	−197(9)
O-4′	6422(5)	6391(11)	3142(5)				
C-4′1	6787(10)	7386(20)	2558(8)				
O-4′1	6225(8)	8401(8)	2237(7)				
C-4′2	8088(10)	6972(21)	2464(10)				

*Lists of anisotropic and isotropic thermal parameters have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/383 *Carbohydr. Res.*, 174 (1988) 145–160.

TABLE II
MOLECULAR DIMENSIONS OF **11**

Bond lengths (Å)

S-6–C-6	1.840(10)	O-5–C-5	1.427(12)
S-6–C-6′	1.829(12)	C-5–C-6	1.522(15)
C-1–O-1	1.384(14)	C-1′–O-1′	1.426(12)
C-1–C-2	1.555(13)	C-1′–C-2′	1.533(16)
C-1–O-5	1.426(13)	O-1′–C-1′1	1.348(16)
O-1–C-2′	1.450(11)	C-1′1–O-1′1	1.217(16)
C-2–O-2	1.397(12)	C-1′1–C-1′2	1.462(18)
C-2–C-3	1.530(14)	O-2′–C-2′	1.413(18)
O-2–C-21	1.342(18)	O-2′–C-5′	1.422(15)
C-21–O-21	1.200(18)	C-2′–C-3′	1.529(18)
C-21–C-22	1.468(21)	C-3′–O-3′	1.469(11)
C-3–O-3	1.452(11)	C-3–C-4′	1.463(14)
C-3–C-4	1.485(14)	O-3′–C-3′1	1.353(14)
O-3–C-31	1.350(15)	C-3′1–O-3′1	1.201(19)
C-31–O-31	1.179(23)	C-3′1–C-3′2	1.532(19)
C-31–C-32	1.516(21)	C-4′–O-4′	1.483(11)
C-4–O-4	1.460(12)	C-4′–C-5′	1.480(16)
C-4–C-5	1.521(13)	O-4′–C-4′1	1.369(18)
O-4–C-41	1.332(14)	C-4′1–O-4′1	1.158(20)
C-41–O-41	1.177(17)	C-4′1–C-4′2	1.531(17)
C-41–C-42	1.525(18)	C-5′–C-6′	1.528(15)

Bond angles (degrees)

C-6–S-6–C-6′	104.9(5)	O-1′–C-1′–C-2′	111.6(7)
O-1–C-1–C-2	106.4(7)	C-1′–O-1′–C-1′1	117.9(9)
O-1–C-1–O-5	112.9(9)	O-1′–C-1′1–O-1′1	122.2(10)
C-2–C-1–O-5	108.5(7)	O-1′–C-1′1–C-1′2	113.8(12)
C-1–O-1–C-2′	117.1(7)	O-1′1–C-1′1–C-1′2	124.0(13)
C-1–C-2–O-2	113.4(8)	C-2′–O-2′–C-5′	111.4(8)
C-1–C-2–C-3	110.2(9)	O-1–C-2′–C-1′	109.7(9)
O-2–C-2–C-3	106.5(7)	O-1–C-2′–O-2′	112.1(7)
C-2–O-2–C-21	117.6(9)	C-1′–C-2′–O-2′	106.7(7)
O-2–C-21–O-21	121.1(13)	O-1–C-2′–C-3′	108.3(7)
O-2–C-21–C-22	111.7(12)	C-1′–C-2′–C-3′	114.5(8)
O-21–C-21–C-22	127.2(15)	O-2′–C-2′–C-3′	105.5(9)
C-2–C-3–O-3	107.5(8)	C-2′–C-3′–O-3′	110.2(7)
C-2–C-3–C-4	112.0(7)	C-2′–C-3′–C-4″	103.0(8)
O-3–C-3–C-4	110.8(7)	O-3′–C-3′–C-4′	107.9(8)
C-3–O-3′–C-31	117.0(10)	C-3′–O-3′–C-3′1	117.9(8)
O-3–C-31–O-31	123.5(12)	O-3′–C-3′1–O-3′1	121.7(11)
O-3–C-31–C-32	111.7(13)	O-3′–C-3′1–C-3′2	111.1(12)
O-31–C-31–C-32	124.4(12)	O-3′1–C-3′1–C-3′2	127.2(12)
C-3–C-4–O-4	107.4(6)	C-3′–C-4′–O-4′	107.4(8)
C-3–C-4–C-5	107.1(8)	C-3′–C-4′–C-5′	106.0(10)
O-4–C-4–C-5	112.9(9)	O-4′–C-4′–C-5′	105.4(7)
C-4–O-4–C-41	116.8(8)	C-4′–O-4′–C-4′1	116.2(9)
O-4–C-41–O-41	124.6(11)	O-4′–C-4′1–O-4′1	125.3(11)
O-4–C-41–C-42	111.0(10)	O-4′–C-4′1–C-4′2	107.8(12)
O-41–C-41–C-42	124.4(11)	O-4′1–C-4′1–C-4′2	126.8(14)
C-1–O-5–C-5	112.2(7)	O-2′–C-5′–C-4′	102.6(8)
C-4–C-5–O-5	104.7(8)	O-2′–C-5′–C-6′	114.3(9)
C-4–C-5–C-6	116.1(8)	C-4′–C-5′–C-6′	112.7(9)
O-5–C-5–C-6	109.7(7)	S-6–C-6′–C-5′	112.7(8)
S-6–C-6–C-5	114.5(7)		

TABLE III

TORSION ANGLES (DEGREES)

Glucopyranosyl ring	
O-5–C-1–C-2–C-3	48.9
C-1–C-2–C-3–C-4	−49.2
C-2–C-3–C-4–C-5	58.1
C-3–C-4–C-5–O-5	−66.9
C-4–C-5–O-5–C-1	72.6
C-5–O-5–C-1–C-2	−63.5
Fructofuranosyl ring	
C-5′–O-2′–C-2′–C-3′	7.2
O-2′–C-2′–C-3′–C-4′	14.4
C-2′–C-3′–C-4′–C-5′	−29.9
C-3′–C-4′–C-5′–O-2′	34.3
C-4′–C-5′–O-2′–C-2′	−25.5
Glycosidic linkage between 5- and 6-membered rings	
O-1–C-1–C-2–C-3	−72.8
C-2–C-1–O-1–C-2′	−164.1
C-1–O-1–C-2′–C-3′	−162.9
O-1–C-2′–C-3′–C-4′	134.6
O-1′–C-1′–C-2′C-3′	−69.2
S-6,6′ Linkage between 5- and 6-membered rings	
O-5–C-1–O-1–C-2′	77.1
C-2–O-1–C-2′–O-2′	−69.7
O-1–C-2′–O-2′–C-5′	−110.5
C-2′–O-2′–C-5′–C-6′	96.8
O-2′–C-5′–C-6′–S-6	56.6
C-5′–C-6′–S-6–C-6	−114.5
C-6′–S-6–C-6–C-5	44.7
S-6–C-6–C-5–O-5	59.1
C-6–C-5–O-5–C-1	−162.1

included in trigonal or tetrahedral positions. Hydrogen atoms in each ring and in each methyl group were given a common refined thermal parameter. The final R value was 0.071 (R_w = 0.075). The structure was given a weighting in the form w = $1/[\sigma^2(F) + 0.003F^2]$. Calculations were carried out using Shelx76[15] and some of our own programmes at the University of Manchester Regional Computer Center. Atomic parameters are given in Table I, molecular dimensions in Table II, and torsion angles in Table III.

Crystal data for **11**: $C_{24}H_{32}O_{15}S$, M = 592.3, monoclinic, space group $P2_1$, a = 11.15(1), b = 9.01(1), c = 14.95(1) Å, β = 101.5(1)°, V = 1471.8 Å^3, D_c = 1.32 g.cm^{-3}, D_m = 1.37 g.dm^{-3}, Z = 2, λ = 0.7107 Å, μ = 1.37 cm^{-1}.

ACKNOWLEDGMENTS

We thank Tate and Lyle Plc for continuing financial support.

REFERENCES

1 L. HOUGH AND S. P. PHADNIS, *Nature (London)*, 263 (1976) 800.
2 P. J. GAREGG AND B. SAMUELSSON, *J. Chem. Soc., Perkin Trans. 1*, (1980) 2866–2869.
3 R. U. LEMIEUX AND J. P. BARRETTE, *Can. J. Chem.*, 38 (1960) 656–662.
4 A. K. M. ANISUZZAMAN AND R. L. WHISTLER, *Carbohydr. Res.*, 61 (1978) 511–518.
5 J. A. BARLTROP, P. M. HAYES, AND M. CALVIN, *J. Am. Chem. Soc.*, 76 (1954) 4348–4362.
6 J. HILL, L. HOUGH, AND A. C. RICHARDSON, *Carbohydr. Res.*, 8 (1968) 19–28, 398–404.
7 M. JESUDASON AND L. N. OWEN, *J. Chem. Soc., Perkin Trans. 1*, (1974) 2024–2030.
8 G. M. BROWN AND H. A. LEVY, *Acta Crystallogr., Sect. B*, 29 (1973) 790–797.
9 D. AVENAL, A. NEUMAN, AND H. GILLIEAR-PANDRAUD, *Acta Crystallogr., Sect. B*, 32 (1976) 2598–2605.
10 A. JEFFREY AND Y. J. PARK, *Acta Crystallogr., Sect. B*, 28 (1972) 257–267.
11 J. B. HENDRICKSON, *J. Am. Chem. Soc.*, 89 (1967) 7036–7043.
12 M. H. ALI, Ph.D. Thesis, University of London, 1985.
13 L. HOUGH, A. K. PALMER, AND A. C. RICHARDSON, *J. Chem. Soc., Perkin Trans. 1*, (1972) 2513–2517.
14 C. H. BOLTON, L. HOUGH, AND R. KHAN, *Carbohydr. Res.*, 21 (1972) 133–143.
15 G. M. SHELDRICK, *Shelx76: Package for Crystal Structure Determination*, University of Cambridge, 1976.