5-Thiopyranoses. Part 11.[1] Isopropylidene Acetals of 5-Thio-D-glucose, 5-Thio-D-allose, and 5-Thio-D-altrose and Some of their Methyl Glycosides.

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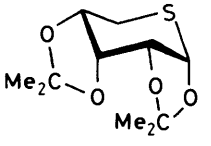
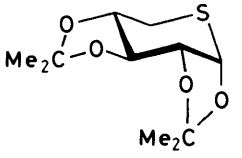
5-Thio-D-glucose (**9**) reacts with acetone in the presence of an acid catalyst to give 1,2-*O*-5,6-*S*,*O*-di-isopropylidene-5-thio-α-D-glucofuranose (**10**). 5-Thio-D-altrose (**37**) similarly gives a 1,2:5,6-diacetal (**39**) but 5-thio-D-allose (**27**) affords 2,3-*O*-5,6-*S*,*O*-di-isopropylidene-5-thio-β-D-allofuranose (**28**). Under kinetic conditions, using 2,2-dimethoxypropane, the major products from 5-thio-D-glucose (**9**) and 5-thio-D-allose (**27**) are 2,3:4,6-di-*O*-isopropylidene-5-thio-D-gluco- and allo-pyranoses (**11a**) and (**32**), even though the former possesses a *trans*-fused dioxolane ring. 1,2:4,6-Di-*O*-isopropylidene-5-thio-α-D-glucopyranose (**14**), which is also produced in the former reaction, has been synthesised by an alternative route. 2,2-Dimethoxypropane and acetone react with methyl 5-thio-α- or β-D-glucopyranosides (**3**) or the related methyl 5-thio-α- or β-D-allopyranosides (**25**) to give the 2,3:4,6-diacetals (**5**) and (**26**) respectively. With acetone alone, the glucosides (**3**) give mainly the 4,6-monoacetals (**4**) together with smaller amounts of the 2,3:4,6- diacetals (**5**); the allosides (**25**) give complex mixtures and methyl 5-thio-α-D-altropyranoside (**40**) gives first the 4,6-acetal (**41**) which then isomerises into the 3,4-acetal (**42**). Methylation of either of the pyranose 2,3:4,6-diacetals (**11a**) or (**32**) leads to the corresponding 2,3:4,6-di-*O*-isopropylidene-5-*S*-methyl-5-thio-*aldehydo* compounds (**44**) and (**45**), respectively.

In an earlier paper[2] in this series it was shown that 5-thio-D-ribose and 5-thio-D-xylose reacted with acetone or 2,2-dimethoxypropane, respectively, in the presence of acids to give 1,2:3,4-di-*O*-isopropylidene-5-thio-α-D-ribo-(**1**) and -xylo-pyranoses (**2**). This behaviour was in sharp contrast to that of



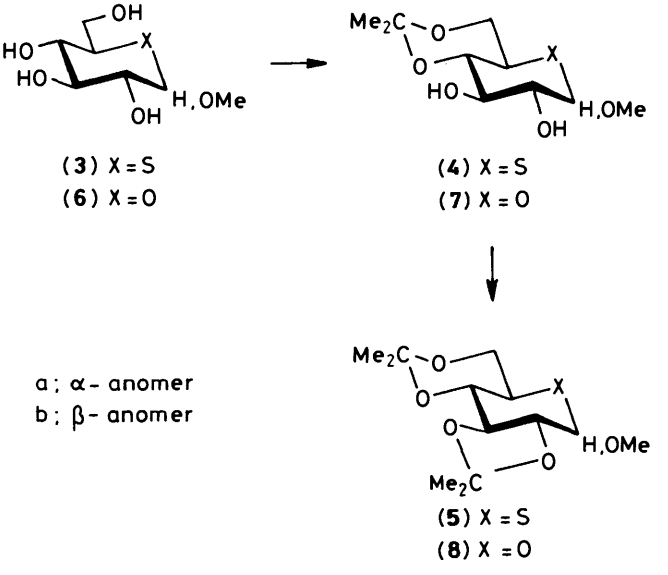
(**1**)



(**2**)

D-ribose and D-xylose, where acetals of the furanose forms are obtained, and was a further demonstration of the preference of these thio sugars for the forms with sulphur in the ring. These investigations have now been extended to some 5-thiohexoses and some of their methyl glycosides. A portion of this work has already been published in preliminary form.[3]

The production of methyl 4,6-*O*-isopropylidene-5-thio-α- and β-D-glucopyranosides (**4**) by epoxide opening reactions and their transformation into the 2,3:4,6-diacetals (**5**) by 2,2-dimethoxypropane was reported in the previous paper in this series. The diacetals (**5**) can also be obtained directly from the glucosides (**3**) by use of 2,2-dimethoxypropane. In view of the ease of formation of the diacetals (**5**), the reaction of the methyl 5-thio-α- and β-D-glucopyranosides (**3**) with acetone in the presence of toluene-*p*-sulphonic acid was investigated. Both gave mixtures of the mono- (**4**) and di-acetals (**5**), the former preponderating. These reactions illustrate the difference in acetal forming reactivity between the *gluco* thiopyranoid and pyranoid ring systems. Methyl α-D-glucopyranoside (**6a**) does not react readily with acetone but with 2,2-dimethoxypropane it is converted into the 4,6-acetal (**7a**) together with a small amount of the 2,3:4,6-diacetal (**8a**).[4] The β-anomer (**6b**) behaves similarly.[5] Better yields of the 2,3:4,6-diacetals (**8**) were obtained by the use of 2-methoxypropene as the isopropylidenating reagent.[6] In the same paper it was pointed out that the *trans*-fused 1,3-dioxolane increased the puckering of the pyranose chair. Lambert and Wharry[7] have shown that such puckering is also introduced when the ring oxygen atom of a pyranose ring is replaced by a sulphur atom and this clearly facilitates the formation of the *trans*-fused 1,3-dioxolane rings in compounds (**2**) and (**5**).



(**3**) X = S
(**6**) X = O
(**4**) X = S
(**7**) X = O
a; α-anomer
b; β-anomer
(**5**) X = S
(**8**) X = O

Treatment of 5-thio-D-glucose (**9**) with acetone in the presence of toluene-*p*-sulphonic acid gave the known[8] 1,2-*O*-5,6-*S*,*O*-di-isopropylidene-5-thio-α-D-glucofuranose (**10**) as the main product. However, when the reaction was repeated for a short time with the addition of 2,2-dimethoxypropane, a different crystalline product was obtained which was shown by *X*-ray crystallography[9] to be 2,3:4,6-di-*O*-isopropylidene-5-thio-α-D-glucopyranose (**11a**). Acetylation of (**11a**) was accom-

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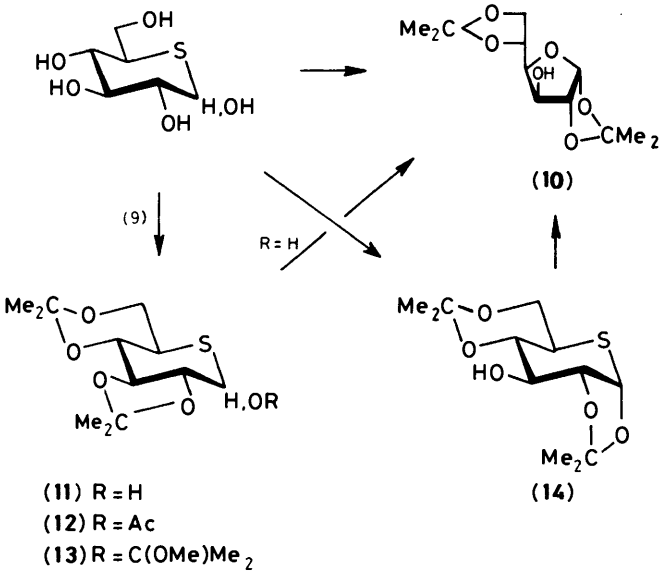
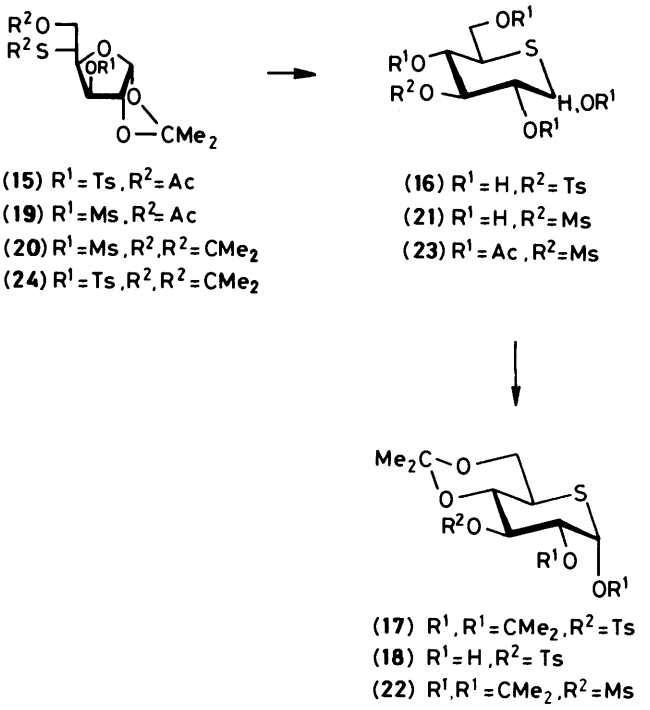


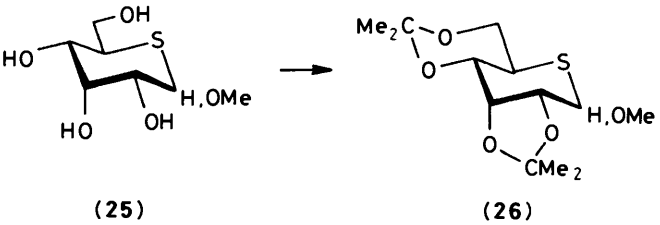


panied by mutarotation and the acetates (**12**) were obtained in the α,β ratio 3:1. Chromatography of the material from the mother liquors of crystallisation of (**11a**) gave a small quantity of higher running material, which was tentatively identified as the 1′-methoxy-1′-methylethyl ether (**13a**), and a fraction that contained a mixture of the diacetals (**10**) and (**11a**) together with a third component. In view of the existence[10,11] of 4,6-*O*-alkylidene-1,2-*O*-isopropylidene-α-D-glucopyranoses this was thought to be the 1,2:4,6-diacetal (**14**) and this was shown to be so by an independent synthesis of the diacetal (**14**) from a suitably protected 5-thio-D-glucose derivative. Brief treatment of 6-*O*-acetyl-5-*S*-acetyl-1,2-*O*-isopropylidene-5-thio-3-*O*-toluene-*p*-sulphonyl-α-D-glucofuranose (**15**) with methanol and hydrochloric acid gave 3-*O*-*p*-tolylsulphonyl-5-thio-D-glucose (**16**)[1] which reacted with 2,2-dimethoxypropane in the presence of acid to give the 1,2:4,6-diacetal (**17**) and a smaller amount of the 4,6-acetal (**18**). Methanolic sodium methoxide cleaved the sulphonate group of (**17**) to give the required diacetal (**14**). A similar series of reactions starting from either of the methanesulphonates (**19**) or (**20**) and proceding *via* syrupy 3-*O*-methylsulphonyl-5-thio-D-glucose (**21**) and its diacetal (**22**) also led to compound (**14**). The methanesulphonate (**21**) was also characterised as the crystalline tetra-acetate (**23a**).

The furanose diacetal (**10**) was obtained when either of the pyranose diacetals (**11a**) or (**14**) was left in acetone containing toluene-*p*-sulphonic acid. Similarly, the pyranose sulphonates (**17**) and (**22**), were also isomerised into the furanose compounds (**24**) and (**20**), respectively, under the same conditions. 5-Thio-D-glucose (**9**) thus differs from 5-thio-D-ribose and 5-thio-D-xylose, where the pyranoid diacetals (**1**) and (**2**) were both kinetic and thermodynamic products, in that the pyranose diacetal (**11a**) is the product obtained under kinetic reaction conditions but the furanose diacetal (**10**) is the thermodynamic product. The same considerations apply to the sulphonate esters (**17**) and (**22**), and (**20**) and (**24**).

The formation of the diacetal (**11a**) possessing a *trans*-fused, 1,3-dioxolane ring system in preference to the *cis*-fused isomer (**14**) is unusual though previous examples have been reported in *septanoses*[12] and in 1,6-deoxy-1,6-epithio-hexitols[13] where fusion to a seven-membered ring occurs. Inspection of models, and, in the case of (**11a**), the *X*-ray study, suggests that the $^4C_1$ conformation of (**11a**) is less distorted than that of (**14**) which is flattened in the region of C-1 and C-2 by the *cis*-fused 1,3-dioxolane ring. Evidence for this flattening also comes from comparison of the ^{1}H n.m.r. spectra (see Table 1) [the spectrum of (**14**) was not completely resolved] with those of the 4,6-acetal (**18**) and the tetra-acetate (**23**). Thus (**18**) and (**23**) have the expected values for $J_{1,2}$ and $J_{2,3}$, about 3 and 9 Hz, respectively, whereas the corresponding values for (**17**) and (**22**) are about 5 and 7 Hz, respectively. It is interesting to note that, after this part of the work was completed, 1,2:4,6-di-*O*-isopropylidene-α-D-glucopyranose was reported[14] as one of the products of kinetic isopropylidenation of sucrose though it has not been observed in similar reactions of D-glucose.

Treatment of either methyl 5-thio-α-D-allopyranoside (**25a**)[8] or the β-anomer (**25b**)[8] with acetone containing toluene-*p*-sulphonic acid gave products which appeared to be mixtures of two or more mono-acetals as well as diacetals; these mixtures were not investigated further. When the reactions were repeated with the addition of 2,2-dimethoxypropane, single products were obtained in both cases and shown to be the methyl 2,3:4,6-di-*O*-isopropylidene-5-thio-α- and -β-D-allopyranosides (**26a**) and (**26b**), respectively. The presence of both 1,3-dioxane and 1,3-dioxolane systems was shown by ^{13}C n.m.r. spectroscopy[15] (see Table 2). Both diacetals (**26**) exist, as expected, in the $^4C_1$ conformation ($J_{4,5}$ 10.5 and 10.0 Hz, respectively) though some distortion is caused by the *cis*-fused 2,3-acetal as shown by the low value of $J_{1,2}$ (3.0 Hz) for the β-anomer (**26b**), similar behaviour has been reported for ordinary D-allopyranose acetals.[16]



A single crystalline product, identified as 2,3:5,6-di-*O*-isopropylidene-5-thio-β-D-allofuranoside (**28**), was obtained when 5-thio-D-allose (**27**) was left in acetone containing toluene-*p*-sulphonic acid. The ^{13}C n.m.r. spectrum (see Table 2) showed

Table 1. ^{1}H N.m.r. data

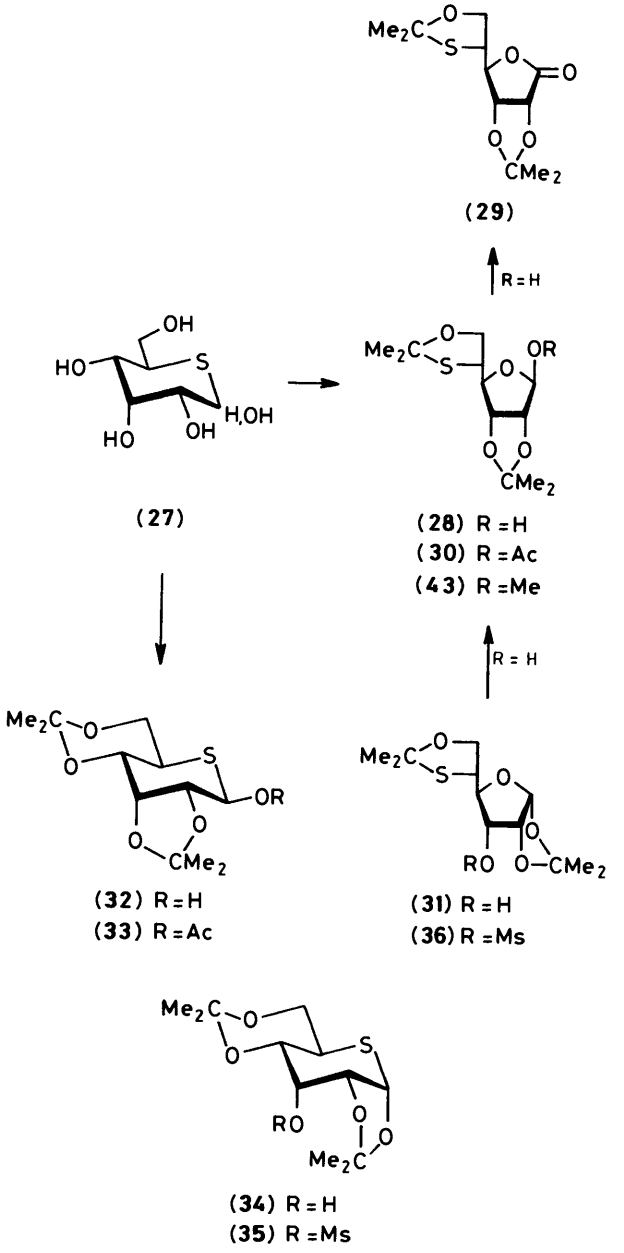
Compd.	1-H	2-H	3-H	4-H	5-H	6-H	6′-H	Other signals	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	Other couplings
(11a)	5.34	4.2	⟷	3.7	3.37	4.2⟷	3.7	3.53 (OH); 1.58, 1.49(3) ($2CMe_2$)	1.0							2.0 ($J_{1,OH}$)
(12a)[a]	6.09	4.1	⟷	3.5	3.10	4.1⟷	3.5	2.09 (COMe); 1.50, 1.37(3) ($2CMe_2$)	2.0							
(12b)[a]	5.88	4.1	⟷				2.9	2.11 (COMe); 1.51, 1.42, 1.38(2) ($2CMe_2$)	10.0							
(14)[a]	4.95	3.9	⟷	3.4	3.03	3.9⟷	3.4	2.86 (OH); 1.49, 1.47, 1.36(2) ($2CMe_2$)	5.0							
(17)[a,b]	5.04	4.12	4.59	3.77	3.18	3.80	3.57	2.43 (ArMe); 1.63, 1.38, 1.23, 1.14 ($2CMe_2$)	5.0	7.0	9.0	10.0	5.5	10.0	11.0	
(18)[b,c]	5.16	4.01	4.82	3.88	3.38	3.85	3.68	3.91 (OH); 2.45 (ArMe); 2.19 (OH); 1.26, 1.05 (CMe_2)	3.0	9.0	9.0	10.0	4.5	12.0	11.0	
(22)	5.16	4.27	4.58	3.92	3.26	2.90	3.73	3.10 (SO_2Me); 1.62; 1.50, 1.42(2) ($2CMe_3$)	5.0	7.5	9.5	10.0	6.0	10.0	11.0	
(23a)	6.16	5.31	5.04	5.40	3.58	4.40	4.09	3.00 (SO_2Me); 2.20, 2.16, 2.09(2) (4COMe)	3.0	9.5	9.0	10.0	5.0	3.0	12.0	
(26a)[c]	4.56	4.42	4.36	4.06	3.45	3.87	3.76	3.42 (OMe); 1.62, 1.52, 1.48, 1.41 ($2CMe_2$)	4.0	6.0	3.5	10.5	5.5	11.0	11.5	
(26b)[c]	4.42	4.58	4.34	4.41	3.40	⟷3.77	⟷	3.41 (OMe); 1.53, 1.44, 1.40, 1.33 ($2CMe_2$)	3.0	7.5	2.0	10.0	8.0	8.0		
(28)	5.42	⟷4.61	⟷	4.13	3.67	4.38	4.09	3.23 (OH); 1.71, 1.62, 1.49, 1.33 ($2CMe_2$)	<0.5		<0.5	11.0	2.5	4.5	9.5	3.0 ($J_{1,OH}$)
(29)		4.81	4.73	4.59	3.63	4.37	4.17	1.72, 1.63, 1.48, 1.40 ($2CMe_3$)		5.5	<0.5	8.0	2.0	5.0	10.5	
(30)	5.94	⟷4.47	⟷	4.21	3.36	3.89	4.10	1.98 (COMe); 1.63, 1.56, 1.44, 1.28 ($2CMe_2$)	<0.5		<0.5	11.0	3.0	5.0	10.0	
(32)[c]	4.90	4.57	4.32	4.54	3.46	3.80	3.79	2.60 (OH); 1.59, 1.52, 1.47, 1.38 ($2CMe_2$)	3.0	7.5	2.5	10.0	9.0	7.5		3.0 ($J_{1,OH}$)
(33)	5.62	4.33	4.3	4.0	3.29	3.65	3.63	2.03 (COMe); 1.53, 1.48, 1.42, 1.33 ($2CMe_2$)	3.0	7.5		9.5	9.5	7.0		
(35)	5.14	4.33	4.84	3.94	3.49	3.89	3.62	3.14 (SO_2Me); 1.70, 1.51, 1.40(2) ($2CMe_2$)	6.0	5.0	1.5	10.0	5.5	9.0	10.0	
(38)	5.94	4.76	4.94	4.15	3.76	4.46	4.07	3.12 (SO_2Me); 1.68, 1.60, 1.52, 1.31 ($2CMe_2$)	3.5	<0.5	<0.5	11.0	1.5	4.5	10.0	
(39)	5.90	4.49	4.14	3.9	3.7	4.39	3.85	2.90 (OH); 1.67; 1.58, 1.49, 1.29 ($2CMe_2$)	4.0	<0.5	<0.5		2.0	5.0	10.0	
(43)[d]	4.95	4.53	4.46	4.41	3.50	4.46	3.92	2.92 (OMe); 1.54, 1.45(2), 1.10 ($2CMe_2$)	<0.5	6.0	<0.5	11.5	2.0	5.0	9.5	
(44)	9.54	4.42	4.86	4.00	2.67	3.93	3.76	2.12 (SMe); 1.58, 1.41(2), 1.36 ($2CMe_2$)	3.0	7.5	3.0	11.0	6.0	9.5	12.0	
(46)[d]	3.65[e]	4.38	4.61	3.60	3.08	3.97	3.66	2.40 (OH); 1.83 (SMe); 1.53, 1.46, 1.42, 1.17 ($2CMe_2$)	4.0[f]	8.0	1.5	11.0	5.5	11.0	12.0	

[a] In carbon tetrachloride. [b] Also showed signal in the aromatic region. [c] At 220 MHz. [d] In deuteriobenzene. [e] 1–H = 1′–H. [f] $J_{1,2} = J_{1',2}$.

Table 2. ^{13}C N.m.r. data

Compd.	C-1, C-2, C-3	C-4	C-5	C-6	OMe	O_2CMe_2	$OSCMe_2$	O_2CMe_2	$OSCMe_2$
(**4a**)	83.5, 79.5, 75.6	74.1	37.4	61.3	56.9	109.6, 99.2		29.2, 26.8, 26.2, 18.9	
(**14**)	80.3, 76.0, 74.4	74.3	35.6	61.4		109.9, 99.7		29.5, 28.3, 26.2, 19.2	
(**26a**)	81.0, 76.9, 74.1	71.8	30.5	62.7	57.2	110.9, 99.7		29.5, 25.6(2), 18.9	
(**26b**)	83.5, 77.4, 73.2	68.9	30.9	65.5	56.3	110.5, 100.2		29.7, 26.2, 24.3, 19.0	
(**28**)	103.4, 89.0, 85.8	84.0	53.5	71.8		112.5	93.3	26.4, 24.9	31.6, 31.1
(**31**)[a]	103.5, 80.7, 73.9	79.4	52.5	71.7		112.9	94.9	26.5, 26.4	30.9(2)
(**32**)	77.8, 73.8, 73.4	69.4	30.9	65.0		110.2, 99.9		29.5, 26.1, 24.1, 18.8	
(**43**)	110.0, 88.8, 85.2	83.8	53.2	71.9	54.8	112.4	93.2	26.4, 24.9	31.6, 30.9

[a] Ref. 8.

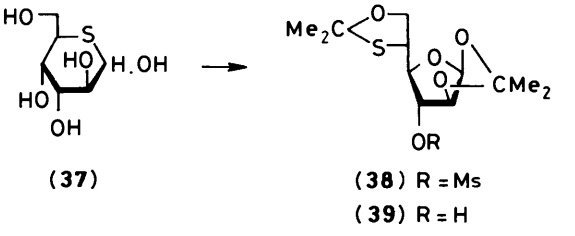


the presence of 1,3-dioxolane and 1,3-oxathiolane[8] ring systems. Oxidation of (**28**) gave the γ-lactone (**29**), confirming the furanose ring system, and the negative rotation of (**28**) and the derived acetate (**30**) suggested the β-configuration as did the lack of coupling between 1-H and 2-H in the ^1H n.m.r. spectra of (**28**) and (**30**). When the known[8] isomeric 1,2:5,6-diacetal (**31**) was left in acidified acetone it was converted into the 2,3:5,6-diacetal (**28**). In these respects the chemistry of 5-thio-D-allose (**27**) is closely similar to that of D-allose itself.[17]

Under kinetic isopropylidenation conditions 2,2-dimethoxypropane in *N*,*N*-dimethylformamide containing toluene-*p*-sulphonic acid, 5-thio-D-allose (**27**) gave a major product and two minor ones. The major product was crystalline and was shown to be 2,3:4,6-di-*O*-isopropylidene-5-thio-β-D-allopyranose (**32**); its ^1H n.m.r. spectrum showed a strong resemblance to that of the β-glucoside (**26b**) and it gave a syrupy acetate (**33**) whose ^1H n.m.r. spectrum differed from that of (**32**) only in the downfield shift of 1-H (see Table 1). One of the minor products was the furanoid diacetal (**28**) and the other was a syrup which was not investigated further. These results may be compared with those[16] for D-allose, which reacted under kinetic conditions (with 2-methoxypropene in place of 2,2-dimethoxypropane) to give mainly pyranose products, 4,6-*O*-isopropylidene-(major) and 2,3:4,6-di-*O*-isopropylidene-β-D-allopyranose (minor) together with a small amount of 2,3:5,6-di-*O*-isopropylidene-β-D-allofuranose.

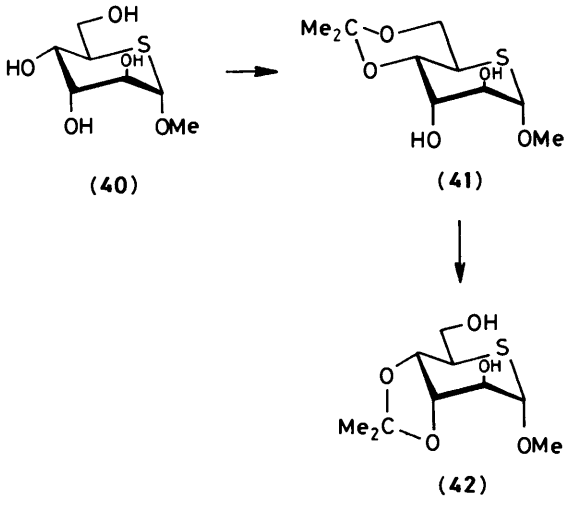
Although the fourth possible 5-thio-D-allose di-isopropylidene derivative, the 1,2:4,6 pyranoid diacetal (**34**), was not obtained in the present work, the related methanesulphonate (**35**) was prepared from the furanoid isomer (**36**) as described earlier for the corresponding *gluco* compound (**22**).

Treatment of 5-thio-D-altrose (**37**) with acetone and toluene-*p*-sulphonic acid or sulphuric acid gave a syrupy product which appeared to be a mixture of two components which could not be separated by chromatography. Methylsulphonylation of the mixture gave a crystalline sulphonate ester which was identified as 1,2-*O*-5,6-*S*,*O*-di-isopropylidene-3-*O*-methylsulphonyl-5-thio-β-D-altrofuranose (**38**) from consideration and comparison

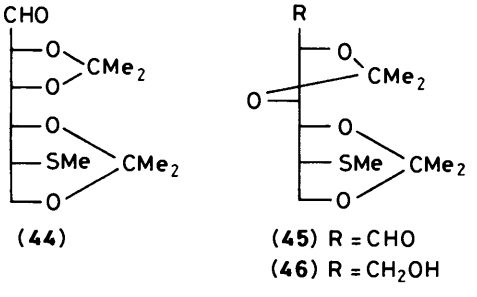


of its ^1H n.m.r. spectrum with that of the parent diacetal (**38**) obtained by saponification of (**39**). Thus the coupling constants for both compounds were similar (see Table 1) and in keeping with a furanose 1,2-acetal with a *cis-trans-trans* arrangement for 1-, 2-, 3-, and 4-H. The location of the sulphonate group of (**38**) and the free hydroxy group of (**39**) at 3-C followed from the large chemical shift difference for 3-H in the spectra of the two compounds. D-Altrose also reacts with acetone to give 1,2:5,6-di-*O*-isopropylidene-β-D-altrofuranose.[18] Reaction of 5-thio-D-

altrose (**37**) with 2,2-dimethoxypropane gave a complex mixture that was not investigated further. The 4,6- and 3,4-*O*-isopropylidene acetals (**41**) and (**42**) of methyl 5-thio-α-D-altropyranoside (**40**) were described in an earlier paper.[1] When the altroside (**40**) was allowed to react with acetone in the presence of toluene-*p*-sulphonic acid, t.l.c. of the reaction mixture suggested that the 4,6-acetal (**41**) was the kinetic product which then isomerised into the 3,4-acetal (**42**). Similar behaviour has been noted in the reaction of methyl α-D-altropyranoside with acetone.[19]

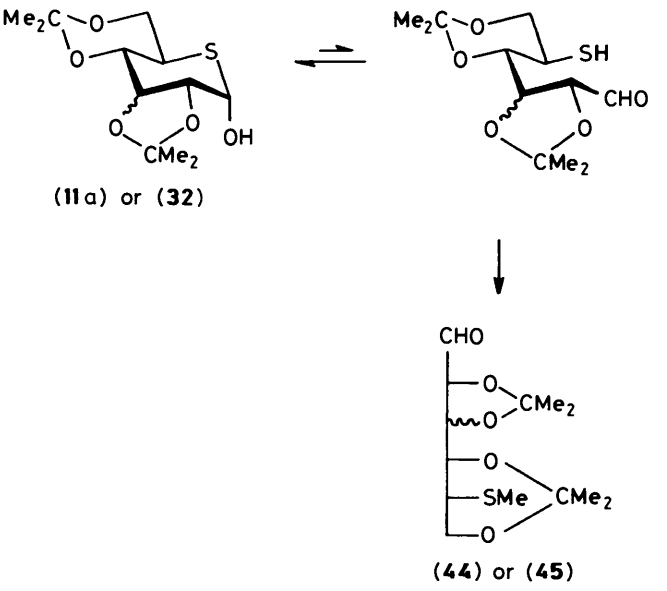


An unusual observation was made when, in the course of proving their structures, the *allo* diacetals (**28**) and (**32**), each containing a free hydroxy group at C–1, were subjected to Purdie methylation. The furanose diacetal (**28**) behaved as expected and gave the related β-glycoside (**43**) which could also be obtained, together with the α-anomer, from the reaction of 5-thio-D-allose (**27**) with methanol, acetone, and 2,2-dimethoxypropane containing an acid catalyst as described[20] for D-allose. Instead of the expected glycoside (**26b**), methylation of the pyranose diacetal (**32**) gave a syrupy product whose ^{1}H n.m.r. spectrum showed the presence of an aldehyde and a thiomethyl group in addition to two isopropylidene groups. The open chain structure (**44**) was assigned to this product. Methylation of the related *gluco* diacetal (**11a**) gave a similar product (**45**) which was further characterised by reduction to the 5-thiohexitol (**46**).



The formation of the aldehydes (**44**) and (**45**) is presumably due to the existence of an equilibrium between the pyranose diacetals (**32**) and (**11a**) and a small amount of open chain forms (see the Scheme) whose thiol groups are preferentially methylated.

In contrast to di-*O*-isopropylidene hexofuranoses, where the 5,6-acetal is more easily hydrolysed, no selectivity was observed in hydrolyses of the *gluco* and *allo* diacetals (**10**) and (**31**) which required relatively vigorous conditions (hot aqueous acetic acid). Evidently the 1,3-oxathiolane group is more resistant to hydrolysis than the corresponding 1,3-dioxolane system. The glucopyranose diacetals (**11**) and (**14**) were much more easily hydrolysed (1 and 4 h, respectively, in cold aqueous acetic acid); the presence of monoacetals during the course of the hydrolyses was observed by t.l.c. but these intermediates were never present in significant amounts.



Scheme.

Experimental

Melting points are uncorrected. Optical rotations were measured in chloroform solution. N.m.r. spectra were recorded, unless otherwise stated, at 90 MHz (^{1}H) and 22.63 MHz (^{13}C) in deuteriochloroform solution with tetramethylsilane as an internal standard. Silica gel was used for t.l.c. (Gelman, ITLC Type SA) and column chromatography (Merck Kieselgel 7734). Organic extracts were dried with anhydrous magnesium sulphate and evaporations were carried out under reduced pressure with bath temperature < 50 °C.

Methyl 2,3:4,6-*Di*-O-*isopropylidene*-5-*thio*-α- *and* β-D-*gluco*-*pyranosides* (**5**).—(*a*) α-*Anomer* (**5a**). Methyl 5-thio-α-D-glucopyranoside (**3a**)[8] (83 mg) was stirred with acetone (8 ml) and 2,2-dimethoxypropane (4 ml) containing toluene-*p*-sulphonic acid (40 mg) at 20 °C for 30 min. The mixture was neutralised (Na_2CO_3), evaporated to dryness and the residue was partitioned between water and dichloromethane. Evaporation of the dried organic extract left a crystalline residue, which recrystallised from light petroleum, to give the diacetal (**5a**)[1] (74 mg, 64%) m.p. and mixed m.p. 133—135 °C.

(*b*) β-*Anomer* (**5b**). Methyl 5-thio-β-D-glucopyranoside (**3b**)[8] (80 mg) was treated as described above for the α-anomer (**3a**) to give the diacetal (**5b**)[1] (50 mg, 45%), m.p. and mixed m.p. 144—145 °C (from di-isopropyl ether).

Reaction of Methyl 5-*thio*-D-*glucopyranosides* (**3**) *with Acetone.*—(*a*) α-*Anomer* (**3a**). A solution of methyl 5-thio-α-D-glucopyranoside (**3a**)[8] (118 mg) in acetone (10 ml) containing toluene-*p*-sulphonic acid (50 mg) was left at 20 °C for 40 min and then neutralised (Na_2CO_3), filtered, and evaporated to give a syrupy product (137 mg). Chromatography on silica and elution with ethyl acetate gave first the diacetal (**5a**) (37 mg,

23%), m.p. and mixed m.p. 133—135 °C, and then the syrupy monoacetal (**4a**)[1] (69 mg, 50%), indistinguishable from authentic material by t.l.c. and n.m.r. spectroscopy.

(*b*) β-*Anomer* (**3b**). Treatment of the β-glucoside (**3b**)[8] (35 mg), as described above for the α-anomer, gave the diacetal (**5b**) (5 mg, 12%), m.p. and mixed m.p. 144—145 °C, and the monoacetal (**4b**)[1] (21 mg, 47%), m.p. and mixed m.p. 137—139 °C.

2,3:4,6-*Di*-O-*isopropylidene*-5-*thio*-α-D-*glucopyranose* (**11a**).—5-Thio-D-glucose (**9**) (200 mg) was stirred with acetone (5 ml) and 2,2-dimethoxypropane (2.5 ml) containing toluene-*p*-sulphonic acid (50 mg) for 20 min at 20 °C. The resultant solution was neutralised (Na_2CO_3) and evaporated, the residue was partitioned between dichloromethane and water. The product (300 mg) from the organic layer crystallised from acetone–di-isopropyl ether to give the *diacetal* (**11a**) (90 mg, 32%), m.p. 214—216 °C, $[\alpha]_D$ + 137° (final) (*c*, 1.0) (Found: C, 51.9; H, 7.3%; M^+, 276.1020. $C_{12}H_{20}O_5S$ requires C, 52.15; H, 7.3%; *M*, 276.1031). Chromatography of the material from the mother liquors on silica and elution with benzene–ether gave first a mobile syrup (70 mg), [$\delta_H(CCl_4$; *inter alia*) 3.23 (3 H, s, OMe), and 1.50 and 1.38 (18 H, 2 × s, ratio 1:5, 3 × CMe_2)], tentatively identified as the ether (**13a**), which decomposed when allowed to stand to give the diacetal (**11a**), m.p. and mixed m.p. 214—216 °C. Further elution gave a mixture (70 mg, 25%) shown by t.l.c. and ^1H n.m.r. spectroscopy, to consist of the diacetals (**10**), (**11a**), and (**14**) in approximately equal amounts.

1-O-*Acetyl*-2,3:4,6-*di*-O-*isopropylidene*-5-*thio*-α- *and* β-D-*glucopyranoses* (**12**).—A solution of the diacetal (**11a**) (72 mg) in pyridine (1.0 ml) and acetic anhydride (0.5 ml) was left for 15 h at 20 °C. The solvents were removed and the residue was dissolved in dichloromethane, and washed with ice-cold dilute sulphuric acid and dilute potassium hydrogen carbonate. The dried solution was evaporated to a syrup (83 mg, 100%) whose ^1H n.m.r. spectrum suggested a 3:1 mixture of the α- and β-tetra-acetates (**12a** and **b**). Crystallisation from light petroleum gave the β-*anomer* (**12b**) (17 mg, 18%), m.p. 172—174 °C, $[\alpha]_D$ − 44° (*c*, 0.7) (Found: C, 53.4; H, 6.9%; M^+, 318.1137. $C_{14}H_{22}O_6S$ requires C, 52.8; H, 7.0%; *M*, 318.1137). The mother liquors were concentrated and cooled to − 10 °C to give the α-*anomer* (**12a**) (35 mg, 42%), m.p. 79—81 °C, $[\alpha]_D$ + 202° (*c*, 0.8) (Found: C, 52.95; H, 6.9%).

1,2-O-5,6-S,O-*Di-isopropylidene*-5-*thio*-α-D-*glucofuranose* (**10**).—(*a*) *From* 5-*thio*-D-*glucose* (**9**). A mixture of (**9**) (50 mg) and acetone (5 ml) containing toluene-*p*-sulphonic acid (25 mg) was stirred at 20 °C for 24 h. The resultant solution was neutralised (Na_2CO_3), filtered, and evaporated. The residue was dissolved in dichloromethane and filtered through a little silica gel. Evaporation of the solvent and crystallisation from light petroleum gave the diacetal (**10**)[8] (25 mg, 36%), m.p. and mixed m.p. 56—58 °C.

(*b*) *From* 1,2:4,6-*di*-O-*isopropylidene*-5-*thio*-α-D-*glucopyranose* (**14**). The diacetal (**14**) (30 mg) was left in acetone (1 ml) containing toluene-*p*-sulphonic acid (10 mg). After 20 h at 20 °C the reaction was worked up as in (*a*) above to give the diacetal (**10**) (25 mg) identified by ^1H n.m.r. spectroscopy and conversion into the more easily crystallised methanesulphonate (**20**),[8] m.p. and mixed m.p. 145—147 °C.

(*c*) *From* 2,3:4,6-*di*-O-*isopropylidene*-5-*thio*-α-D-*glucopyranose* (**11a**). Treatment of the diacetal (**11a**) (35 mg) as described in (*b*) above also gave the diacetal (**10**) (25 mg) again identified as the methanesulphonate (**20**), m.p. and mixed m.p. 145—147 °C.

Isopropylidenation of 5-*Thio*-3-O-*toluene*-p-*sulphonyl*-D-*glucose* (**16**).—A solution of 6-*O*-acetyl-5-*S*-acetyl-1,2-*O*-isopropylidene-5-thio-3-toluene-*p*-sulphonyl-α-D-glucofuranose (**15**)[21] (470 mg) in methanol (10 ml), concentrated hydrochloric acid (0.5 ml), and water (0.5 ml) was heated under reflux for 45 min, neutralised ($PbCO_3$), and filtered. The solvents were removed and the residue was partitioned between water and dichloromethane. Evaporation of the aqueous layer gave 5-thio-3-*O*-*p*-tolylsulphonyl-D-glucose (310 mg) as a syrup. This was dissolved in acetone (3.5 ml) to which 2,2-dimethoxypropane (3.5 ml) and toluene-*p*-sulphonic acid (80 mg) were added. After 15 min at 20 °C the mixture was neutralised (Na_2CO_3), evaporated to dryness, and the residue was partitioned between water and dichloromethane. The residue from the organic layer was chromatographed on silica and eluted with benzene–ether to give first, the *diacetal* (**17**) (140 mg, 33%), m.p. 82—83 °C (from di-isopropyl ether), $[\alpha]_D$ + 109° (*c*, 0.9) (Found: C, 52.5, H, 5.9. $C_{19}H_{26}O_7S$ requires C, 53.0; H, 6.1%). Further elution with ether gave the *monoacetal* (**18**) (409 mg, 10%), m.p. 112—114 °C (decomp.) (from dichloromethane–di-isopropyl ether), $[\alpha]_D$ + 66° (*c*, 0.6) (Found: C, 49.2; H, 5.7. $C_{16}H_{22}O_7S_2$ requires C, 49.2; H, 5.7%).

1,2:4,6-*Di*-O-*isopropylidene*-3-O-*methylsulphonyl*-5-*thio*-α-D-*glucopyranose* (**22**).—(*a*) *From* 6-O-*acetyl*-5-S-*acetyl*-1,2-O-*isopropylidene*-3-O-*methylsulphonyl*-5-*thio*-α-D-*glucofuranose* (**19**). The diacetate (**19**)[8] (400 mg) was converted into syrupy 3-*O*-methylsulphonyl-5-thio-D-glucose (**21**) and then into the diacetal (**22**) (150 mg, 42%) as described above for the corresponding toluene-*p*-sulphonate (**15**). The *diacetal* (**22**) had m.p. 130—131 °C (decomp.) from ethanol, $[\alpha]_D$ + 145° (*c*, 1.5) (Found: C, 43.9; H, 6.25%; M^+, 354.0811. $C_{13}H_{22}O_7S_2$ requires C, 44.0; H, 6.3%; *M*, 354.0807).

(*b*) *From* 1,2-O-5,6-S,O-*di-isopropylidene*-3-O-*methylsulphonyl*-5-*thio*-α-D-*glucofuranose* (**20**). A solution of the furanose (**20**) (50 mg) in trifluoroacetic acid (2 ml) and water (1 ml) was left at 20 °C for 120 min before being evaporated. The resultant 3-*O*-methylsulphonyl-5-thio-D-glucose (**21**) was treated with 2,2-dimethoxypropane, acetone, and toluene-*p*-sulphonic acid as described above, to give the diacetal (**22**) (30 mg, 67%), m.p. 130—131 °C (decomp.).

1,2:4,6-*Di*-O-*isopropylidene*-5-*thio*-α-D-*glucopyranose* (**14**).—(*a*) *From the methanesulphonate* (**22**). A solution of the sulphonate (**22**) (50 mg) in methanol (3 ml) containing sodium methoxide [from sodium (100 mg)] has heated under reflux for 9 h. The mixture was neutralised (CO_2) and evaporated to dryness. The residue was partitioned between water and dichloromethane. Evaporation of the dried organic extract and crystallisation of the residue from light petroleum gave the *diacetal* (**14**) (24 mg, 62%), m.p. 99—101 °C, $[\alpha]_D$ + 180° (*c*, 0.7) (Found: C, 52.5; H, 7.2%; M^+, 276.1031. $C_{12}H_{20}O_5S$ requires C, 52.15; H, 7.3%; *M*, 276.1031).

(*b*) *From the toluene*-p-*sulphonate* (**17**). Similar treatment of the sulphonate (**17**) (50 mg) gave the diacetal (**14**) (12 mg, 30%), m.p. and mixed m.p. 99—101 °C.

1,2,4,6-*Tetra*-O-*acetyl*-3-O-*methylsulphonyl*-5-*thio*-α-D-*glucopyranose* (**23**).—The syrupy methanesulphonate (**21**) (50 mg) was acetylated in the usual way with acetic anhydride (1 ml) and pyridine (2 ml) for 15 h at 20 °C to yield a syrup (75 mg) which crystallised from ethanol to give the *tetra-acetate* (**23a**) (33 mg, 41%), m.p. 105—107 °C, $[\alpha]_D$ + 153° (*c*, 0.5) (Found: C, 40.4; H, 4.8. $C_{15}H_{22}O_{11}S_2$ requires C, 40.7; H, 5.0%).

Isomerisation of the 1,2:4,6-*Di*-O-*isopropylidene*-5-*thio*-α-D-*glucopyranose Sulphonates* (**17**) *and* (**22**).—(*a*) *The toluene*-p-*sulphonate* (**17**). A solution of the sulphonate (**17**) (50 mg) in acetone (1 ml) containing toluene-*p*-sulphonic acid (10 mg) was kept at 20 °C for 5 days. The mixture was neutralised (Na_2CO_3)

and worked up in the usual way to give, after chromatography on silica and elution with benzene–ether, the 1,2:5,6-diacetal sulphonate (**24**) (35 mg, 70%), m.p. and mixed m.p. 91—93 °C (from ethanol).

(*b*) *The methanesulphonate* (**21**). The sulphonate (**21**) (40 mg) was treated as described in (*a*) above to give the isomeric sulphonate (**20**) (35 mg, 87%), m.p. and mixed m.p. 143—145 °C (from ethanol).

Methyl 2,3:4,6-*Di*-O-*isopropylidene*-5-*thio*-D-*allopyranosides* (**26**).—(*a*) α-*Anomer* (**26a**). Methyl 5-thio-α-D-allopyranoside (**25a**)[8] (50 mg) was dissolved, with stirring, in a mixture of acetone (5 ml) and 2,2-dimethoxypropane (2.5 ml) containing toluene-*p*-sulphonic acid (30 mg). After 15 min at 20 °C, the mixture was neutralised ($NaCO_3$) and evaporated to dryness. The residue was partitioned between water and dichloromethane and the dried organic extract was evaporated to give a crystalline residue (85 mg). Chromatography on silica eluting with benzene–ether (9:1) and crystallisation from light petroleum gave the *diacetal* (**26a**) (64 mg, 93%), m.p. 79—81 °C, $[\alpha]_D$ + 220° (*c*, 0.5) (Found: C, 53.9; H, 7.5. $C_{13}H_{22}O_5S$ requires C, 53.8; H, 7.6%).

(*b*) β-*Anomer* (**26b**). Treatment of methyl 5-thio-β-D-allopyranoside (**25b**)[8] (89 mg) as described above for the α-anomer (**25a**) gave the β-*diacetal* (**26b**) (110 mg, 94%) as a syrup $[\alpha]_D$ −51° (*c*, 1.2) (Found: M^+, 290.1201. $C_{13}H_{22}O_5S$ requires *M*, 290.1188).

2,3-O-5,6-S,O-*Di-isopropylidene*-5-*thio*-β-*allofuranose* (**28**).—(*a*) *From* 5-*thio*-D-*allose* (**27**). 5-Thio-D-allose (**27**)[8] (50 mg) was stirred with acetone (5 ml) containing toluene-*p*-sulphonic acid (25 mg) for 3 h at 20 °C. The mixture was neutralised (Na_2CO_3) and worked-up as in the previous experiment to give the *diacetal* (**28**) (60 mg, 85%), m.p. 138—139 °C (from di-isopropyl ether), $[\alpha]_D$ − 83° (final) (*c*, 0.8) (Found: C, 52.3; H, 7.2; M^+, 276.1023. $C_{12}H_{20}O_5S$ requires C, 52.15; H, 7.3%, *M*, 276.1031).

(*b*) *From* 1,2-O-5,6-S,O-*di-isopropylidene*-5-*thio*-α-D-*allofuranose* (**31**). A solution of the diacetal (**31**)[8] (50 mg) in acetone (3 ml) containing toluene-*p*-sulphonic acid (35 mg) was left overnight at 20 °C. Work-up as described above gave the isomeric diacetal (**28**) (43 mg, 86%) m.p. and mixed m.p. 138—139 °C.

2,3-O-5,6-S,O-*Di-isopropylidene*-5-*thio*-D-*allono*-1,4-*lactone* (**29**).—A solution of the diacetal (**28**) (115 mg) in dimethyl sulphoxide (2 ml) and acetic anhydride (1.2 ml) was kept at 50 °C for 8 h. The solvents were evaporated (60 °C/1 mmHg) and the residue was partitioned between dichloromethane and aqueous sodium chloride. The residue from the dried organic extract was chromatographed on silica (10 g), eluting with benzene–ether (4:1), to give the *lactone* (**29**) (74 mg, 64%), m.p. 97—98 °C (from light petroleum), $[\alpha]_D$ − 100° (*c*, 1.0) (Found: C, 52.5; H, 6.7; M^+, 274.0878. $C_{12}H_{18}O_5S$ requires C, 52.5; H, 6.6%; *M*, 274.0875), $\nu_{max.}$ 1 773 cm (CO).

1-O-*Acetyl*-2,3-O-5,6-S,O-*di-isopropylidene*-5-*thio*-β-D-*allofuranose* (**30**).—The diacetal (**28**) (44 mg) was acetylated with acetic anhydride (0.5 ml) and pyridine (1 ml) for 15 h at 20 °C. Work-up in the usual way gave the *acetate* (**30**) (50 mg, 93%), m.p. 90—91 °C (from light petroleum), $[\alpha]_D$ − 94° (*c*, 0.8) (Found: C, 52.5; H, 7.3; M^+, 318.1141. $C_{14}H_{22}O_6S$ requires C, 52.8; H, 7.0%; *M*, 318.1137).

2,3:4,6-*Di*-O-*isopropylidene*-5-*thio*-β-D-*allopyranose* (**32**).—To a stirred solution of 5-thio-D-allose (**27**) (230 mg) in *N*,*N*-dimethylformamide (2 ml) was added acetone (20 ml), 2,2-dimethoxypropane (10 ml) and toluene-*p*-sulphonic acid (250 mg). After 4 min at 40 °C the mixture was neutralised (Na_2CO_3), evaporated to dryness and worked-up as in the previous experiments to give a mixture (230 mg). This was chromatographed on silica (40 g) and eluted with benzene–ether (4:1). First eluted was a syrup (22 mg) and then the diacetal (**28**) (25 mg), m.p. and mixed m.p. 137—140 °C. Last eluted was *diacetal* (**32**) (110 mg, 34%) which, after crystallisation from di-isopropyl ether, had m.p. 173—175 °C, $[\alpha]_D$ + 28° (final), (*c*, 0.4) (Found: C, 52.2; H, 6.9. $C_{12}H_{20}O_5S$ requires C, 52.15; H, 7.3%).

1-O-*Acetyl*-2,3:4,6-*di*-O-*isopropylidene*-5-*thio*-β-D-*allopyranose* (**33**).—The diacetal (**33**) (37 mg) was acetylated in the usual way with acetic anhydride (0.3 ml) in pyridine (0.5 ml) for 15 h at 20 °C to give the *acetate* (**33**) as a syrup (38 mg, 88%), $[\alpha]_D$ − 87° (*c*, 1.2) (Found: M^+, 318.1146. $C_{14}H_{22}O_6S$ requires *M*, 318.1137).

1,2:4,6-*Di*-O-*isopropylidene*-3-O-*methyl-sulphonyl*-5-*thio*-α-D-*allopyranose* (**35**).—A solution of the methanesulphonate (**36**)[8] (250 mg) in trifluoroacetic acid (7.5 ml) and water (0.5 ml) was kept at 20 °C for 30 min. The solvents were evaporated and the residue was partitioned between water and dichloromethane. Evaporation of the aqueous extract gave crude 5-thio-D-allose 3-O-methanesulphonate which was stirred with acetone (4 ml) and 2,2-dimethoxypropane (4 ml) containing toluene-*p*-sulphonic acid (0.6 g) for 40 min at 20 °C. Work-up as in earlier experiments and chromatography on silica (10 g), eluting with benzene–ether (9:1), gave first a syrup (20 mg) and then the *diacetal sulphonate* (**35**) (90 mg, 36%), m.p. 97—99 °C (decomp.) (from di-isopropyl ether), $[\alpha]_D$ + 93° (*c*, 0.5) (Found: C, 43.8; H, 6.1. $C_{13}H_{22}O_7S_2$ requires C, 44.0; H, 6.3%).

1,2-O-5,6-S,O-*Di-isopropylidene*-3-O-*methylsulphonyl*-5-*thio*-β-D-*altrofuranose* (**38**).—5-Thio-D-altrose (**37**)[1] (150 mg) was stirred with acetone (7 ml) containing toluene-*p*-sulphonic acid (150 mg) for 24 h at 20 °C [a similar result was obtained using sulphuric acid (0.3 ml) for 20 min at 20 °C]. Neutralisation (Na_2CO_3) and work-up as in earlier experiments gave a syrupy product (137 mg) whose ^1H n.m.r. spectrum suggested it to be a mixture of two components in the ratio 9:1 in which the major product was the diacetal (**39**). Attempts to isolate a pure sample by chromatography were unsuccessful. The mixture was dissolved in dichloromethane (4 ml) containing trimethylamine (0.5 ml) and cooled to 0 °C while a solution of methanesulphonyl chloride (0.15 ml) in dichloromethane (4 ml) was added. After 15 min the mixture was washed sequentially with dilute hydrochloric acid and dilute potassium hydrogen carbonate, dried, and evaporated to give a crystalline residue (130 mg). This was further purified by passage through silica in benzene–ether (4:1) to give the *sulphonate* (**38**) (166 mg, 61%), m.p. 131—133 °C (from ethanol), $[\alpha]_D$ − 29° (*c*, 1.1) (Found: C, 43.8; H, 6.2%; M^+, 354.0827. $C_{13}H_{22}O_7S_2$ requires C, 44.0; H, 6.3%; *M*, 354.0807).

1,2-O-5,6-S,O-*Di-isopropylidene*-5-*thio*-β-D-*altrofuranose* (**39**).—A solution of the methanesulphonate (**38**) (80 mg) in methanol (5 ml) containing sodium methoxide [from sodium (80 mg)] was heated under reflux for 2 h. The mixture was neutralised (CO_2), evaporated to dryness and partitioned between water and dichloromethane. The dried organic extract was evaporated and the residue was passed through a little silica in benzene–ether (4:1) to give the *diacetal* (**39**) (55 mg, 85%), m.p. 99—101 °C (from light petroleum), $[\alpha]_D$ − 37° (*c*, 1.2) (Found: C, 52.1; H, 7.2%; M^+, 276.1017. $C_{12}H_{20}O_5S$ requires C, 52.15; H, 7.3%; *M*, 276.1031).

Methyl 2,3-O-5,6-S,O-*Di-isopropylidene*-5-*thio*-β-D-*allofuranoside* (**43**).—(*a*) *From* 5-*thio*-D-*allose* (**27**). A solution of 5-thio-

D-allose (**27**) (85 mg) in a mixture of methanol (0.6 ml), acetone (0.6 ml), 2,2-dimethoxypropane (1 ml) and concentrated hydrochloric acid (90.02 ml) was heated under reflux for 2 h. The mixture was neutralised (Na_2CO_3) and evaporated to dryness. The residue was partitioned between water and dichloromethane and the organic extract was dried and evaporated to give a mixture (120 mg). Chromatography on silica (15 g) and elution with benzene–ether (9:1) gave first the β-*alloside* (**43**) (80 mg, 64%), m.p. 92—95 °C (from light petroleum), $[\alpha]_D$ − 105° (*c*, 0.9) (Found: C, 53.9; H, 7.5%; M^+, 290.1200. $C_{12}H_{22}O_5S$ requires C, 53.8; H, 7.6%; *M*, 290.1188). Further elution gave a syrup (25 mg), tentatively identified as the α-anomer, $[\alpha]_D$ − 16° (*c*, 1.1), [δ_H (*inter alia*) 3.46 (3 H, s, OMe) and 1.70, 1.61, 1.57, and 1.36 (12 H, 4 × s, 2 × CMe_2)].

(*b*) *From the diacetal* (**32**). A mixture of the diacetal (**32**) (115 mg), freshly prepared dry silver oxide (150 mg) and iodomethane (10 ml) was heated and stirred under reflux for 5 h. The cooled mixture was filtered, evaporated to dryness, and the residue chromatographed as in (*a*) to give first the β-alloside (**43**) (95 mg, 79%) m.p. and mixed m.p. 92—95 °C, and the α-anomer (20 mg).

2,3:4,6-*Di*-O-*isopropylidene*-5-S-*methyl*-5-*thio*-aldehydo-D-*allose* (**44**).—The diacetal (**32**) (240 mg) was methylated using silver oxide (302 mg) and iodomethane (10 ml) as described in the previous experiment. Chromatography of the product on silica (15 g) eluting with benzene–ether (2:1) gave the *sulphide* (**44**) (83 mg, 33%) as a syrup, $[\alpha]_D$ − 21° (*c*, 1.1) (Found: M^+, 290.1202. $C_{13}H_{22}O_5S$ requires *M*, 290.1188).

2,3:4,6-*Di*-O-*isopropylidene*-5-S-*methyl*-5-*thio*-D-*glucitol* (**46**).—The *gluco*-diacetal (**11**) (70 mg) was methylated as described above for the *allo*-isomer (**44**). The resultant *aldehydo* derivative (**45**) (65 mg), $[\alpha]_D$ − 40° (*c*, 1.1), [δ_H (*inter alia*) 9.77 (1 H, d, *J* 2 Hz, 1-H), 2.12 (3 H, s, SMe), and 1.40 (12 H, s, 2 × CMe_2)], was reduced in ethanol (2 ml) and water (2 ml) with sodium borohydride (100 mg) overnight at 20 °C. The solvents were removed and the residue was partitioned between dichloromethane and water. The organic extract was dried and evaporated to give the *glucitol* (**46**) (60 mg, 81%) as a syrup, $[\alpha]_D$ − 51° (*c*, 0.9) (Found: M^+, 292.1378. $C_{13}H_{24}O_5S$ requires *M*, 292.1344).

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