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REACTIONS OF 4,6-DISULPHONATES OF METHYL D-GLUCOPYRANOSIDES AND METHYL D-GALACTOPYRANOSIDES WITH THIO-NUCLEOPHILES*

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ABSTRACT

The reactions of some 4,6-disulphonates of methyl 2,3-di-*O*-acyl-(and di-*O*-methyl)-D-glucopyranosides and -galactopyranosides, with thiocyanate, thioacetate, and thiobenzoate anions, have been studied under a variety of conditions. In the glucoside series, somewhat similar reactivity is shown by isomers differing only in anomeric configuration, and there is no very great difference between the reactivities of a 2,3-dibenzoate and its 2,3-di-*O*-methyl analogue. In contrast to the situation in the β-D-galactoside series, the presence of *O*-benzoyl groups in an α-D-galactoside does not have an unfavourable effect on displacement at C-4. Two hexose derivatives containing the novel 4,6-epithio bridge are described.

INTRODUCTION

Syntheses of thio sugars involving reaction of a methyl 4-*O*-sulphonyl- or 4,6-di-*O*-sulphonyl-hexopyranoside with thiolate anions have been described by several groups of investigators[1–4], and these studies have provided further examples of the considerable variations in the susceptibility of sulphonyloxy groups to undergo S_N2 displacement[5]. These differences can often be qualitatively explained by steric and polar factors[6], but the low reactivity of methyl 2,3,6-tri-*O*-benzoyl-4-*O*-methylsulphonyl-β-D-galactopyranoside[1] (**35**), compared with the α anomer[2] (**28**), appears to be anomalous. We have reported[1] on the reaction of thionucleophiles with 4,6-disulphonates in the methyl β-D-galactoside series, and we now describe experiments made with the analogous derivatives of methyl α- and β-D-glucopyranoside and of methyl α-D-galactopyranoside. The aim was to effect either displacement of both sulphonyloxy groups or selective displacement at the primary position; products obtained from the latter process would be of interest as sources (by desulphuration at C-6) of 6-deoxy sugars from which, by subsequent displacement of the 4-sulphonate group, 6-deoxy-thiofuranose sugars might be derived. Because of the considerable variations in the conditions used, the relative reactivities of different substrates

*Dedicated to the memory of Sir Edmund Hirst, C.B.E., F.R.S.
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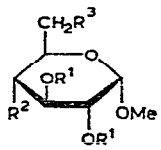
towards a particular reagent cannot always be assessed, but good comparability was possible in a number of experiments, and certain general conclusions can be drawn.

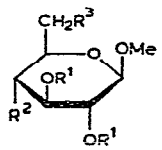
RESULTS AND DISCUSSION

The compounds used for most of the reactions were the 4,6-di-*O*-*p*-tolylsulphonyl derivatives of methyl 2,3-di-*O*-acetyl-, -di-*O*-benzoyl-, and -di-*O*-methyl-α- (or -β-)-D-glucopyranoside, and the 4,6-di-*O*-methylsulphonyl derivatives of methyl 2,3-di-*O*-benzoyl- and -di-*O*-methyl-α-D-galactopyranoside, which were prepared by conventional methods, but with some modifications (see Experimental), from the methyl 4,6-*O*-benzylidene-D-glycosides. The disulphonates were treated with potassium thiocyanate, potassium thioacetate, or potassium thiobenzoate, under the conditions specified in Table I, and the yields refer to isolated materials, except in the two designated experiments when they were calculated from the p.m.r. spectrum of the total product. The absence of a figure in one of the last two columns of Table I does not necessarily mean that none of that substitution product was formed, only that it was not recognised during isolation of the product indicated. Most of the reactions were performed for synthetic purposes, and yields generally were not optimised. Although neighbouring-group participation is sterically possible in the glucoside series[3], no evidence for its occurrence was encountered.

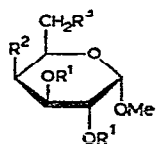
Comparison of results for the α- and β-D-glucoside series can be made by consideration of Expts. 6, 7, 8, 9, and 12 in conjunction with 13, 14, 15, 17, and 18, respectively. Clearly there is no very great difference between the reactivities within an



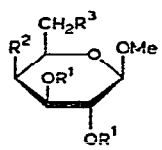
	R^1	R^2	R^3
1	Ac	OTs	OTs
2	Ac	OTs	SCN
3	Ac	OH	SCN
4	Ac	OTs	SAc
5	Ac	OTs	SBz
6	Bz	OTs	OTs
7	Bz	OTs	SCN
8	Bz	OTs	SBz
9	Bz	SBz	SBz
10	Bz	SBz	OBz
11	Me	OTs	OTs
12	Me	OTs	SCN
13	Me	OTs	SAc
14	Me	OTs	SBz
15	Me	SAc	SAc
16	Me	SBz	SBz



	R^1	R^2	R^3
17	Bz	OTs	OTs
18	Bz	OTs	SCN
19	Bz	OTs	SBz
20	Bz	SBz	OBz
21	Me	OTs	OTs
22	Me	OTs	SCN
23	Me	OTs	SBz



	R^1	R^2	R^3
24	Ac	SCN	SCN
25	Ac	SAc	SAc
26	Bz	OMs	OMs
27	Bz	OMs	SBz
28	Bz	OMs	OBz
29	Bz	SCN	SCN
30	Bz	SAc	SAc
31	Me	OMs	OMs
32	Me	OMs	SBz
33	Me	SCN	SCN
34	Me	SBz	SBz



	R^1	R^2	R^3
35	Bz	OMs	OBz
36	Bz	SCN	SCN
37	Bz	SBz	SBz
38	Me	OMs	OMs
39	Me	SBz	SBz

TABLE I

REACTIONS OF 4,6-DI-*O*-SULPHONYL DERIVATIVES OF METHYL PYRANOSIDES WITH THIO-NUCLEOPHILES

Expt. No.	*O-Substituents*		*Weight (g)*	*Reagent*	*Weight (g)*	*Solvent*	*Vol. (ml)*	*Time (h)*	*Temp. (degrees)*	*Product[a] yield (%)*	
	2,3-Di	*4,6-Di*								*6*	*4,6*
α-D-Glucosides											
1	Ac	Ts	0.33	KSCN	0.35	MeCOEt	5	24	Reflux	81	
2	Ac	Ts	4.0	KSCN	2.0	$HCONMe_2$	25	130	100		23
3	Ac	Ts	0.30	KSAc	0.50	Me_2CO	3	15	Reflux	62	
4	Ac	Ts	1.0	KSAc	1.0	$HCONMe_2$	10	5	120		25
5	Ac	Ts	0.21	KSBz	0.77	Me_2CO	3	16	Reflux	31	
6	Bz	Ts	0.27	KSCN	0.74	Me_2CO	3	38	Reflux	89	
7	Bz	Ts	9.9	KSCN	17.0	$HCONMe_2$	120	37	110		57
8	Bz	Ts	0.22	KSBz	0.38	Me_2CO	3	30	Reflux	58	
9	Me	Ts	0.47	KSCN	1.1	Me_2CO	5	20	Reflux	30	
10	Me	Ts	0.25	KSCN	1.3	$HCONMe_2$	5	32	120		85
11	Me	Ts	1.33	KSAc	2.6	Me_2CO	16	21	Reflux	60	
12	Me	Ts	0.20	KSBz	0.60	Me_2CO	2	18	Reflux	74	22
β-D-Glucosides											
13	Bz	Ts	0.27	KSCN	0.77	Me_2CO	6	38	Reflux	78[b]	
14	Bz	Ts	0.20	KSCN	0.34	$HCONMe_2$	3	37	110	23	44
15	Bz	Ts	0.21	KSBz	0.38	Me_2CO	3	30	Reflux	69	25
16	Bz	Ts	0.21	KSBz	0.41	$HCONMe_2$	3	6	76	82	10
17	Me	Ts	0.20	KSCN	0.47	Me_2CO	2	20	Reflux	50[b]	
18	Me	Ts	0.20	KSBz	0.60	Me_2CO	2	18	Reflux	75	23
19	Me	Ts	0.17	KSBz	0.34	$HCONMe_2$	3	6	76	90	
α-D-Galactosides											
20	Bz	Ms	0.53	KSBz	1.0	$HCONMe_2$	10	6	70	55	8
21	Me	Ms	0.41	KSAc	0.61	$HCONMe_2$	5	3	110		100
22	Me	Ms	0.53	KSBz	1.0	$HCONMe_2$	10	6	70	21	10
23	Me	Ms	0.51	KSBz	1.3	$HCONMe_2$	5	3	120	12	39

[a]The 6-substitution product still carries the sulphonyloxy function at C-4; the 4,6-disubstitution product has the inverted configuration at C-4. For characterisation of products, see Experimental. [b]Estimated from the p.m.r. spectrum.

anomeric pair. The yield of the 4,6-dithiocyanate **29** (57%) from the di-*p*-tolylsulphonate **6** is higher than that (39%) reported[3] (under more drastic conditions) from the corresponding dimethanesulphonate.

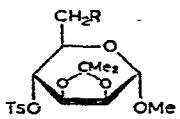
Comparison of the results of experiments 9, 10, 12, 17, 18, and 19 with those of 6, 7, 8, 13, 15, and 16, respectively, is less reliable, because the reaction durations for a particular pair of compounds were not always the same. However, there is evidently no very large difference between the reactivities of a 2,3-dibenzoate and its 2,3-di-*O*-methyl analogue, in contrast to the situation in the β-D-galactose series[1], where only the di-*O*-methyl compound **38** readily underwent displacement. Noteworthy, however, is the particularly smooth reaction of the dimethanesulphonate **31** with potassium thioacetate (Expt. 21).

Reaction of the 6-thiolbenzoate **27**, obtained as the major product from Expt. 20, with potassium thiobenzoate in *N*,*N*-dimethylformamide at 120° (4 h) gave the 4,6-di-*S*-benzoyl compound **9** in 54% yield. In agreement with reports that methyl 2,3,6-tri-*O*-benzoyl-4-*O*-methylsulphonyl-α-D-galactopyranoside (**28**) readily undergoes displacement at C-4 by azide[7], benzoate[7], and thiocyanate[2], this result again indicates that the presence of *O*-benzoyl groups in the α-D-galactoside compounds has no marked inhibiting effect on such substitutions. Indeed, the 6-thiolbenzoate **32** reacted with potassium thiobenzoate, under the same conditions used for the reaction on **27**, to give the 4,6-di-*S*-benzoyl compound **16** in 57% yield, showing that the 2,3-di-*O*-benzoyl and the 2,3-di-*O*-methyl compounds **27** and **32** have almost identical reactivities.

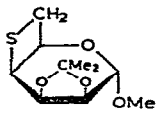
Among the several experiments[1,8] that had demonstrated the difficulty of effecting displacement reactions on methyl 2,3,6-tri-*O*-benzoyl-4-*O*-methylsulphonyl-β-D-galactopyranoside (**35**) was one in which the compound was treated with potassium thiobenzoate in *N*,*N*-dimethylformamide at 95° for 65 h. Repetition of this experiment has confirmed the original observation that no thiobenzoate can be detected in the tarry product. However, when the duration of the reaction was reduced to 18 h, a much cleaner product was obtained which contained ~30% of methyl 2,3,6-tri-*O*-benzoyl-4-*S*-benzoyl-4-thio-β-D-glucopyranoside (**20**), although it could not be completely purified, and a similar yield of the crude α-D anomer **10** was obtained, under the same conditions, from the α-D-galactoside **28**. This evidence suggests that the supposedly low reactivity of the β-D-galactoside **35** is illusory, but that the β-D compound is much more prone to decomposition (with concomitant destruction of displacement product already formed) than the α-D anomer **28**; it seems unlikely, however, that such an explanation can account for all of the results reported[1,8] in the β-D-galactoside series.

Reaction of methyl 2,3-*O*-isopropylidene-4,6-di-*O*-*p*-tolylsulphonyl-α-D-mannoside (**40**) with potassium thiobenzoate in *N*,*N*-dimethylformamide (2.5 h at 120°) gave methyl 6-*S*-benzoyl-2,3-*O*-isopropylidene-6-thio-4-*O*-*p*-tolylsulphonyl-α-D-mannoside (**41**). On treatment of **41** with ethanolic sodium ethoxide, debenzoylation and intramolecular displacement of the 4-sulphonate occurred, to give the 4,6-episulphide **42**, and a similar episulphide (**43**) was likewise obtained from methyl

6-*S*-acetyl-2,3-di-*O*-methyl-6-thio-4-*O*-*p*-tolylsulphonyl-α-D-glucoside (**13**). Although 1,6-[9], 2,6-[10], and 3,6-epithio derivatives[11] of aldohexoses are known, 4,6-episulphides have not hitherto been described, the only thietanes known in the sugar field being esters of methyl 3,5-dideoxy-3,5-epithio-α- and -β-D-xylofuranoside[12]. The 4,6-bridge was not affected by lithium aluminium hydride, confirming the known resistance of the thietane ring towards nucleophilic reagents[13].



40 R = OTs
41 R = SBz



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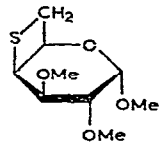

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Base-catalysed solvolysis of the dithiocyanate **29** has been reported[3] to give only the 4,6-cyclic disulphide, because of the susceptibility of the 4,6-dithiol to oxidation. We have found that the S–CN bonds can be reductively cleaved by zinc and acetic acid, and that by incorporating acetic anhydride in the medium, the dithiol can be trapped as the 4,6-di-*S*-acetyl derivative **30**. Similarly, reductive acetylation of the corresponding 2,3-diacetate **24** gave the tetra-acetyl derivative **25**.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Optical rotations were measured, for chloroform solutions, with a Perkin–Elmer 141 polarimeter. Infrared spectra were recorded (for chloroform solutions unless otherwise specified) with a Perkin–Elmer 700 spectrophotometer. A Varian T-60 instrument was used to record p.m.r. spectra of solutions in deuteriochloroform. The adsorbent for t.l.c. was Kieselgel GF_{254} (Merck) and, for column chromatography, silica gel MFC (Hopkin and Williams). Light petroleum refers to the fraction with b.p. 40–60°.

*Methyl 2,3-di-*O*-acetyl-4,6-di-*O*-p-tolylsulphonyl-α-D-glucopyranoside* (**1**). — Methyl *2,3*-di-*O*-acetyl-*4,6*-*O*-benzylidene-α-D-glucopyranoside[14] (7.3 g) in ethyl acetate (140 ml) and methanol (35 ml) was shaken with 10% palladium–charcoal (0.4 g) under hydrogen until absorption ceased (20 h). Evaporation of the filtered solution gave methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside (5.6 g), m.p. 99–100° (from light petroleum), $[\alpha]_D^{20}$ +134° (*c* 1.0); lit.[15], oil, $[\alpha]_D^{20}$ +138° (Found: C, 47.5; H, 6.5. $C_{11}H_{16}O_8$ calc.: C, 47.4; H, 6.5%).

A solution of the diol (5.5 g) in chloroform (10 ml) was treated at 0° with a solution of toluene-*p*-sulphonyl chloride (8.0 g) in pyridine (10 ml) and chloroform (5 ml). After 30 min, the mixture was left at ambient temperature for 70 h, and then worked up in the usual way to give **1** (6.5 g), m.p. 157–159° (from ether–chloroform), $[\alpha]_D^{21}$ +89° (*c* 5) (Found: C, 51.1; H, 5.4; S, 10.8. $C_{25}H_{30}O_{12}S$ calc.: C, 51.1; H, 5.15; S, 10.9%).

*Methyl 2,3-di-*O*-benzoyl-4,6-di-*O*-p-tolylsulphonyl-α-*D*-glucopyranoside* (**6**). — Hydrogenolysis of methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside[16] (4.1 g), by the foregoing procedure, gave the 4,6-diol (3.0 g) as a glass, $[\alpha]_D^{21}$ +146° (*c* 0.9, ethanol) (lit.[17], +154°), which on treatment with toluene-*p*-sulphonyl chloride (5.0 g) in pyridine (70 ml), under the conditions described for the diacetate, gave **6** (3.8 g), m.p. 133–134°, $[\alpha]_D^{25}$ +93° (*c* 1.4), ν_{max} 1380 cm^{-1} (OTs); lit.[18], m.p. 122–124°, $[\alpha]_D$ +95°; and[19] m.p. 128–129°.

When the diol (3.0 g) was similarly treated with less toluene-*p*-sulphonyl chloride (1.5 g), the main product, purified by column chromatography (ether), was methyl 2,3-di-*O*-benzoyl-6-*O*-*p*-tolylsulphonyl-α-D-glucopyranoside, m.p. 150–151° (from ethanol–chloroform); ν_{max} 3500 (OH) and 1375 (OTs) cm^{-1} (Found: C, 60.5; H, 5.1; S, 5.7. $C_{28}H_{28}O_{10}S$ calc.: C, 60.5; H, 5.1; S, 5.8%).

*Methyl 2,3-di-*O*-methyl-4,6-di-*O*-p-tolylsulphonyl-α-*D*-glucopyranoside* (**11**). — By the methods described above, methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-α-D-glucopyranoside[14] (2.7 g) was converted into methyl 2,3-di-*O*-methyl-α-D-glucopyranoside (1.4 g), m.p. 84° (lit.[20] m.p. 82–85°), and thence into **11** (1.5 g), m.p. 123–124°, $[\alpha]_D^{20}$ +80° (*c* 2.8), ν_{max}^{Nujol} 1390 cm^{-1} (OTs) (Found: C, 51.8; H, 5.75; S, 12.4. $C_{23}H_{30}O_{10}S_2$ calc.: C, 52.1; H, 5.7; S, 12.1%).

*Methyl 2,3-di-*O*-benzoyl-4,6-di-*O*-p-tolylsulphonyl-β-*D*-glucopyranoside* (**17**). — Prepared from methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside[16] by Kaufmann's method[21], **17** (overall yield, 35%) had m.p. 173–173.5° (from ethanol), $[\alpha]_D^{22}$ +46° (*c* 1.6), ν_{max} 1725 (OBz) and 1360 (OTs) cm^{-1}; lit.[21], m.p. 176–177°, $[\alpha]_D^{24}$ + 22°.

*Methyl 2,3-di-*O*-methyl-4,6-di-*O*-p-tolylsulphonyl-β-*D*-glucopyranoside* (**21**). — A solution of methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-β-D-glucopyranoside[14] (4.0 g) in acetone (100 ml) and 1% hydrochloric acid (10 ml) was boiled under reflux for 6 h, then neutralised with barium carbonate, filtered, and concentrated. A solution of the oily residue in chloroform was washed with aqueous sodium hydrogen sulphite and water, dried, and evaporated to give the 4,6-diol (2.3 g), $[\alpha]_D^{20}$ −40° (*c* 1.6); lit.[22], $[\alpha]_D$ −45°. By the foregoing procedure, the diol (2.0 g) was converted into **21** (3.5 g), m.p. 147–149°, $[\alpha]_D^{22}$ −15° (*c* 1.6), ν_{max} 1360 cm^{-1} (OTs) (Found: C, 52.3; H, 5.8; S, 12.0. $C_{23}H_{30}O_{10}S_2$ calc.: C, 52.1; H, 5.7; S, 12.1%).

*Methyl 2,3-di-*O*-benzoyl-4,6-di-*O*-methylsulphonyl-α-*D*-galactopyranoside* (**26**). — Methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside[23] (16.0 g) was hydrolysed in a boiling mixture of acetone (400 ml) and 1% hydrochloric acid (40 ml) for 5 h. The crude diol, isolated by the procedure described in the preceding experiment, was a glass (12.5 g); this was dissolved in pyridine (60 ml), the solution was cooled to 0°, and methanesulphonyl chloride (14 ml) was slowly added. The mixture was left at ambient temperature for 48 h and then poured onto a column of silica gel and eluted with ether; this procedure removed a red, tarry impurity. The pale-yellow eluate was evaporated, and the residual syrup purified by t.l.c. (ether) to give **26** as a glass (7.7 g), $[\alpha]_D^{21}$ +122° (*c* 1.2), ν_{max} 1720 (OBz) and 1360 cm^{-1} (OMs) (Found: C, 49.2; H, 4.4; S, 11.2. $C_{23}H_{26}O_{12}S_2$ calc.: C, 49.5; H, 4.7; S, 11.5%).

Methyl 2,3-di-O-methyl-4,6-di-O-methylsulphonyl-α-D-galactopyranoside (**31**). — A solution of methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-α-D-galactopyranoside[24] (15 g) in methanol (300 ml) and 10% hydrochloric acid (3 ml) was boiled under reflux for 5 h, then neutralised with barium carbonate, and evaporated. The residue was extracted with acetone, and the extract was concentrated to an oil, which was freed from benzaldehyde dimethyl acetal by being washed several times with light petroleum. The crude diol was dissolved in pyridine (10 ml) and treated at 0° with methanesulphonyl chloride (10 ml). The mixture was left for 4 h at ambient temperature, and then gradually diluted with water. Extraction with chloroform gave **31** as a glass (11.1 g), $[\alpha]_D^{20}$ +104° (*c* 1.1), ν_{max} (film) 1360 cm^{-1} (OMs) (Found: C, 34.9; H, 5.7; S, 16.95. $C_{11}H_{22}O_{10}S_2$ calc.: C, 34.9; H, 5.9; S, 16.95%). P.m.r. data: τ 4.78 (bd, 1 H, J ~2 Hz, H-4), 5.00 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 5.4–6.0 (m, 3 H), 6.38 and 6.40 (2 s, 6 H, MeO-2,3), 6.50 (s, 3 H, MeO-1), and 6.80 and 6.90 (2 s, 6 H, 2 SO_2Me).

General method for the reactions of disulphonates with nucleophiles. — The quantities used, and the conditions, for each numbered experiment are given in Table I. Reactions were carried out in an atmosphere of nitrogen. The work-up procedure involved concentration under reduced pressure, dilution of the residue with water, and extraction with ether, chloroform, or dichloromethane. The extract was washed with water, dried over magnesium sulphate, and evaporated, and the residue was then purified and identified as indicated in the following paragraphs.

Reactions of methyl 2,3-di-O-acetyl-4,6-di-O-p-tolylsulphonyl-α-D-glucopyranoside. — Expt. 1. The crude product was transferred to a column of silica gel and eluted with ether to give methyl 2,3-di-*O*-acetyl-6-deoxy-6-thiocyanato-4-*O*-*p*-tolylsulphonyl-α-D-glucopyranoside (**2**, 0.21 g) as an oil, $[\alpha]_D^{24}$ +96° (*c* 1.1), ν_{max} 2180 (SCN) and 1380 (OTs) cm^{-1} (Found: C, 48.2; H, 4.9; N, 2.95; S, 13.2. $C_{19}H_{23}NO_9S_2$ calc.: C, 48.2; H, 4.9; N, 3.0; S, 13.5%).

Expt. 2. Crystallisation from ether–light petroleum gave methyl 2,3-di-*O*-acetyl-4,6-dideoxy-4,6-dithiocyanato-α-D-galactopyranoside (**24**, 0.57 g), m.p. 181–183.5°, $[\alpha]_D^{25}$ +138° (*c* 1.3); lit.[3], m.p. 183–185°, $[\alpha]_D$ +134°.

Expt. 3. Column chromatography (ether) gave methyl 2,3-di-*O*-acetyl-6-*S*-acetyl-6-thio-4-*O*-*p*-tolylsulphonyl-α-D-glucopyranoside (**4**, 0.15 g) as an oil, $[\alpha]_D^{28}$ +106° (*c* 4.6), ν_{max} 1685 (SAc) and 1375 (OTs) cm^{-1} (Found: C, 48.7; H, 5.4; S, 13.2. $C_{20}H_{26}O_{10}S_2$ calc.: C, 49.0; H, 5.3; S, 13.1%).

Expt. 4. Crystallisation from ether–light petroleum gave methyl 2,3-di-*O*-acetyl-4,6-di-*S*-acetyl-4,6-dithio-α-D-galactopyranoside (**25**, 0.17 g), m.p. 97–98°, $[\alpha]_D^{24}$ +94.5° (*c* 2.2), ν_{max} 1690 cm^{-1} (SAc) (Found: C, 45.65; H, 5.7; S, 16.4. $C_{15}H_{22}O_8S_2$ calc.: C, 45.7; H, 5.6; S, 16.3%).

Expt. 5. Purification by t.l.c. (ether) gave methyl 2,3-di-*O*-acetyl-6-*S*-benzoyl-6-thio-4-*O*-*p*-tolylsulphonyl-α-D-glucopyranoside (**5**, 60 mg), $[\alpha]_D^{28}$ +92° (*c* 2.7), ν_{max} 1660 (SBz) and 1380 (OTs) cm^{-1} (Found: C, 54.2; H, 5.2; S, 11.7. $C_{25}H_{28}O_{10}S_2$ calc.: C, 54.3; H, 5.1; S, 11.6%).

Reactions of methyl 2,3-di-O-benzoyl-4,6-di-O-p-tolylsulphonyl-α-D-gluco-

pyranoside. — *Expt. 6.* Crystallisation from carbon tetrachloride gave methyl 2,3-di-*O*-benzoyl-6-deoxy-6-thiocyanato-4-*O*-*p*-tolylsulphonyl-α-D-glucopyranoside (**7**, 0.20 g), m.p. 181–182° $[\alpha]_D^{21}$ +121° (*c* 2.9), ν_{max} 2180 (SCN) and 1380 (OTs) cm^{-1} (Found: C, 58.3; H, 4.55; N, 2.0; S, 10.6. $C_{29}H_{27}NO_9S_2$ calc.: C, 58.3; H, 4.55; N, 2.3; S, 10.7%).

Expt. 7. Crystallisation from ethanol gave methyl 2,3-di-*O*-benzoyl-4,6-dideoxy-4,6-dithiocyanato-α-D-galactopyranoside (**29**, 3.9 g), m.p. 211–212°, $[\alpha]_D^{25}$ +95° (*c* 2.1); lit.[3], m.p. 212–214°, $[\alpha]_D^{25}$ +93.5°.

Expt. 8. Purification by column chromatography (ether) gave methyl 2,3-di-*O*-benzoyl-6-*S*-benzoyl-6-thio-4-*O*-*p*-tolylsulphonyl-α-D-glucopyranoside (**8**, 0.12 g), m.p. 175–176° (from methanol), $[\alpha]_D^{28}$ +67° (*c* 10.6), ν_{max} 1660 (SBz) and 1375 (OTs) cm^{-1} (Found: C, 63.7; H, 4.8; S, 9.5. $C_{35}H_{32}O_{10}S_2$ calc.: C, 63.6; H, 4.9; S, 9.7%).

*Reactions of methyl 2,3-di-*O*-methyl-4,6-di-*O*-p-tolylsulphonyl-α-D-gluco-pyranoside.* — *Expt. 9.* Preparative t.l.c. (ether) gave, as the main (faster running) component, methyl 6-deoxy-2,3-di-*O*-methyl-6-thiocyanato-4-*O*-*p*-tolylsulphonyl-α-D-glucopyranoside (**12**, 0.12 g), an oil, $[\alpha]_D^{24}$ +97° (*c* 4.8), ν_{max} 2180 (SCN) and 1370 (OTs) cm^{-1} (Found: C, 48.8; H, 5.5; N, 3.3; S, 15.1. $C_{17}H_{23}NO_7S_2$ calc.: C, 48.9; H, 5.55; N, 3.4; S, 15.4%).

A second component (40 mg) was identified as starting material.

Expt. 10. Preparative t.l.c. (chloroform) gave methyl 4,6-dideoxy-2,3-di-*O*-methyl-4,6-dithiocyanato-α-D-galactopyranoside (**33**, 0.12 g), m.p. 91–94° (from aqueous ethanol), $[\alpha]_D^{20}$ +182° (*c* 0.4), ν_{max} 2175 cm^{-1} (SCN) (Found: C, 43.4; H, 5.1; N, 9.0; S, 21.3. $C_{11}H_{16}N_2O_4S_2$ calc.: C, 43.4; H, 5.3; N, 9.2; S, 21.1%). P.m.r. data: τ 5.10 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 5.6 (m, 1 H), 5.9 (m, 1 H), 6.15 (m, 1 H), 6.42 (s, 9 H, OMe), and 6.5–6.75 (m, 3 H).

Expt. 11. Preparative t.l.c. (ether) gave methyl 6-*S*-acetyl-2,3-di-*O*-methyl-6-thio-4-*O*-*p*-tolylsulphonyl-α-D-glucopyranoside (**13**, 0.65 g) as an oil, $[\alpha]_D^{20}$ +50° (*c* 2.6), ν_{max} 1695 (SAc) and 1365 (OTs) cm^{-1} (Found: C, 49.9; H, 6.0; S, 14.9. $C_{18}H_{26}O_8S_2$ calc.: C, 49.8; H, 6.0; S, 14.8%).

Expt. 12. Preparative t.l.c. (dichloromethane) gave (*i*) methyl 6-*S*-benzoyl-2,3-di-*O*-methyl-6-thio-4-*O*-*p*-tolylsulphonyl-α-D-glucopyranoside (**14**, 0.14 g) as a glass, $[\alpha]_D^{20}$ +77° (*c* 2.3), ν_{max} 1660 (SBz) and 1360 (OTs) cm^{-1} (Found: C, 55.6; H, 5.8; S, 12.6. $C_{23}H_{28}O_5S_2$ calc.: C, 55.6; H, 5.7; S, 12.9%). P.m.r. data: τ 1.8–2.7 (m, 9 H, aromatic), 5.15 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 5.50 (t, 1 H, $J_{3,4} = J_{4,5} = 9$ Hz, H-4), 5.8–6.4 (m, 2 H), 6.50 and 6.60 (2 s, 6 H, MeO-2,3), 6.85 (s, 3 H, MeO-1), 6.4–7.3 (m, 3 H), and 7.55 (s, 3 H, Ar-Me). The other product (*ii*) was methyl 4,6-di-*S*-benzoyl-2,3-di-*O*-methyl-4,6-dithio-α-D-galactopyranoside (**34**, 39 mg), a glass, ν_{max} 1660 cm^{-1} (SBz) (Found: C, 57.7; H, 5.6; S, 12.7. $C_{23}H_{26}O_6S_2$ calc.: C, 59.7; H, 5.7; S, 13.9%). P.m.r. data: τ 1.8–2.75 (m, 10 H, aromatic), 5.08 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.15 (q, 1 H, $J_{3,4}$ 6, $J_{4,5}$ 2 Hz, H-4), 5.6–6.2 (m, 2 H), 6.40, 6.50, 6.53 (3 s, 9 H, 3 OMe), and 6.1–6.8 (m, 3 H).

*Reactions of methyl 2,3-di-*O*-benzoyl-4,6-di-*O*-p-tolylsulphonyl-β-D-gluco-pyranoside.* — *Expt. 13.* Preparative t.l.c. (chloroform) gave an oil (0.23 g), the p.m.r.

spectrum of which (compared with that of authentic material obtained from Expt. 14) showed it to be the 6-thiocyanate **18** mixed with ~22% of starting material.

Expt. 14. Preparative t.l.c. (dichloromethane) gave two products. (*i*) Methyl 2,3-di-*O*-benzoyl-6-deoxy-6-thiocyanato-4-*O*-*p*-tolylsulphonyl-β-D-glucopyranoside (**18**, 41 mg), a glass, $[\alpha]_D^{20}$ +43° (*c* 0.7), ν_{max} 2200 (SCN) and 1370 (OTs) cm^{-1} (Found: C, 58.5; H, 4.75; N, 2.3; S, 10.9. $C_{29}H_{27}NO_9S_2$ calc.: C, 58.3; H, 4.55; *N*, 2.3; S, 10.7%). P.m.r. data: τ 1.8–3.2 (m, 14 H, aromatic), 4.28 (t, 1 H, $J_{2,3} = J_{3,4} = 9$ Hz, H-3), 4.60 (t, 1 H, $J_{1,2}$ 7, $J_{2,3}$ 9 Hz, H-2), 5.10 (t, 1 H, $J_{3,4}$ 9, $J_{4,5}$ 10 Hz, H-4), 5.20 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), 5.7–7.0 (m, 3 H), 6.40 (s, 3 H, OMe), and 7.93 (s, 3 H, Ar-Me). (*ii*) Methyl 2,3-di-*O*-benzoyl-4,6-dideoxy-4,6-dithiocyanato-β-D-galactopyranoside (**36**, 66 mg), m.p. 166–167°, $[\alpha]_D^{20}$ −20° (*c* 0.6), ν_{max} 2200 cm^{-1} (SCN) (Found: C, 57.1; H, 4.4; N, 5.8; S, 12.9. $C_{21}H_{20}N_2O_6S_2$ calc.: C, 57.0; H, 4.2; N, 5.8; S, 13.2%). P.m.r. data: τ 1.8–2.8 (m, 10 H, aromatic), 4.1–4.5 (m, 2 H), 5.20 (t, 1 H, *J* 4.5 Hz, H-4), 5.45–5.75 (m, 2 H), 6.35 (s, 3 H, OMe), and 6.3–6.7 (m, 2 H).

Expt. 15. Preparative t.l.c. (dichloromethane) gave two products. (*i*) Methyl 2,3-di-*O*-benzoyl-6-*S*-benzoyl-6-thio-4-*O*-*p*-tolylsulphonyl-β-D-glucopyranoside (**19**, 136 mg), a glass, $[\alpha]_D^{20}$ +39° (*c* 1.2), ν_{max} 1660 (SBz) and 1350 (OTs) cm^{-1} (Found: C, 62.0; H, 4.8; S, 9.3. $C_{35}H_{32}O_{10}S_2$ calc.: C, 62.1; H, 4.8; S, 9.5%). P.m.r. data: τ 1.8–3.2 (m, 19 H, aromatic), 4.23 (t, 1 H, $J_{2,3} = J_{3,4} = 9$ Hz, H-3), 4.60 (q, 1 H, $J_{1,2}$ 7, $J_{2,3}$ 9 Hz, H-2), 5.05 (t, 1 H, *J* 9 Hz, H-4), 5.50 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), 5.8–6.3 (m, 2 H), 6.53 (s, 3 H, OMe), 6.7–7.1 (m, 1 H), 7.90 (s, 3 H, Ar-Me). (*ii*) Methyl 2,3-di-*O*-benzoyl-4,6-di-*S*-benzoyl-4,6-dithio-β-D-galactopyranoside (**37**, 47 mg), a glass, $[\alpha]_D^{20}$ −8.8° (*c* 1.3), ν_{max} 1660 cm^{-1} (SBz) (Found: C, 65.2; H, 4.8; S, 9.6. $C_{35}H_{30}O_8S_2$ calc.: C, 65.4; H, 4.7; S, 10.0%). P.m.r. data: τ 1.8–2.8 (m, 20 H, aromatic), 4.0–4.5 (m, 2 H), 5.00 (q, 1 H, *J* 2 and 4 Hz, H-4), 5.30 (d, 1 H, $J_{2,3}$ 8 Hz, H-3), 5.55–5.9 (m, 1 H), 6.40 (s, 3 H, OMe), and 6.35–6.6 (m, 2 H).

Expt. 16. Preparative t.l.c. (dichloromethane) gave the monosubstituted product **19** (162 mg) and the bisthiobenzoate **37** (19 mg), spectroscopically identical to the products obtained from the preceding experiment.

*Reactions of methyl 2,3-di-*O*-methyl-4,6-di-*O*-p-tolylsulphonyl-β-D-gluco-pyranoside. — Expt. 17.* The product could not be separated from remaining starting material. From the relative integrals of *C*-methyl and *O*-methyl signals in the p.m.r. spectrum of the mixture, ~50% of methyl 6-deoxy-2,3-di-*O*-methyl-6-thiocyanato-4-*O*-*p*-tolylsulphonyl-β-D-glucopyranoside (**22**) appeared to be present.

Expt. 18. Separation by preparative t.l.c. gave two main products. (*i*) Methyl 6-*S*-benzoyl-2,3-di-*O*-methyl-6-thio-4-*O*-*p*-tolylsulphonyl-β-D-glucopyranoside (**23**, (141 mg), a glass, $[\alpha]_D$ +0.4° (*c* 1.6), ν_{max} 1660 (SBz) and 1365 cm^{-1} (OTs) (Found: C, 55.4; H, 5.5; S, 13.0. $C_{23}H_{28}O_8S_2$ calc.: C, 55.6; H, 5.7; S, 12.9%). P.m.r. data: τ 1.8–2.8 (m, 9 H, aromatic), 5.53 (t, 1 H, $J_{2,3} = J_{3,4} = 9$ Hz, H-4), 5.85 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), 6.50 (2 s, 6 H, MeO-2,3), 6.0–6.6 (m, 3 H), 6.88 (s, 3 H, MeO-1), and 7.55 (s, 3 H, Ar-Me). (*ii*) Methyl 4,6-di-*S*-benzoyl-2,3-di-*O*-methyl-4,6-dithio-β-D-galactopyranoside (**39**, 41 mg), a glass, $[\alpha]_D^{20}$ −29° (*c* 2.7), ν_{max} 1660 cm^{-1} (SBz)

(Found: C, 59.6; H, 5.8; $C_{23}H_{26}O_6S_2$ calc.: C, 59.7; H, 5.7%). P.m.r. data: τ 1.7–2.7 (m, 10 H, aromatic), 5.20 (q, 1 H, $J_{2,3}$ 5, $J_{3,4}$ 1 Hz, H-4), 5.75 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), 5.85–6.7 (m, 3 H), 6.40 (s, 6 H, MeO-2,3), 6.55 (s, 3 H, MeO-1), and 6.8–7.2 (m, 2 H).

Expt. 19. Purification by t.l.c. (dichloromethane) gave the monosubstitution product **23** (142 mg), spectroscopically identical with that obtained from the preceding experiment.

Reaction of methyl 2,3-di-O-benzoyl-4,6-di-O-methylsulphonyl-α-D-galactopyranoside. — Expt. 20. Separation by t.l.c. (chloroform) gave some recovered substrate (62 mg) and two products. (*i*) Methyl 2,3-di-*O*-benzoyl-6-*S*-benzoyl-4-*O*-methylsulphonyl-6-thio-α-D-galactopyranoside (**27**, 314 mg), an oil, $[\alpha]_D^{20}$ +72° (*c* 1.0), ν_{max} 1660 (SBz) and 1355 (OMs) cm^{-1} (Found: C, 57.8; H, 4.8; S, 10.2. $C_{29}H_{28}O_{10}S_2$ calc.: C, 58.0; H, 4.7; S, 10.7%). P.m.r. data, τ 1.8–2.8 (m, 15 H, aromatic), 4.0–4.5 (m, 3 H), 4.80 (d, 1 H), 5.75 (q, 1 H, $J_{5,6}$ 15, $J_{5,6'}$ 7, $J_{4,5}$ <1 Hz, H-5), 6.53 (s, 3 H, OMe), 6.5–6.7 (m, 2 H), and 6.90 (s, 3 H, SO_2Me). (*ii*) Methyl 2,3-di-*O*-benzoyl-4,6-di-*S*-benzoyl-4,6-dithio-α-D-glucopyranoside (**9**, 50 mg), a glass, $[\alpha]_D^{21}$ +91° (*c* 1.5), ν_{max} 1660 cm^{-1} (SBz) (Found: C, 65.35; H, 4.9; S, 10.0. $C_{35}H_{30}O_8S_2$ calc.: C, 65.4; H, 4.7; S, 10.0%). P.m.r. data: τ 1.8–2.8 (m, 20 H, aromatic) and 6.55 (s, 3 H, OMe); other resonances not identifiable.

The 6-thiobenzoate **27** (102 mg) was heated with potassium thiobenzoate (197 mg) in *N*,*N*-dimethylformamide (2 ml) for 4 h at 120°. The product was purified by preparative t.l.c. (dichloromethane) to give the 4,6-bisthiobenzoate **9** (59 mg), identified by the i.r. spectrum, and some recovered **27** (27 mg).

Reactions of methyl 2,3-di-O-methyl-4,6-di-O-methylsulphonyl-α-D-galactopyranoside. — Expt. 21. Purification by t.l.c. (dichloromethane) gave methyl 4,6-di-*S*-acetyl-2,3-di-*O*-methyl-4,6-dithio-α-D-glucopyranoside (**15**, 370 mg), m.p. 60–64°, $[\alpha]_D^{26}$ +99° (*c* 2.7), ν_{max} 1690 cm^{-1} (SAc) (Found: C, 45.8; H, 6.8; S, 19.15. $C_{13}H_{22}O_6S_2$ calc.: C, 45.9; H, 7.0; S, 18.85%). P.m.r. data: τ 5.10 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 6.40 (s, 6 H, MeO-2,3), 6.50 (s, 3 H, MeO-1), 5.8–7.2 (m, 6 H), 7.55 and 7.63 (2 s, 6 H, 2 SAc).

Expt. 22. Preparative t.l.c. (chloroform) gave, in addition to recovered substrate (286 mg), two products. (*i*) Methyl 6-*S*-benzoyl-2,3-di-*O*-methyl-4-*O*-methylsulphonyl 6-thio-α-D-galactopyranoside (**32**, 123 mg), a glass $[\alpha]_D^{20}$ +99° (*c* 1.2), ν_{max} 1660 (SBz) and 1360 (OMs) cm^{-1} (Found: C, 48.6; H, 5.7; S, 14.9. $C_{17}H_{24}O_8S_2$ calc.: C, 48.6; H, 5.75; S, 15.25%). P.m.r. data: τ 1.8–2.8 (m, 5 H, aromatic), 4.80 (bs, 1 H, H-4), 5.05 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 5.9–6.25 (m, 1 H), 6.43 and 6.45 (2 s, 6 H, MeO-2,3), 6.58 (s, 3 H, MeO-1), 6.80 (s, 3 H, SO_2Me), and 6.3–7.0 (m, 4 H). (*ii*) Methyl 4,6-di-*S*-benzoyl-2,3-di-*O*-methyl-4,6-dithio-α-D-glucopyranoside (**16**, 64 mg), a glass, $[\alpha]_D^{21}$ +55° (*c* 0.4), ν_{max} 1660 (SBz) (Found: C, 59.95; H, 5.7; S, 13.7. $C_{23}H_{26}O_6S_2$ calc.: C, 59.7; H, 5.7; S, 13.9%). P.m.r. data: τ 1.7–2.8 (m, 10 H, aromatic), 5.05 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 6.40 (s, 6 H, MeO-2,3), 6.55 (s, 3 H, MeO-1), and 5.9–7.1 (m, 6 H).

Expt. 23. By preparative t.l.c. (ether–light petroleum, 2:1), two products were

obtained: (*i*) the 6-*S*-benzoyl compound **32** (70 mg), and (*ii*) the 4,6-di-*S*-benzoyl compound **16** (244 mg), both identified spectroscopically by comparison with the products from Expt. 22.

Reaction of compound **32** (100 mg) with potassium thiobenzoate (196 mg) in *N*,*N*-dimethylformamide (2 ml) for 4 h at 120° gave compound **16** (62 mg), identified spectroscopically; some compound **32** (20 mg) was recovered.

*Methyl 2,3-di-*O*-acetyl-6-deoxy-6-thiocyanato-α-*D*-glucopyranoside* (**3**). — Toluene-*p*-sulphonyl chloride (5.0 g) was added to a cooled solution of methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside (5.2 g) in pyridine (80 ml); after 2 h at 0°, the mixture was left at ambient temperature for 92 h. After isolation in the usual way, the crude 6-*O*-*p*-tolylsulphonyl derivative (3.2 g), $[\alpha]_D$ +100° (*c* 1.1), was treated with potassium thiocyanate (6.8 g) in *N*,*N*-dimethylformamide (80 ml) for 120 h at 135°. Isolation by the standard procedure gave an oil which was purified by column chromatography (ether–light petroleum, 1:1) to give the title compound **3** (1.1 g), m.p. 86° (from ether–light petroleum), $[\alpha]_D^{18}$ +148° (*c* 1.1), ν_{max} 2160 (SCN) and 1740 (OAc) cm^{-1} (Found: C, 45.5; H, 5.15; N, 4.1; S, 9.85. $C_{12}H_{17}NO_7S$ calc.: C, 45.1; H, 5.4; N, 4.4; S, 10.0%).

*Reaction of methyl 2,3,6-tri-*O*-benzoyl-4-*O*-methylsulphonyl-α-*D*-galacto-pyranoside* (**28**) *with potassium thiobenzoate.* — A solution of **28**[7] (75 mg) and the reagent (150 mg) in *N*,*N*-dimethylformamide (2 ml) was heated at 95° for 18 h. After the usual work-up, separation by t.l.c. afforded **28** (31 mg), and a syrup (28 mg), $[\alpha]_D^{21}$ +146° (*c* 2.5), ν_{max} (film) 1660 cm^{-1} (SBz) (OMs absent), which was mainly methyl 2,3,6-tri-*O*-benzoyl-4-*S*-benzoyl-4-thio-α-D-glucopyranoside (**10**), but which could not be obtained analytically pure; the ratio of aromatic to methoxyl protons in the p.m.r. spectrum was approximately correct for this structure.

*Reaction of methyl 2,3,6-tri-*O*-benzoyl-4-*O*-methylsulphonyl-β-*D*-galacto-pyranoside* (**35**) *with potassium thiobenzoate.* — Under the conditions described for the preceding experiment, **35**[1] (75 mg) gave recovered substrate (31 mg), and a syrup (27 mg), $[\alpha]_D^{21}$ +55° (*c* 2.5), ν_{max} (film) 1660 cm^{-1} (SBz) (OMs absent), which was mainly methyl 2,3,6-tri-*O*-benzoyl-4-*S*-benzoyl-4-thio-β-D-glucopyranoside (**20**), but could not be completely purified; the poorly resolved p.m.r. spectrum again supported the structure.

Repetition of the reaction, at 95° for 65 h, gave a black oil from which t.l.c. failed to yield any product containing a thiolbenzoate function.

*Methyl 2,3-*O*-isopropylidene-4,6-di-*O*-p-tolylsulphonyl-α-*D*-mannopyranoside* (**40**). — Toluene-*p*-sulphonyl chloride (3.0 g) was added in portions to a solution of methyl 2,3-*O*-isopropylidene-α-D-mannopyranoside[25] (1.73 g) in pyridine (10 ml) at 0°. The mixture was left at ambient temperature for 50 h, then water (3 ml) was added, and after 10 min the solution was poured into 2M hydrochloric acid (125 ml) at 0°. Extraction with chloroform, and evaporation of the washed and dried extract, gave an oil, which was purified by column chromatography (dichloromethane). The major component (1.71 g) was **40**, $[\alpha]_D^{25}$ +5.3° (*c* 2.4), ν_{max} 1375 cm^{-1} (OTs) (Found: C, 53.0; H, 5.7; S, 11.3. $C_{24}H_{30}O_{10}S_2$ calc.: C, 53.1; H, 5.6; S, 11.8%).

Methyl 6-S-benzoyl-2,3-O-isopropylidene-6-thio-4-O-p-tolylsulphonyl-α-D-mannopyranoside (**41**). — A solution of the disulphonate **40** (0.47 g) and potassium thiobenzoate (1.0 g) in *N,N*-dimethylformamide (8 ml) was heated in a nitrogen atmosphere at 120° for 2 h, then cooled, and partitioned between chloroform and water. Evaporation of the washed and dried organic layer gave an oil, which by two successive treatments by preparative t.l.c. (first in ether, then in dichloromethane) gave **41** (0.28 g) as an oil, $[\alpha]_D^{20}$ +6.5° (*c* 1.3), ν_{max} 1665 (SBz) and 1380 (OTs) cm^{-1} (Found: C, 56.5; H, 5.6; S, 12.9. $C_{24}H_{28}O_8S_2$ calc.: C, 56.7; H, 5.55; S, 12.6%).

Methyl 4,6-dideoxy-4,6-epithio-2,3-O-isopropylidene-α-D-talopyranoside (**42**). — A solution of the *S*-benzoyl compound **41** (150 mg) in 0.05M ethanolic sodium ethoxide (10 ml) was boiled under reflux in an atmosphere of nitrogen for 7 h. The excess of base was neutralised with carbon dioxide, and the solvent was evaporated to an oil, which was taken up in chloroform. The solution was washed, dried, and evaporated, and sublimation of the residue at 40–50°/10^{-5} mmHg gave the episulphide **42** (18 mg), m.p. 78–80°, $[\alpha]_D^{20}$ +241° (*c* 0.2) (Found: C, 51.6; H, 6.9; S, 13.7. $C_{10}H_{16}O_4S$ calc.: C, 51.7; H, 6.9; S, 13.8%).

Methyl 4,6-dideoxy-4,6-epithio-2,3-di-O-methyl-α-D-galactopyranoside (**43**). — Methyl 6-*S*-acetyl-2,3-di-*O*-methyl-6-thio-4-*O*-*p*-tolylsulphonyl-α-D-glucoside (**13**, 4.1 g) was dissolved in a solution prepared from sodium (1.0 g) and ethanol (20 ml). The mixture was kept under nitrogen for 6 h, then neutralised with carbon dioxide, and evaporated. The residue was extracted with ether, and the extract was washed with water, dried, and evaporated to give an oil, which was distilled at 85°/10^{-5} mmHg. The distillate (0.61 g) crystallised completely, and recrystallisation from light petroleum gave **43**, m.p. 45°, $[\alpha]_D^{20}$ +320° (*c* 4.0) (Found: C, 49.3; H, 7.1; S, 14.4. $C_9H_{16}O_4S$ calc.: C, 49.1; H, 7.4; S, 14.55%). P.m.r. data (HA-100): τ 5.12 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 5.4–5.6 (m, 2 H, H-4,5), 6.26 (q, 1 H, $J_{1,2}$ 3, $J_{2,3}$ 9.5 Hz, H-2), 6.53, 6.66, and 6.71 (3 s, each 3 H, 3 OMe), and 6.4–7.5 (m, 3 H, H-3,6).

The episulphide **43** (84 mg) was recovered (identical p.m.r. spectrum) after being treated with lithium aluminium hydride (200 mg) in boiling ether (5 ml) for 2 h.

Reductive fission of thiocyanates. — (*a*) Zinc powder (1.0 g) was added to a solution of methyl 2,3-di-*O*-benzoyl-4,6-dideoxy-4,6-dithiocyanato-α-D-galactopyranoside (**29**, 1.0 g) in acetic acid (5 ml) and acetic anhydride (5 ml). The suspension was stirred and boiled under reflux for 15 h, then poured into water, and filtered. Extraction of the filtrate with ether, followed by washing of the extract with aqueous sodium hydrogen carbonate, drying, and evaporation, gave methyl 4,6-di-*S*-acetyl-2,3-di-*O*-benzoyl-4,6-dithio-α-D-galactopyranoside (**30**, 0.60 g), m.p. 135–136° (from ethanol), $[\alpha]_D^{23}$ +79° (*c* 2.6), ν_{max} 1695 cm^{-1} (SAc) (Found: C, 58.0; H, 5.3; S, 12.0. $C_{25}H_{26}O_8S_2$ calc.: C, 57.9: H, 5.1; S, 12.4%). P.m.r. data: τ 2.0–2.8 (m, 10 H, aromatic), 4.08 (q, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 4 Hz, H-3), 4.75 (q, 1 H, $J_{1,2}$ 4, $J_{2,3}$ 10 Hz, H-2), 4.92 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.3–5.8 (m, 2 H, H-4,5), 6.56 (s, 3 H, OMe), 6.88 (d, 2 H, $J_{5,6}$ 7 Hz, H-6), 7.66 and 7.72 (2 s, 6 H, 2 SAc).

(*b*) Zinc powder (1.5 g) was added to a solution of methyl 2,3-di-*O*-acetyl-4,6-dideoxy-4,6-dithiocyanato-α-D-galactopyranoside (**24**, 3.51 g) in acetic acid (20 ml)

and acetic anhydride (10 ml). Under the conditions described in (*a*), the reaction yielded methyl 2,3-di-*O*-acetyl-4,6-di-*S*-acetyl-4,6-dithio-α-D-galactopyranoside (**25**, 1.6 g), m.p. and mixture m.p. 97–98°, i.r. spectrum identical to that of **25** prepared by displacement.

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