Thio-sugars. Part VII.[1] Syntheses of Trithiocarbonates by Reaction of Methyl 2,3- and 3,4-Anhydroglycopyranosides with Sodium Methyl Xanthate

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Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-guloside and -taloside, and also the corresponding episulphides, react with sodium methyl xanthate to give methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-thiocarbonyldithio-α-D-idoside. The β-anomers of these epoxides and episulphides give the β-form of this *ido*-trithiocarbonate. Other products include methyl 4,6-di-*O*-benzylidene-2,3-dideoxy-α- and -β-D-*threo*-hex-2-enopyranoside, methyl 4,6-di-*O*-benzylidene-2- and -3-thio-α- and -β-D-idoside, the 3-*S*-methyl derivative of the 3-thio-β-D-idoside, and dimethyl trithiocarbonate.

Methyl 2,3-dideoxy-4,6-di-*O*-methyl-2,3-thiocarbonyldithio-α-D-altroside was obtained from methyl 2,3-anhydro-4,6-di-*O*-methyl-α-D-alloside and -mannoside, and from the corresponding episulphides; the *manno*-epoxide and the *allo*-episulphide gave also the *gluco*-2,3-trithiocarbonate.

Methyl 3,4-anhydro-6-deoxy-α-L-taloside gave methyl 2,3,6-trideoxy-2,3- and -3,4-thiocarbonyldithio-α-L-idopyranoside, whereas methyl 3,4,6-trideoxy-3,4-epithio-α-L-altroside gave methyl 3,4,6-trideoxy-3,4-thiocarbonyldithio-α-L-idoside and -mannoside; the 2-*O*-methyl ethers of the last two trithiocarbonates were both obtained from methyl 3,4-anhydro-6-deoxy-2-*O*-methyl-α-L-taloside. Methyl 2,3-anhydro-6-deoxy-α-D-talopyranoside gave methyl 2,3,6-trideoxy-2,3-thiocarbonyldithio-α-D-idopyranoside.

^{1}H N.m.r. parameters for the trithiocarbonates and other products are tabulated.

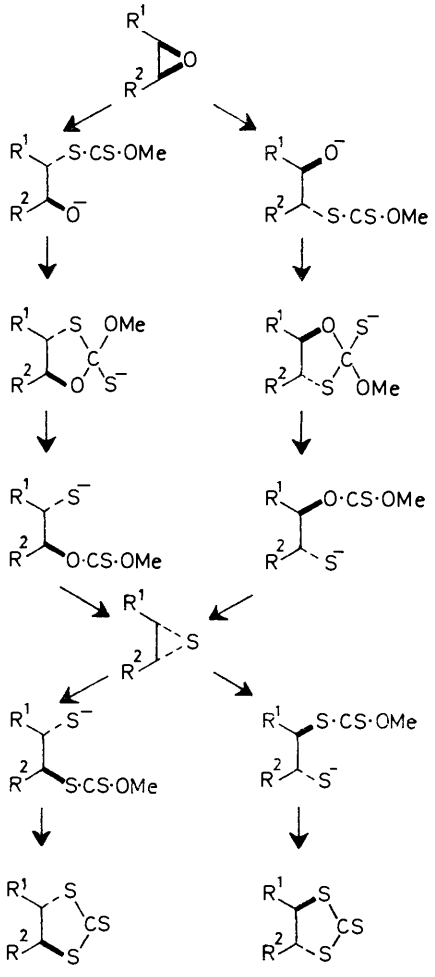
THE reaction of an oxiran with a salt of an *O*-alkyl xanthate proceeds through an episulphide, of opposite configuration, which normally reacts further to give a cyclic trithiocarbonate.[2] Application of the mechanism proposed[3] for a terminal epoxide to the general case indicates that a pair of stereoisomers can, in principle,

[1] Part VI, M. V. Jesudason and L. N. Owen, *J.C.S. Perkin I*, preceding paper.

[2] C. C. J. Culvenor, W. Davies, and K. H. Pausacker, *J. Chem. Soc.*, **1946**, 1050; *cf.* S. Hayashi, M. Furukawa, Y. Fujino, T. Nakao, and K. Nagato, *Chem. and Pharm. Bull* (*Japan*), **1971**, **19**, 1594.

[3] A. M. Creighton and L. N. Owen, *J. Chem. Soc.*, **1960**, 1024.

be formed (Scheme 1), though the only instance where both have been isolated is that of the inositol derivatives reported by McCasland.[4] Three sugar trithiocarbonates have been described, 5,6-dideoxy-1,2-*O*-isopropylidene-5,6-thiocarbonyldithio-β-L-idose [3,5] (incorrectly named as α-L-), the α-D-*gluco*-isomer,[5] and 3,4,6-tri-*O*-acetyl-1,2-dideoxy-1,2-thiocarbonyldithio-β-D-mannose; [6] no such derivative has been made in which the thiocarbonyldithio-bridge is *trans*-fused to the sugar ring, and attempts to prepare such a trithiocarbonate by reaction of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-alloside, the corresponding mannoside, or methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epithio-α-D-mannoside with xanthate were unsuccessful.[7]



SCHEME 1 Reaction of an epoxide with sodium methyl xanthate

The ready formation, from methyl 4,6-*O*-benzylidene-α-D-glucoside, of the *trans*-2,3-carbonate [8] and the *trans*-2,3-thionocarbonate [9] can be attributed to the fact that in the only possible chair conformation ($^4C_1$) for this glycoside the 2- and the 3-hydroxy-group are both equatorial, whereas attack by xanthate on a 2,3-episulphide would be expected to occur in a diaxial manner, and ring closure to give the cyclic trithiocarbonate would require conformational change to a boat ($B_{2,5}$) or skew ($^0S_2$) form; the same situation arises in the epoxide–episulphide transformation.[1] Consequently, particularly when an epoxide is used for the reaction with xanthate, it is understandable that competition by side reactions leads to the unsaturated glycoside and the other products which were obtained (the effect of conformational restraint in preventing the formation of cyclic trithiocarbonates is well exemplified [10] by certain steroid episulphides). It has been shown in the preceding paper [1] that in sugar derivatives which are conformationally less rigid than those containing the *trans*-fused 2-phenyldioxan ring the formation of episulphides from epoxides can proceed more easily, and we have therefore examined the possibility of obtaining trithiocarbonates from such epoxides and episulphides.

Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-guloside (1) on treatment with sodium methyl xanthate gave a mixture which was separated by t.l.c. into the trithiocarbonate (3) (17%), the hydroxy-thiol (4) (18·5%), and unchanged epoxide (20·5%). A 62% yield of the same trithiocarbonate was obtained by reaction of the *talo*-episulphide (7) with the xanthate; methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*threo*-hex-2-enoside (8) (8%) was also isolated, and some episulphide (15%) was recovered. Reaction of the epoxide (1) with nucleophiles normally gives products having the *ido*-configuration,[11] formed by diaxial opening of the $^0H_5$ conformation by attack at C-2, and the allocation of this configuration to the hydroxy-thiol (4), which is presumably formed by solvolysis of the intermediate 3-hydroxy-2-methoxy(thiocarbonyl)thio-compound (compare Scheme 1), is confirmed by the ^{1}H n.m.r. spectrum of the diacetyl derivative (5) (see Table); for the $^4C_1$ conformation the broad singlet assigned to H-3 is incompatible with the alternative *galacto*-configuration. By analogy with methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-taloside (6), which also leads to idose derivatives, by attack at C-3,[11] the episulphide (7) would give a trithiocarbonate having the *ido*-configuration (3) in a boat ($B_{2,5}$) or a skew ($^0S_2$) conformation. The epoxide (6), in accord with this reasoning, gave the same trithiocarbonate (3) (15·5%), the *gulo*-episulphide (2) (19%), and the hydroxy-thiol (9) (16·5%), characterised as the diacetyl derivative (10), the n.m.r. spectrum of which showed a two-proton low-field broad singlet, assigned to H-1 and H-2, again in accord with the *ido*-configuration. There appears to be only one previous

[4] G. E. McCasland, S. Furuta, A. Furst, L. F. Johnson, and J. N. Shoolery, *J. Org. Chem.*, 1963, **28**, 456.
[5] L. D. Hall, L. Hough, and R. A. Pritchard, *J. Chem. Soc.*, 1961, 1537.
[6] S. Ishiguro and S. Tejima, *Chem. and Pharm. Bull.* (*Japan*), 1968, **16**, 2040.
[7] M. Kojima, M. Watanabe, and T. Taguchi, *Tetrahedron Letters*, 1968, 839.
[8] W. M. Doane, B. S. Shasha, E. I. Stout, C. R. Russell, and C. E. Rist, *Carbohydrate Res.*, 1967, **4**, 445; 1969, **11**, 321.
[9] E. I. Stout, W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *Carbohydrate Res.*, 1967, **3**, 354.
[10] D. A. Lightner and C. Djerassi, *Tetrahedron*, 1965, **21**, 583.
[11] N. R. Williams, *Adv. Carbohydrate Chem.*, 1970, **25**, 109.

occasion [7] on which the intermediate episulphide was isolated (in 6% yield) in the epoxide–trithiocarbonate transformation, and the present results indicate that the *gulo*-episulphide, like the *gulo*-epoxide,[1] is less reactive than the *talo*-isomer, a distinction which can be explained [1] on steric grounds. Prolonged treatment of this episulphide (2) with xanthate gave the trithiocarbonate (3), but still some episulphide was recovered.

^{1}H N.m.r. parameters (τ values; J in Hz)

Compound	Solvent	H-1	H-2	H-3	H-4	H-5	H-6	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$
(3)	$CDCl_3$	4·93 (d)						6·6				
(4)	$CDCl_3$	4·99 (s)						0·0	*a*			
(5)	$CDCl_3$	5·02br (s) [b]		5·30br (s) [c]								
(10)	$CDCl_3$	5·28 (m) [d]										
(13)	$CDCl_3$	4·92 (d)	5·49 (q)	5·10 (q)				4·0	14·0	6·0		
(14)	$CDCl_3$	5·21 (d)	7·08 (m)					2·0	2·5 [e]			
(18)	$CDCl_3$	5·38 (s) [f]						0·0				
(19)	$CDCl_3$	5·45 (s) [g]						0·0				
(26)	C_6D_6	5·43 (d)	5·72 (q)	6·18 (q)	6·11 (q)	6·8—7·0 (m)		7·0	12·5	4·3		
(27)	C_6D_6	5·3—5·5 (m)		5·7—6·3 (m)		6·2 (m)	6·9 (m)					
(28)	C_6D_6	5·76 (d)	6·41 (q)	5·61 (q)	←	6·5—6·9 (m)	→ 3·0		12·2	10·0		
(29)	C_6D_6	5·90 (d)	6·30 (q)	5·45 (q)	←	6·4—6·9 (m)	→ 3·0		13·0	9·8		
(33)	$(CD_3)_2SO$	5·09 (d)	5·36 (q)	5·55 (q)	5·7—6·2 (m)		8·80 (d)	7·5	13·0	6·8	*h*	6·5
(34)	$(CD_3)_2SO$	5·53 (d)	6·45 (m)	5·2—5·45 (m)		5·6 (m)	8·62 (d)	6·5	9·5 [i]			6·2
(35)	$CDCl_3$	5·23 (d)	6·65 (q)	5·47 (t)	5·38 (q)	5·8 (m)	8·60 (d)	4·5	9·5	9·5	3·3	6·5
(36)	$(CD_3)_2SO$	5·3—5·7 (m)	6·1 (m)	5·3—5·7 (m)		5·9 (m)	8·76 (d)	2·0, 2·5 [i]				6·0
(37)	$CDCl_3$	5·23 (d)	6·52 (q)	5·34 (q)	5·60 (q)	5·95 (m)	8·75 (d)	1·5	2·3	12·5	9·5	6·0

[a] Also τ 6·46 (1H, d, SH), $J_{2,SH}$ 10·0 Hz. [b] $W_{\frac{1}{2}}$ 6 Hz. [c] $W_{\frac{1}{2}}$ 4 Hz; also τ 7·70 (3H, s, SAc), 7·91 (3H, s, OAc). [d] $W_{\frac{1}{2}}$ 6 Hz; also τ 7·69 (3H, s, SAc), 7·98 (CH, s, OAc). [e] Also $J_{2,SH}$ 10·5 Hz. [f] Also τ 7·79 (3H, s, SMe). [g] Also τ 7·55 (3H, s, SSMe). [h] $J_{4,OH}$ 5·5 Hz. [i] $J_{2,OH}$ 5·5 Hz.

Attack at C-2 in the 2,3-anhydro-β-D-guloside (11) is more hindered than in the α-isomer, and reaction with xanthate was slow. The products were the trithiocarbonate (13) (9%), the hydroxy-thiol (14) (22%), and dimethyl trithiocarbonate, some epoxide being recovered. The n.m.r. spectra of compounds (13) and (14) confirmed the *ido*-configuration, in conformations $B_{2,5}$ (or $^OS_2$) and $^4C_1$, respectively, and spin decoupling established that in the hydroxy-thiol the anomeric proton and the thiol proton were both coupled to the proton resonating as a high-field multiplet, thus locating the thiol group at C-2. The same trithiocarbonate (13) was obtained, in 27% yield, from the *talo*-episulphide (16). A control experiment established that the unexpected product, dimethyl trithiocarbonate, does not arise from the methanolic sodium methyl xanthate reagent alone, and it must be derived from some reaction intermediate, possibly from the 3-hydroxy-2-methoxy-(thiocarbonyl)thio-compound by the mechanism outlined in Scheme 2. It has not previously been reported as a product of the reaction of epoxides with xanthate, but it could easily have been lost or overlooked.

The 2,3-anhydro-β-D-taloside (15) also gave some surprising products. In addition to dimethyl trithiocarbonate and the *ido*-trithiocarbonate (13), 3,3′-dithiobis(methyl 4,6-*O*-benzylidene-3-deoxy-β-D-idopyranoside) (17) (8%), the known [12] methyl 4,6-*O*-benzylidene-3-*S*-methyl-3-thio-β-D-idoside (18) (37%) (further characterised as the 2-*O*-ethoxycarbonyl derivative), and methyl 4,6-*O*-benzylidene-3-*S*-methylthio-3-thio-β-D-idoside (19) (5%) were obtained. The disulphide is evidently formed by aerial oxidation of the β-analogue of the hydroxy-thiol (9), and the *S*-methyl compound (18) could be derived from the intermediate (20), the thiol anion abstracting a methyl group from the thiocarbonate function as an alternative to its normal [3] attack on C-2 to form episulphide. The latter course would be hindered in this instance (unlike the α-isomer) because to attain the necessary *trans*-diaxial arrangement of the substituents at C-2 and C-3, the $B_{2,5}$ (or $^OS_2$) conformation in which the thiol (20) is first generated (from the intermediate cyclic dithiocarbonate) has to change to the $^4C_1$ conformation, and this involves a passing interaction between the anomeric methoxy-group and the large substituent at C-2. The alkylation of thiols by esters, the essential feature of the postulated behaviour of the intermediate (20) and also of Scheme 2, is well known.[13] The constitution of the mixed disulphide (19) is based on the analysis and mass spectrum, the configuration being assumed; the derivation of this product is obscure.

The hindered β-D-*gulo*-episulphide (12) reacted very slowly with xanthate, most of the compound being recovered, but the trithiocarbonate (13) (7%) and methyl 4,6-*O*-benzylidene-2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (21) (16%) were isolated. The formation of olefins in the reactions of epoxides or episulphides with an alkyl xanthate salt has often been reported.[7,10,14]

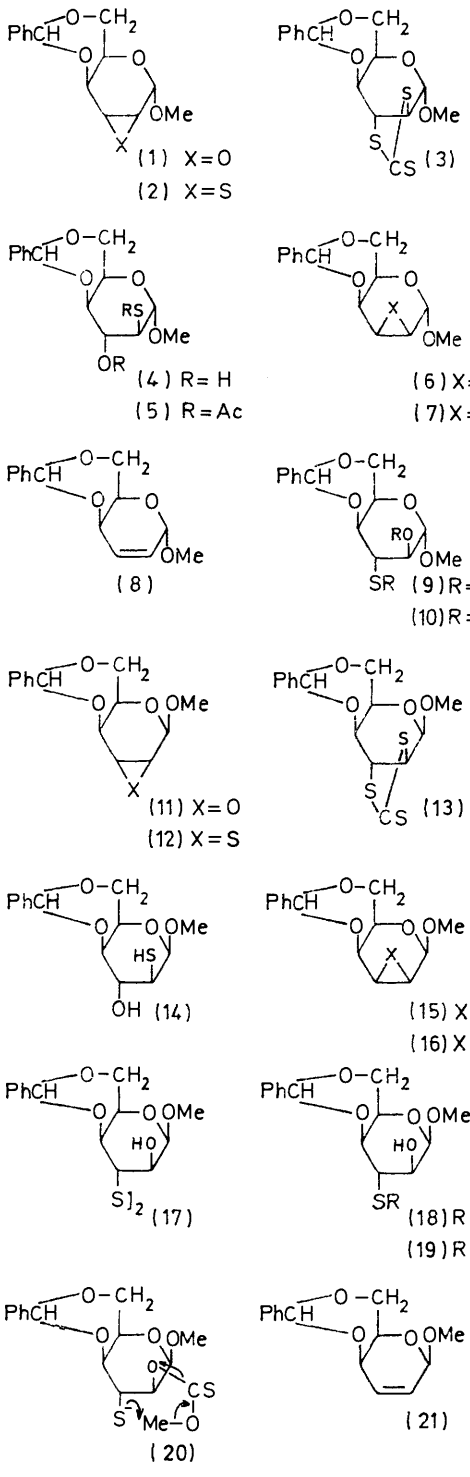
Reaction of methyl 2,3-anhydro-4,6-di-*O*-methyl-α-D-alloside (22) with sodium methyl xanthate gave a single trithiocarbonate, which was also the only product isolated from a similar reaction of methyl 2,3-dideoxy-2,3-epithio-4,6-di-*O*-methyl-α-D-mannoside (25). The

[12] M. Gut, D. A. Prins, and T. Reichstein, *Helv. Chim. Acta*, 1947, **30**, 743.

[13] W. R. Vaughan and J. B. Baumann, *J. Org. Chem.*, 1962, **27**, 739.

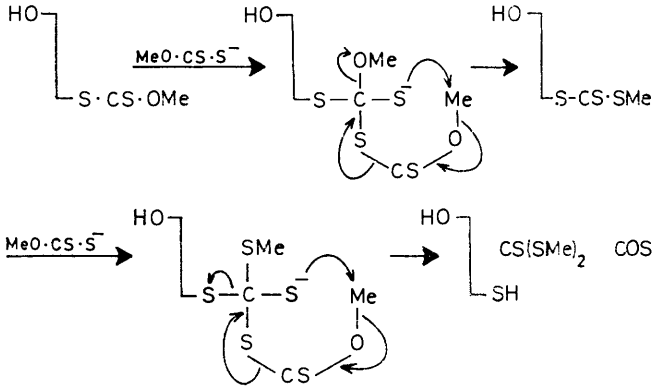
[14] G. E. McCasland, S. Furuta, and A. Furst, *J. Amer. Chem. Soc.*, 1963, **85**, 2866; D. Horton and W. N. Turner, *Tetrahedron Letters*, 1964, 2531; J. F. McGhie, W. A. Ross, F. J. Julietti, G. Swift, G. Usher, N. M. Waldron, and B. E. Grimwood, *Chem. and Ind.*, 1964, 460.

n.m.r. spectrum of the trithiocarbonate could not be satisfactorily analysed, but treatment of the compound with mercuric acetate gave an almost quantitative yield of the dithiocarbonate, and the n.m.r. spectrum of this



revealed a value for $J_{3,4}$ of 4·25 Hz, incompatible with the *trans*-3,4-diaxial protons of a *gluco*-configuration in conformation $^4C_1$. The dithiocarbonate, and consequently the trithiocarbonate, must possess the *altro*-configuration (26) and (27) in conformation $^1C_4$.

Methyl 2,3-anhydro-4,6-di-*O*-methyl-α-D-mannoside (24) gave two trithiocarbonates, one of which was identical with compound (27). The n.m.r. spectrum of the other showed $J_{3,4}$ 9·8 Hz, and this isomer gave a

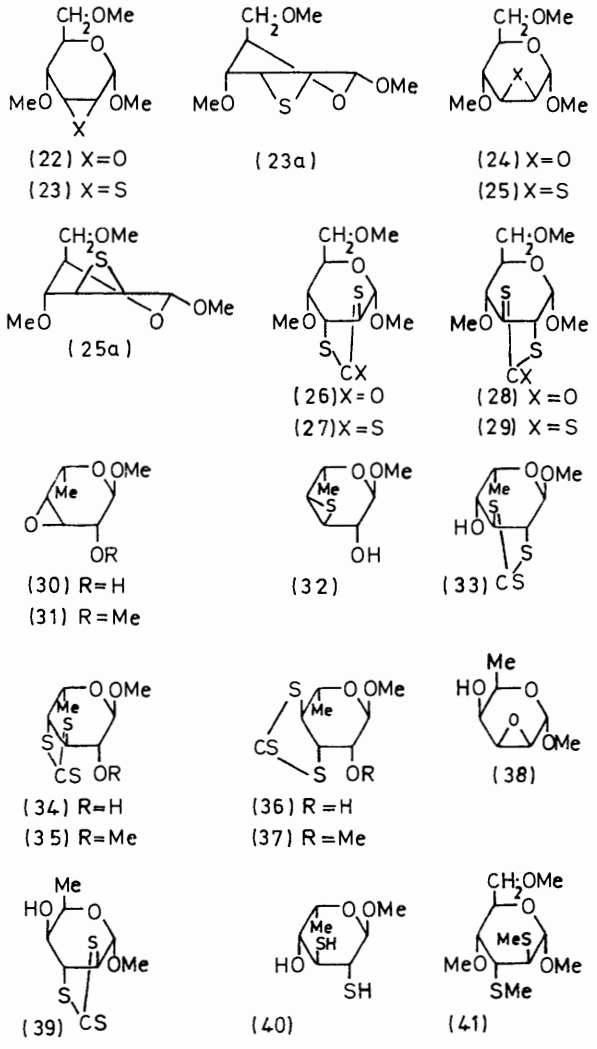


dithiocarbonate which showed $J_{3,4}$ 10·0 and $J_{2,3}$ 12·2 Hz; these couplings are in accord with the *gluco*-configuration (28) and (29) in conformation $^4C_1$. Both trithiocarbonates were also obtained from methyl 2,3-dideoxy-2,3-epithio-4,6-di-*O*-methyl-α-D-alloside (23).

The difference in behaviour between the two episulphides (25) and (23) indicates that the former reacts with xanthate only in the $^OH_5$ conformation, to give a single trithiocarbonate, whilst the latter episulphide reacts in both the $^OH_5$ and the ^5H_O forms. Inspection of models reveals that in the ^5H_O conformation of the *manno*-episulphide (25a) there is severe interaction between the methoxymethyl group (C-6) and the sulphur atom, whereas in the *allo*-isomer (23a) this conformation is relatively unhindered.

Methyl 3,4-anhydro-6-deoxy-α-L-taloside (30) can in principle be converted into a 2,3-*gulo*- as well as a 3,4-*altro*-episulphide,[1] and consequently could give four trithiocarbonates. Two were in fact isolated, in small yield. That one of these was a 2,3-compound was shown by the n.m.r. spectrum; the INDOR technique showed that the hydroxy-group was not at C-2, because it, and the anomeric proton, were not coupled to a common proton. Furthermore, by comparison with other trithiocarbonates (see Table), the $J_{1,2}$ value (7·5 Hz) favours a diaxial disposition of H-1 and H-2, as in the *ido*-compound (33) (conformation $^4C_1$) rather than the axial–equatorial arrangement in the alternative *galacto*-isomer. The second product was identified as a 3,4-trithiocarbonate because it was also obtained from methyl 3,4,6-trideoxy-3,4-epithio-α-L-altroside (32), and it is formulated as the *ido*-compound (34); another trithiocarbonate was also isolated from the latter reaction and must have the *manno*-configuration (36) (conformation $^1C_4$). Comparison of the n.m.r. spectra of (34) and (36) supports these conclusions.

Methyl 2,3-anhydro-6-deoxy-α-D-talopyranoside (38), which in principle can also lead to four trithiocarbonates, gave only one. The physical properties and spectra were identical with those of compound (33) except that the optical rotation was of opposite sign; consequently it is the D-*ido*-compound (39).



Methyl 3,4-anhydro-6-deoxy-2-*O*-methyl-α-L-taloside (31) gave two trithiocarbonates. The one in major amount was the mannoside (37) and the minor product was the idoside (35), as shown by comparison of the coupling constants with those of the 2-hydroxy-analogues (36) and (34).

Reduction of trithiocarbonates with lithium aluminium hydride leads to dithiols,[15] and, as a test example, the 6-deoxy-L-*ido*-compound (33) by this procedure gave methyl 6-deoxy-2,3-dithio-α-L-idopyranoside (40). Hydrolysis of trithiocarbonates is usually difficult, but dithiocarbonates (of the carbonyldithio-type) are less resistant,[16] and treatment of the *altro*-dithiocarbonate (26) with sodium methoxide, followed by methylation *in situ*, gave methyl 4,6-di-*O*-methyl-2,3-di-*S*-methyl-2,3-dithio-α-D-altroside (41).

EXPERIMENTAL

Instrumentation and general techniques were as described in the preceding paper,[1] where references to the sources of epoxides and preparations of episulphides can also be found. All n.m.r. spectra were recorded at 100 MHz.

General Method.—Carbon disulphide (3—5 ml) was added to a cooled solution prepared from sodium (0·15 g for the benzylidene compounds; 0·25 g for the others) and methanol (15—30 ml). After addition of the epoxide or episulphide (1 mmol), the solution was gently boiled under reflux for the time specified. It was then cooled, diluted with water, and extracted with chloroform. The dried extract was concentrated, and the residue then treated as subsequently described. The quantity of epoxide or episulphide actually used is individually specified, the amounts of other reagents being proportional to those indicated above.

Reactions of Epoxides.—(*a*) Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-guloside (260 mg) after 48 h gave a mixture, separated by t.l.c. (chloroform; followed by ether–chloroform, 2 : 1) into (i) *methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-2,3-*thiocarbonyldithio*-α-D-*idoside* (3) (60 mg), m.p. 248—249° (from chloroform–ether), $[\alpha]_D^{27}$ +33·6° (*c* 0·9) (Found: C, 50·5; H, 4·55; S, 27·2. $C_{15}H_{16}O_4S_3$ requires C, 50·6; H, 4·5; S, 27·0%), (ii) unchanged epoxide (53 mg), and (iii) *methyl* 4,6-O-*benzylidene*-2-*thio*-α-D-*idoside* (4) (59 mg), m.p. 122—126° (from ether–petroleum), $[\alpha]_D^{27}$ +25·8° (*c* 0·7) (Found: C, 56·1; H, 6·0; S, 11·3; thiol S, 11·6. $C_{14}H_{18}O_5S$ requires C, 56·4; H, 6·1; S, 10·8%).

Acetylation of the thiol (4) with acetic anhydride–pyridine gave *methyl* 3-O-*acetyl*-2-S-*acetyl*-4,6-O-*benzylidene*-2-*thio*-α-D-*idoside* (5), m.p. 205—206° (from chloroform–ether) (Found: C, 56·35; H, 5·6; S, 8·8. $C_{18}H_{22}O_7S$ requires C, 56·5; H, 5·8; S, 8·4%).

(*b*) Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-taloside (210 mg) after 64 h gave a mixture, separated by t.l.c. (chloroform) into (i) the same trithiocarbonate (3) (44 mg), m.p. and mixed m.p. 248—249°, (ii) methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epithio-α-D-guloside (2) (42 mg), m.p. and mixed m.p. 113—115°, and (iii) methyl 4,6-*O*-benzylidene-3-thio-α-D-idoside (9) (39 mg), m.p. 95—101°.

Acetylation (acetic anhydride–pyridine) of the thiol (9) gave *methyl* 2-O-*acetyl*-3-S-*acetyl*-4,6-O-*benzylidene*-3-*thio*-α-D-*idoside* (10), m.p. 216—218° (from chloroform–ether) (Found: C, 56·4; H, 5·55; S, 8·35. $C_{18}H_{22}O_7S$ requires C, 56·5; H, 5·8; S, 8·4%).

(*c*) Methyl 2,3-anhydro-4,6-*O*-benzylidene-β-D-guloside (200 mg) after 48 h gave a mixture, separated by t.l.c. (chloroform; then ether) into (i) dimethyl trithiocarbonate (8 mg), τ 7·23 (s), M^+ 138 (Calc. for $C_3H_6S_3$: *M*, 138), identical with an authentic sample,[17] (ii) unchanged epoxide (75 mg), (iii) *methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-2,3-*thiocarbonyldithio*-β-D-*idoside* (13) (24 mg), m.p. 158—161° (from ether–petroleum), $[\alpha]_D^{22}$ −2·6° (*c* 0·15) (Found: C, 50·35; H, 4·7; S, 26·8. $C_{15}H_{16}O_4S_3$ requires C, 50·6; H, 4·5; S, 27·0%), and (iv) *methyl* 4,6-O-*benzylidene*-2-*thio*-β-D-*idoside* (14) (50 mg), m.p. 136—138° (from ether), $[\alpha]_D^{20}$ −67·6° (*c* 0·6) (Found: C, 56·1; H, 6·1; S, 10·9; thiol S, 10·1. $C_{14}H_{18}O_5S$ requires C, 56·4; S, 6·1; S, 10·75%).

(*d*) Methyl 2,3-anhydro-4,6-*O*-benzylidene-β-D-taloside

[15] S. M. Iqbal and L. N. Owen, *J. Chem. Soc.*, 1960, 1030.
[16] M. V. Jesudason and L. N. Owen, *J.C.S. Perkin I*, 1974, 1443.
[17] E. Wertheim, *J. Amer. Chem. Soc.*, 1926, **48**, 826.

(264 mg) after 48 h gave a mixture, separated by t.l.c. (chloroform) into (i) dimethyl trithiocarbonate (36 mg) [identified as in (*c*)], (ii) the same trithiocarbonate (13) (7 mg), and, after further purification by t.l.c. (ether), (iii) *methyl* 4,6-O-*benzylidene*-3-S-*methylthio*-3-*thio*-β-D-*idoside* (19) (18 mg), m.p. 98—110° (decomp.) (from chloroform–ether), $[\alpha]_D^{23}$ −116° (*c* 0·14) (Found: C, 52·3; H, 5·7; S, 18·4%; M^+, 344. $C_{15}H_{20}O_5S_2$ requires C, 52·3; H, 5·85; S, 18·6%; *M*, 344), (iv) methyl 4,6-*O*-benzylidene-3-*S*-methyl-3-thio-β-D-idoside (18) (116 mg), m.p. 102—103° (from ether), $[\alpha]_D^{16}$ −60·2° (*c* 0·9) (Found: C, 57·4; H, 6·3; S, 10·5. Calc. for $C_{15}H_{20}O_5S$: C, 57·7; H, 6·45; S, 10·3%) (lit.,[12] m.p. 104—105°, $[\alpha]_D^{16}$ −59·3°), and (v) 3,3′-*dithiobis*-(*methyl* 4,6-O-*benzylidene*-3-*deoxy*-β-D-*idopyranoside*) (17) (23 mg), m.p. 196—198° (from chloroform–ether), $[\alpha]_D^{20}$ −16·3° (*c* 0·55) (Found: C, 56·7; H, 5·85; S, 11·2%; M^+, 594. $C_{28}H_{34}O_{10}S_2$ requires C, 56·55; H, 5·8; S, 10·8%; *M*, 594).

Reaction of the 3-*S*-methyl compound (18) (45 mg) in pyridine (0·5 ml) with ethyl chloroformate for 1 h, followed by dilution with water and extraction with chloroform, gave methyl 4,6-*O*-benzylidene-2-*O*-ethoxycarbonyl-3-*S*-methyl-3-thio-β-D-idoside (37 mg), m.p. 148—149° (from ether–petroleum), $[\alpha]_D^{21}$ −4·7° (*c* 1·2) (lit.,[12] m.p. 149°, $[\alpha]_D$ −3·7 ± 2°).

(*e*) Methyl 2,3-anhydro-4,6-di-*O*-methyl-α-D-alloside (1·03 g) after 46 h gave an oil, which when purified by column chromatography (ether) furnished *methyl* 2,3-*dideoxy*-4,6-*di*-O-*methyl*-2,3-*thiocarbonyldithio*-α-D-*altroside* (27) (0·42 g), m.p. 66·5—68° (from ether–petroleum), $[\alpha]_D^{23}$ +4·8° (*c* 0·6) (Found: C, 40·7; H, 5·4; S, 32·7. $C_{10}H_{16}O_4S_3$ requires C, 40·5; H, 5·4; S, 32·5%).

A mixture of this trithiocarbonate (0·40 g), mercuric acetate (1·2 g), and acetic acid (15 ml) was stirred at 40° for 45 min and then diluted with chloroform and filtered. The filtrate was concentrated, and the residue was stirred with water and extracted with chloroform. The extract was washed successively with aqueous sodium hydrogen carbonate and with water, then dried and evaporated to give *methyl* 2,3-*dideoxy*-4,6-*di*-O-*methyl*-2,3-*carbonyldithio*-α-D-*altroside* (26) (0·38 g), m.p. 69° (from ether–petroleum), $[\alpha]_D^{23}$ +148° (*c* 0·5) (Found: C, 43·0; H, 5·7; S, 22·7. $C_{10}H_{16}O_5S_2$ requires C, 42·8; H, 5·75; S, 22·9%).

(*f*) Methyl 2,3-anhydro-4,6-di-*O*-methyl-α-D-mannoside (0·43 g) after 48 h, and purification of the product by column chromatography (ether) gave a mixture (0·26 g) which was separated by t.l.c. (ether–petroleum, 2 : 1) into (i) the same trithiocarbonate (27) described in (*e*) (0·10 g), m.p. and mixed m.p. 66—68°, and (ii) *methyl* 2,3-*dideoxy*-4,6-*di*-O-*methyl*-2,3-*thiocarbonyldithio*-α-D-*glucoside* (29) (0·16 g), a yellow oil, $[\alpha]_D^{18}$ +96·5° (*c* 0·5) (Found: C, 41·15; H, 5·5; S, 33·1. $C_{10}H_{16}O_4S_3$ requires C, 40·5; H, 5·4; S, 32·5%).

Treatment of the trithiocarbonate (29) (100 mg) with mercuric acetate (0·3 g) and acetic acid (5 ml) under the conditions described in (*e*) gave *methyl* 2,3-*dideoxy*-4,6-*di*-O-*methyl*-2,3-*carbonyldithio*-α-D-*glucoside* (28) (85 mg), m.p. 70—71° (from ether–petroleum), $[\alpha]_D^{26}$ +19·6° (*c* 0·6) (Found: C, 42·8; H, 5·7; S, 22·8. $C_{10}H_{16}O_5S_2$ requires C, 42·8; H, 5·75; S, 22·9%); the m.p. was depressed to 60—64° on admixture with the *altro*-isomer described in (*e*).

(*g*) Methyl 3,4-anhydro-6-deoxy-α-L-taloside (730 mg) after 18 h gave an oil, which on trituration with carbon tetrachloride gave a yellow solid (106 mg) (Found: C, 38·2; H, 4·8; S, 37·9. Calc. for $C_8H_{12}O_3S_3$: C, 38·1; H, 4·8; S, 38·1%). The ^{1}H n.m.r. spectrum indicated that it was a mixture, and separation by t.l.c. [petroleum (b.p. 60—80°)–ethyl acetate, 2 : 1] gave (i) *methyl* 2,3,6-*trideoxy*-2,3-*thiocarbonyldithio*-α-L-*idopyranoside* (33) (42 mg), m.p. 120—124° (from chloroform–carbon tetrachloride), $[\alpha]_D^{23}$ +30·4° (*c* 0·8), and (ii) *methyl* 3,4,6-*trideoxy*-3,4-*thiocarbonyldithio*-α-L-*idopyranoside* (34) (45 mg), m.p. 194—197° (from chloroform–carbon tetrachloride), $[\alpha]_D^{23}$ −77·9° (*c* 0·7).

(*h*) Methyl 2,3-anhydro-6-deoxy-α-D-talopyranoside (prepared from methyl 6-deoxy-3,4-*O*-isopropylidene-2-*O*-tosyl-α-D-galactoside[18] by the method described[19] for the L-isomer) (220 mg) after 20 h gave, after purification of the product by t.l.c. (petroleum–ethyl acetate, 2 : 1), *methyl* 2,3,6-*trideoxy*-2,3-*thiocarbonyldithio*-α-D-*idopyranoside* (39) (62 mg), m.p. 120—124° (from chloroform–carbon tetrachloride), $[\alpha]_D$ −30·3° (*c* 0·6). The i.r. and n.m.r. spectra were identical with those of the L-enantiomer described in (*g*).

(*i*) Methyl 3,4-anhydro-6-deoxy-2-*O*-methyl-α-L-talopyranoside (250 mg) after 12 h, and purification of the product by t.l.c. [petroleum (b.p. 60—80°)–ethyl acetate, 2 : 1] gave a yellow solid (140 mg), m.p. 78—89° (from petroleum) (Found: C, 40·7; H, 5·35; S, 36·1. Calc. for $C_9H_{14}O_3S_3$: C, 40·6; H, 5·3; S, 36·1%). The ^{1}H n.m.r. spectrum showed this to be a 1 : 5 mixture, and separation by t.l.c. (ether–petroleum, 1 : 3) gave (i) *methyl* 3,4,6-*trideoxy*-2-O-*methyl*-3,4-*thiocarbonyldithio*-α-L-*idoside* (35) (23 mg), m.p. 95—98° (from petroleum), $[\alpha]_D^{23}$ −183° (*c* 0·3), and (ii) *methyl* 3,4,6-*trideoxy*-2-O-*methyl*-3,4-*thiocarbonyldithio*-α-L-*mannoside* (37) (110 mg), m.p. 94—96° (from petroleum), $[\alpha]_D^{23}$ −131° (*c* 0·6).

Reactions of Episulphides.—(*a*) Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epithio-α-D-taloside (60 mg) after 24 h gave a product which was separated by t.l.c. (chloroform–ether) into (i) the trithiocarbonate (3) (47 mg), m.p. 237—243°, spectroscopically identical with that obtained in epoxide reaction (*a*), (ii) methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (8) (5 mg), identified by the i.r. spectrum,[1] and (iii) recovered episulphide (9 mg). A longer reaction time resulted in decomposition and the yield of trithiocarbonate was less.

(*b*) Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epithio-α-D-guloside (198 mg) after 72 h gave, after separation of the product by t.l.c. (chloroform) (i) the trithiocarbonate (3) (88 mg), m.p. and mixed m.p. 242—244° [see reaction (*a*)], and (ii) unchanged episulphide (70 mg).

(*c*) Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epithio-β-D-taloside (100 mg) after 48 h gave a product which was separated by t.l.c. (ether) into (i) the trithiocarbonate (13) (34 mg), m.p. 158—161°, identical with that obtained in epoxide reaction (*c*), and (ii) unchanged episulphide (20 mg).

(*d*) Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epithio-β-D-guloside (75 mg) after 72 h, and separation of the product by t.l.c. (ether) gave (i) the trithiocarbonate (13) (7 mg) [see reaction (*c*)], (ii) methyl 4,6-*O*-benzylidene-2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (21) (11 mg), identified spectroscopically,[1] and (iii) unchanged episulphide (55 mg).

(*e*) Methyl 2,3-dideoxy-2,3-epithio-4,6-di-*O*-methyl-α-D-mannoside (86 mg) after 48 h gave, by column chromatography (ether), the trithiocarbonate (27) (60 mg), m.p. and mixed m.p. 66—68° [see epoxide reaction (*e*)].

[18] B. Iselin and T. Reichstein, *Helv. Chim. Acta*, 1946, **29**, 508.
[19] E. E. Percival and E. G. V. Percival, *J. Chem. Soc.*, 1950, 690; G. Charalambous and E. E. Percival, *ibid.*, 1954, 2443.

(*f*) Methyl 2,3-dideoxy-2,3-epithio-4,6-di-*O*-methyl-α-D-alloside (95 mg) after 48 h gave, by column chromatography (ether), a mixture, which was separated by t.l.c. (ether–petroleum, 2 : 1) into (i) the trithiocarbonate (27) (59 mg), m.p. and mixed m.p. 65—68° [see reaction (*e*)], and (ii) the trithiocarbonate (29) (29 mg), identified spectroscopically [see epoxide reaction (*f*)].

(*g*) Methyl 3,4,6-trideoxy-3,4-epithio-α-L-altropyranoside (50 mg) after 18 h gave, by t.l.c. (petroleum–ethyl acetate, 2 : 1), (i) *methyl* 3,4,6-*trideoxy*-3,4-*thiocarbonyldithio*-α-L-*mannoside* (36) (33 mg), m.p. 121—123°, $[\alpha]_D^{20}$ −148° (*c* 0·5) (Found: C, 38·2; H, 4·8; S, 38·05. $C_8H_{12}O_3S_3$ requires C, 38·1; H, 4·8; S, 38·1%), and (ii) the trithiocarbonate (34) (14 mg), m.p. and mixed m.p. 189—195° [see epoxide reaction (*g*)].

Methyl 6-*Deoxy*-2,3-*dithio*-α-L-*idopyranoside* (40).—A solution of methyl 2,3,6-trideoxy-2,3-thiocarbonyldithio-α-L-idopyranoside (33) (78 mg) in dry ether (5 ml) was slowly added to a stirred slurry of lithium aluminium hydride (150 mg) in dry ether (2 ml), so that the yellow colour was continually destroyed. The mixture was stirred at ambient temperature for a further hour, and it was then acidified with dilute hydrochloric acid. The ethereal layer was removed and combined with ethereal extracts of the aqueous portion, and the organic solution was washed with aqueous sodium hydrogen carbonate, then dried and evaporated to give the *dithiol*, an oil (64 mg), $[\alpha]_D$ −11·9° (*c* 0·4) (Found: C, 40·25; H, 6·5; S, 30·3. $C_7H_{14}O_3S_2$ requires C, 40·0; H, 6·7; S, 30·5%).

Methyl 4,6-*Di*-O-*methyl*-2,3-*di*-S-*methyl*-2,3-*dithio*-α-D-*altroside* (41).—Methyl 2,3-dideoxy-4,6-di-*O*-methyl-2,3-carbonyldithio-α-D-altroside (26) (160 mg) was dissolved in a solution prepared from sodium (39 mg) and methanol (10 ml). After 1 h under nitrogen the mixture was treated with more sodium methoxide solution [from sodium (48 mg) and methanol (5 ml)], followed by methyl iodide (5 ml), and it was then stirred for 4 h before being diluted with water and extracted with chloroform to give an oil. This was purified by t.l.c. (ether) and distilled to give the *di*-S-*methyl compound* (95 mg), b.p. 88—92° at 0·2 mmHg, $[\alpha]_D^{20}$ +92° (*c* 0·5) (Found: C, 46·7; H, 7·8; S, 22·5. $C_{11}H_{22}O_4S_2$ requires C, 46·8; H, 7·85; S, 22·7%).

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