Carbohydrate Research, 119 (1983) 85–93
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE PREPARATION AND X-RAY CRYSTALLOGRAPHIC CHARACTERISATION OF METHYL 4,6-*O*-BENZYLIDENE-2,3-DI-*C*-METHYL-2-*O*-(METHYLTHIO)METHYL-α-D-ALLOPYRANOSIDE, AND ITS CONVERSION INTO METHYL 2,3-DIDEOXY-2,3-DI-*C*-METHYL-α-D-*glycero*-HEXOPYRANOSID-4-ULOSE

VERNON G. S. BOX*†, LYNDA I. BOX, EARLE V. E. ROBERTS,
Chemistry Department, University of The West Indies, Kingston 7 (Jamaica)

JOHN F. BLOUNT, AND LOUIS J. TODARO
Hoffmann La-Roche, Nutley, New Jersey 07110 (U.S.A.)

(Received May 13th, 1982, accepted for publication in revised form, October 2nd, 1982)

ABSTRACT

The preparation of the title compound from methyl 4,6-*O*-benzylidene-2-*C*-methyl-2-*O*-(methylthio)methyl-α-D-*ribo*-hexopyranosid-3-ulose and its single-crystal X-ray structural characterisation is described. Consistent with the chemistry of methyl 4,6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose[1], the Grignard reduction of the two 2-*C*-methyl-α-D-*ribo*-hexopyranosid-3-uloses examined produced *allo* compounds stereoselectively. Methyl 4,6-*O*-benzylidene-2,3-di-*C*-methyl-2-*O*-(methylthio)methyl-α-D-allopyranoside was dehydrated to the hex-3-enopyranoside[2], which was converted into methyl 2,3-dideoxy-2,3-di-*C*-methyl-α-D-*glycero*-hex-2-enopyranosid-4-ulose by an acid-catalysed fragmentation-process[2].

INTRODUCTION

The synthesis of singly branched sugars has been thoroughly explored. We wished to prepare, by Grignard reaction, some doubly branched-chain sugars, in order to observe the stereochemical consequences of reducing a carbonyl group flanked by a carbon atom bearing a methyl and a free or derivatised hydroxyl group. This report describes Grignard reactions of the glycos-3-uloses **1** and **2** with methylmagnesium iodide.

RESULTS AND DISCUSSION

The reduction of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*ribo*-hexo-

*To whom correspondence should be addressed.
†Present address: Schering Corporation, 60 Orange St., Bloomfield, New Jersey 07003, U.S.A.

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pyranosid-3-ulose (**3**) by hydride donors and Grignard reagents has been investigated[1] and shown to proceed stereospecifically to yield *allo* compounds. It therefore seemed reasonable to expect the *allo* compounds **4** and **5** by reduction of **1** and **2**, respectively, as the major, if not the sole products.

Inch *et al.*[3] demonstrated that the stereoselectivity of reduction of glycosuloses may be affected by substituents on the adjacent carbon atoms. Our investigation would not only reveal the effect of replacement of H-2 by a methyl group, but also demonstrate the effect of the (methylthio)methyl group on the stereoselectivity of the Grignard reduction.

Oxidation of **6** with dimethyl sulphoxide–phosphorus pentaoxide provided **2** (ref. 4) in 53% yield, whereas dimethyl sulphoxide–acetic anhydride gave **1** in 39% yield.

The reaction of **1** with methylmagnesium iodide in 1:1 ether–benzene provided 89% of one compound, which was converted into the corresponding diol by cleavage of the (methylthio)methyl ether with methyl iodide–potassium carbonate in acetone[5].

The Grignard reduction of **2** with methylmagnesium iodide in ether–benzene gave two products, one (79%) identical with the previously prepared diol, and an isomeric diol in 18% yield.

Both diols were inert to buffered sodium periodate solutions and were largely recovered after 7 days[6]. Both diols resisted benzoylation and acetylation, even when the reactions were attempted in the presence of 4-dimethylaminopyridine[7]. Neither compound gave an isopropylidene acetal with acetone–anhydrous copper(II) sulphate, and neither gave isolable carbonates from phosgene–pyridine at 0°.

The single-crystal X-ray structural analysis of the (methylthio)methyl ether obtained from the Grignard reaction of the glycosulose 1, showed that ths ether was the *allo* compound **4**. A stereoscopic ORTEP drawing of **4** is given in Fig. 1, and a list of the final atomic parameters is presented in Table I.

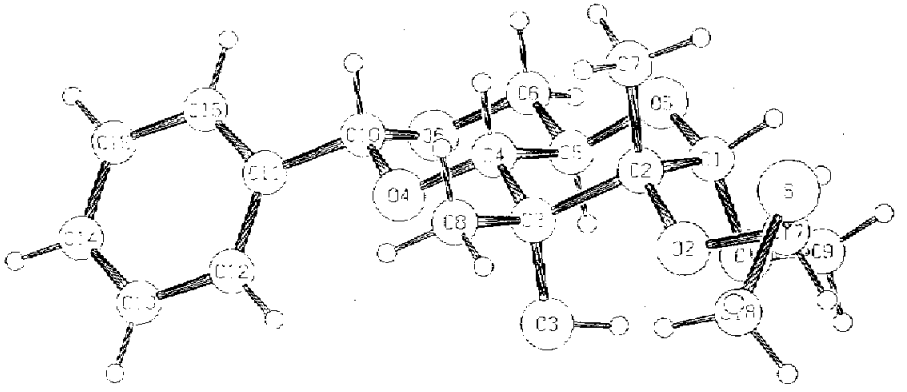


Fig. 1. Stereoscopic ORTEP drawing of compound **4**.

TABLE I

FINAL ATOMIC PARAMETERS FOR **4**, WITH STANDARD DEVIATIONS IN PARENTHESES

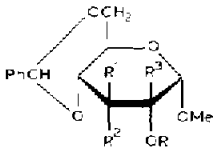
Atom	*X*	*Y*	*Z*	*B*
S	0.2716(2)	0 0409(1)	0 3775(1)	[a]
O-1	0.6550(4)	0 2446(3)	0 2343(2)	[a]
O-2	0.4083(4)	0.2149(2)	0.3273(2)	[a]
O-3	0 4721(4)	0.4087(2)	0 2926(2)	[a]
O-4	0.6638(3)	0.5309(2)	0 3877(2)	[a]
O-5	0 8288(4)	0 2834(2)	0.3344(2)	[a]
O-6	0.9275(4)	0 5526(2)	0 3555(2)	[a]
C-1	0 6939(6)	0 2287(4)	0.3107(3)	[a]
C-2	0.5501(6)	.0 2532(3)	0 3624(3)	[a]
C-3	0 5204(5)	0.3726(3)	0.3650(2)	[a]
C-4	0 6784(6)	0 4219(3)	0.3859(3)	[a]
C-5	0.8055(6)	0.3920(3)	0.3300(3)	[a]
C-6	0 9565(6)	0.4451(4)	0.3513(3)	[a]
C-7	0.5766(6)	0 2060(4)	0 4409(3)	[a]
C-8	0.3918(6)	0 4006(4)	0.4219(3)	[a]
C-9	0.7692(8)	0 2080(5)	0 1821(3)	[a]
C-10	0.8082(6)	0.5766(3)	0 4095(3)	[a]
C-11	0 7942(6)	0 6901(3)	0 4143(3)	[a]
C-12	0 6730(7)	0.7430(4)	0.3788(3)	[a]
C-13	0.6642(8)	0 8491(4)	0.3858(3)	[a]
C-14	0 7725(9)	0 9020(4)	0.4274(4)	[a]
C-15	0.8916(9)	0 8499(5)	0 4625(4)	[a]
C-16	0 9018(7)	0 7437(4)	0 4562(3)	[a]
C-17	0 3967(6)	0.1084(4)	0.3123(3)	[a]
C-18	0.0877(8)	0.0977(5)	0 3516(4)	[a]
HO-3	0 523	0 361	0 255	5.0
H-1	0 718	0.154	0.317	5 0
H-4	0.710	0.398	0.438	4.0
H-5	0 774	0 412	0.277	5.0
H-6A	0.994	0 419	0.402	8.0
H-6B	1.038	0 431	0.312	8 0
H-7A	0 589	0.130	0.436	6.0
H-7B	0 484	0 221	0.475	6 0
H-7C	0.674	0.236	0 464	6.0
H-8A	0.377	0 477	0 423	6.0
H-8B	0.423	0.377	0.474	6 0
H-8C	0 291	0 367	0 407	6 0
H-9A	0 734	0 222	0.129	10.0
H-9B	0 783	0.132	0 189	10.0
H-9C	0 872	0.244	0 192	10 0
H-10	0.840	0 549	0.461	5.0
H-12	0.593	0 705	0.348	7.0
H-13	0 577	0 887	0 360	8 0
H-14	0 765	0 978	0 432	8.0
H-15	0.972	0 888	0.493	8 0
H-16	0 989	0 706	0 483	7 0
H-17A	0.505	0 078	0.315	6.0
H-17B	0 354	0 099	0 259	6.0
H-18A	0 002	0.068	0 384	9.0
H-18B	0 066	0 084	0 296	9.0
H-18C	0.093	0 174	0 360	9.0

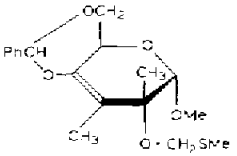
[a] Anisotropic thermal parameters are given in Table III

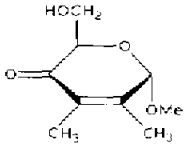
The Grignard reactions of glycosuloses **1** and **2** thus both provided *allo* compounds, the reaction of **1** proceeding stereospecifically and that of **2** stereoselectively. The axial methyl group at C-2, is therefore, not a very important factor in determining the mode of addition of the Grignard reagent to the caronyl group at C-3.

The inertness of the diols **5** and **7** to the reactions described must be attributable to the tertiary nature of these groups and to the severe crowding about C-2 and C-3 (ref. 6).

The stereospecific formation of the *allo* compound **4** was useful, because this compound is ideally suited for transformation into a hex-2-enopyranosid-4-ulose by the dehydration–fragmentation sequence that we have described[2].







8 9

1 R = CH_2—S—CH_3, R^1 and R^2 = O, R^3 = CH_3
2 R = H, R^1 and R^2 = O, R^3 = CH_3
3 R = Bz, R^1 are R^2 = O, R^3 = H
4 R = CH_2—S—CH_3, R^1 = CH_3, R^2 = OH, R^3 = CH_3
5 R = H, R^1 = CH_3, R^2 = OH, R^3 = CH_3
6 R = H, R^1 = OH, R^2 = H, R^3 = CH_3
7 R = H, R^1 = OH, R^2 = CH_3, R^3 = CH_3
10 R = H, R^2 = O—SO—S—CH_3, R^1 = R^3 = CH_3
11 R^2 and R = O—SO—, R^1 = R^3 = CH_3

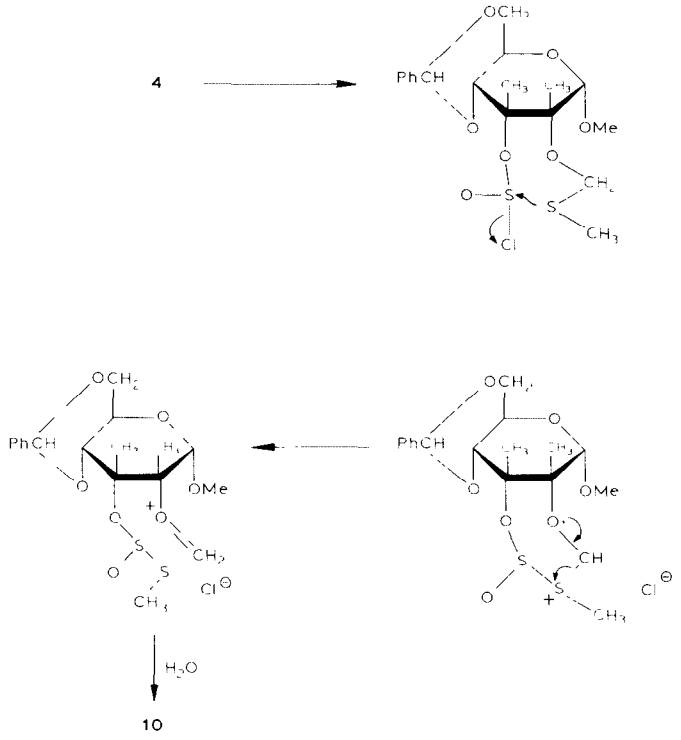
Exposure of the alcohol **4** to thionyl chloride in pyridine at 0°, followed by aqueous isolation, afforded three compounds identified as **8**, **9**, and **10**, in 64, 4, and 12% yields, respectively.

The identities of compounds **8** and **9** were obvious from examination of their i.r., u.v., and n.m.r. spectra. Furthermore, treating the alkene **8** with very dilute methanolic hydrogen chloride gave the hex-2-enopyranosid-4-ulose **9** in 87% yield, as expected[2].

The crystalline product **10** showed signals in its n.m.r. spectrum at δ 1.60, 1.73, 2.15, and 3.40 (each 3 H, s) corresponding to the 3-*C*-methyl, 2-*C*-methyl, an -*S*-methyl, and an -*O*-methyl groups, respectively. Other signals observed were at δ 4.45, 5.53 (each 1 H, s, H-1 and C*H*-Ph, respectively) and a multiplet centred at δ 7.37 (aromatic protons). The n.m.r. spectrum showed signals of only four other protons in the δ 3.5–4.5 region, corresponding to H-4, H-5, H-6, and H-6′. The absence of any signal corresponding to the two protons of an -O-CH_2SCH_3 group unequivocally ruled out the presence of the (methylthio)methyl group.

The low-resolution mass spectrum of compound **10** showed a highest-mass peak of *m/z* 356, corresponding to an efficient loss of CH_3SH to give the cyclic sul-

phite **11**. Indeed, combustion analysis of **10** gave data corresponding to those expected for the cyclic sulphite. However, the fact that the n.m.r. spectrum of **10** showed signals for the -SCH_3 group unequivocally ruled out the formulation of this compound as a cyclic sulphite, and taken with the data already given, leads to formulation of **10** as the unusual thiosulphite structure shown. The formation of **10** might occur as shown in Scheme 1.



Scheme 1

This preparation of the doubly branched hex-2-enopyranosid-4-ulose **9** should be generally applicable to the preparation of other doubly branched enones.

The key reaction of the sequence was the protection of the 2-hydroxyl group as the (methylthio)methyl ether, before reaction of the glycos-3-ulose with the Grignard reagent, and hence the stereospecific or stereoselective preparation of the desired, partially protected sugar having the *allo* configuration. It has been suggested[8] that all *allo* compounds having a hydroxyl group at C-3 will undergo dehydration, in E1 or E2 reactions, towards C-4, and there are now several examples of this reaction pathway. Thus the reactions of the sequence seem to be generally applicable to the syntheses of doubly branched-chain hex-2-enopyranosid-4-uloses.

EXPERIMENTAL

General methods. — Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded with a Perkin–Elmer 735 B i.r. spectrophotometer and are for chloroform solutions, unless otherwise stated. N.m.r. spectra were recorded with a Jeol JNM-PMX60 spectrometer and are for chloroform-*d* solutions unless otherwise stated. Chemical shifts were measured relative to tetramethylsilane as the internal standard. Specific rotations were recorded for chloroform solutions, unless otherwise stated. Thin-layer and preparative-layer chromatography were effected on silica gel $PF_{254+366}$ (Merck). Chromatograms were observed under a Hanovia Chromatolite u.v. lamp and spots made visible by exposure to iodine vapour. The petroleum ether used as a solvent or eluant had a boiling range 60–80°. Solutions were dried with sodium sulphate. Evaporations were conducted with a rotary evaporator (Buchi) evacuated by a water pump.

*Methyl 4,6-O-benzylidene-2-C-methyl-2-O-(methylthio)methyl-α-*D*-ribo-hexopyranosid-3-ulose* (**1**). — Acetic anhydride (47 mL) was added to a solution of methyl 4,6-*O*-benzylidene-2-C-methyl-α-D-glucopyranoside (**6**, 4.7393 g, 16.0 mol) in dimethyl sulphoxide (75 mL). The mixture was stirred for 18 h at room temperature and then poured into cold, saturated sodium carbonate (600 mL). The aqueous solution was extracted with chloroform (8 × 100 mL) and the organic solution washed with brine (2 × 150 mL), dried, and evaporated to a yellow gum (6.2794 g). Column chromatography (2:1 toluene–ethyl acetate) yielded yellow crystals (2.2856 g, 38.6%) of the required ketone **1**. Recrystallisation from chloroform–petroleum ether yielded colourless plates, m.p. 178–181°, $[\alpha]_D^{25}$ +97.6° (*c* 1.09), ν_{max} 1756 cm^{-1}; n.m.r. δ 1.63 (3 H, s, C-CH_3), 2.27 (3 H, s, S-CH_3), 3.42 (3 H, s, O-CH_3), 4.82 (1 H, s, H-1), 4.93 (2 H, s, O-CH_2-S), 5.58 (1 H, s, PhC*H*), and 7.40 (5 H, m, C_6H_5).

Anal. Calc. for $C_{17}H_{22}O_6S$: C, 57.62; H, 6.26; S, 9.04. Found: C, 58.06; H, 6.11; S, 9.25.

*Methyl 4,6-O-benzylidene-2-C-methyl-α-*D*-ribo-hexopyranosid-3-ulose* (**2**). — A solution of methyl 4,6-*O*-benzylidene-2-C-methyl-α-D-glucopyranoside (**6**, 0.7651 g, 2.6 mmol) in dimethyl sulphoxide (5 mL) was added to a cooled suspension of phosphorus pentaoxide (0.25 g, 1.8 mmol) in dimethyl sulphoxide (10 mL). The stirred mixture was allowed to warm to room temperature and, after 23 h, the brown solution was poured into cold, saturated sodium carbonate solution (100 mL) and extracted with chloroform (5 × 50 mL). The crude gum obtained (0.7434 g) was resolved by p.l.c. (2:1 toluene–ethyl acetate), providing white crystals of **2** (0.3550 g, 53% based on reacted starting material), and **6** (90.6 mg). Recrystallisation of **2** from ethyl acetate–petroleum ether gave white crystals, m.p. 173–174°, $[\alpha]_D^{28}$ +90.6° (*c* 0.88); ν_{max} 1744 cm^{-1}; n.m.r. δ 1.57 (3 H, s, C-CH_3), 3.40 (3 H, s, O-CH_3), 4.73 (1 H, s, H-1), 5.57 (1 H, s, Ph-CH), and 7.40 (5 H, m, C_6H_5).

Anal. Calc. for $C_{15}H_{18}O_6$: C, 61.21; H, 6.17; O, 32.62. Found: C, 61.29; H, 6.32; O, 32.39.

Methyl 4,6-O-benzylidene-2,3-di-C-methyl-2-O-(methylthio)methyl-α-D-allopyranoside (**4**). — A solution of compound **1** (1.0066 g, 2.7 mmol) in sodium-dried benzene (100 mL) was added with stirring to an ethereal solution of methylmagnesium iodide, made from magnesium (2.00 g, 83.3 mmol) and methyl iodide, (6.4 mL, 102.8 mmol) in sodium-dried ether (100 mL), and the mixture was stirred for 18 h at room temperature, after which time it was poured into cold, saturated ammonium chloride (300 mL). The organic layer was separated and the aqueous solution extracted with chloroform (4 × 100 mL). The combined organic solutions were washed with brine (2 × 100 mL), dried, and evaporated to a pale-yellow gum (1.112 g) which, on being kept in a desiccator overnight, gave **4** as crystals (0.9372 g, 89.1%) which were recrystallised from chloroform–petroleum ether to give colourless plates, m.p. 106–107°, $[\alpha]_D^{28}$ +16.6° (*c* 1.45); ν_{max} 3580 cm^{-1}; n.m.r δ 1.30, 1.40, 2.23 and 3.42 (each 3 H, s, 2 × C-CH_3, S-CH_3, and O-CH_3 respectively), 4.68 (2 H, s, O-CH_2-S), 4.75 and 5.53 (each 1 H, s, H-1 and PhCH-), and 7.40 (5 H, m, C_6H_5); *m/z* 370 (M^+).

Anal. Calc. for $C_{18}H_{26}O_6S$: C, 58.37; H, 7.08; O, 25.92; S, 8.64. Found: C, 57.76; H, 7.13; O, 25.50; S, 8.43.

Methyl 4,6-O-benzylidene-2,3-di-C-methyl-α-D-allopyranoside (**5**). — Methyl iodide (0.15 mL, 2.4 mmol) was added to a suspension of potassium carbonate (0.1247 g, 0.9 mmol) in a solution of compound **4** (0.1426 g, 0.4 mmol) in acetone (5 mL), and the mixture was stirred for 8 days at room temperature. After removal of the acetone, the solid was dissolved in water and the aqueous solution extracted with chloroform (5 × 5 mL). The organic solution was dried and evaporated to a solid (0.1376 g) that was purified by column chromatography (4:1 benzene–ethyl acetate) to yield **5** as crystals (90.0 mg, 75.3%), m.p. 97–117°. Recrystallisation from chloroform–petroleum ether gave crystals, m.p. 164–166°, $[\alpha]_D^{28}$ +54.6° (*c* 2.01); ν_{max} 3530 and 3480 cm^{-1}; n.m.r. δ 1.28 (6 H, s, 2 × C-CH_3), 3.40 (3 H, s, O-CH_3), 4.37 (1 H, s, H-1), and 5.50 (1 H, s, Ph-CH); *m/z* 310 (M^+).

Anal. Calc. for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15; O, 30.93. Found: C, 62.15; H, 7.33; O, 30.52.

Methyl 4,6-O-benzylidene-2,3-di-C-methyl-α-D-gluco- and allopyranosides (**7**) *and* (**5**). — A slurry of compound **2** (0.7198 g, 2.5 mmol) in sodium-dried benzene (100 mL) was added to the Grignard reagent prepared from magnesium (2.0 g, 83.3 mmol) and methyl iodide (5 mL, 80.3 mmol) in diethyl ether (75 mL). The mixture was stirred for 24 h at room temperature and then poured into cold, saturated ammonium chloride (100 mL). The organic solution was separated, and the aqueous solution extracted with ethyl acetate (5 × 25 mL). The combined organic solutions were dried and evaporated to a yellow gum (1.0685 g) that was shown by t.l.c. (2:1 toluene–ethyl acetate) to consist of two components. P.l.c. (2:1 toluene–ethyl acetate) yielded white crystals of **5** (0.5987 g, 78.9%) and a colourless gum **7**, (0.1386 g, 18.3%).

Compound **7** showed ν_{max} 3550 and 350 cm^{-1}; n.m.r. δ 1.40, 1.45 and 3.37 (each 3 H, s, 2 × C-CH_3 and O-CH_3), 4.40 (1 H, s, H-1), and 5.47 (1 H, s, Ph-CH).

*Methyl 4,6-O-benzylidene-3-deoxy-2,3-di-C-methyl-2-O-(methylthio)methyl-α-*D*-erythro-hex-3-enopyranoside* (**8**) *and methyl 4,6-O-benzylidene-2,3-di-C-methyl-3-O-(methylthio)sulphinyl-α-*D*-allopyranoside* (**10**). — Thionyl chloride (0.1 mL, 1.378 mmol) was added to a cooled solution of **2** (0.2930 g, 0.792 mmol) in pyridine (10 mL) and the solution was allowed to warm up to, and was stirred at, room temperature for 2.5 h, and then it was poured into brine (100 mL) and extracted with ethyl acetate (2 × 100 mL). The organic solution was washed with brine (150 mL), dried, and evaporated to a brown gum (0.2833 G), which was readily resolved by p.l.c. (toluene–ethyl acetate, 2:1) to yield **8** (0.1806 g, 64.2%) as a colourless gum; **10** (0.0338 g, 12.5%) as white crystals, which were recrystallised from acetone–light petroleum to give plates m.p. 219–222°; and **9** (0.0054 g, 3.7%).

The alkene **8** showed signals in the n.m.r. spectrum at δ 1.72 (3 H, d, *J* 2.0 Hz, 3-CCH_3, long-range coupled to H-5), 1.42, 2.20 and 3.47 (each 3 H, s, 2-CCH_3, -SCH_3, and -OCH_3 respectively), 4.33 (1 H, m, H-5), 4.45 and 4.82 (each 1 H, d, *J* 11.0 Hz, -O-CH_2S), 4.58 and 5.47 (each 1 H, s, H-1 and PhC*H* respectively), and 7.40 (5 H, m).

Compound **8** was unstable at room temperature.

The *allo* compound **10** was recrystallised from acetone–water as white needles, m.p. 163–169°; *m/z* 356 (M^+); ν_{max} 3400 cm^{-1}; n.m.r. δ 1.60, 1.73, 2.15 and 3.40 (each 3 H, s, 3-CCH_3, 2-CCH_3, -SCH_3, and -OCH_3, respectively), 4.45 and 5.53 (each 1 H, s, H-1 and Ph-C*H*, respectively), and 7.37 (5 H, m).

*Methyl 2,3-dideoxy-2,3-di-C-methyl-α-*D*-glycero-hex-2-enopyranosid-4-ulose* (**9**). — Concentrated hydrochloric acid (0.1 mL) was added to a solution of **8** (0.1159 g, 0.329 mmol) in methanol (10 mL) and the solution stirred for 20 min at room temperature. Concentrated aqueous ammonia solution (5 mL) was added to the mixture, which was then evaporated to a solid (0.0581 G). Purification by p.l.c. (toluene–ethyl acetate, 7:1) yielded **9** (0.0530 g, 86.6%), which was recrystallised from chloroform–light petroleum to yield needles m.p. 114–115°, *m/z* 186 (M^+); ν_{max} 3175 and 1667 cm^{-1}; λ_{max} 235 and 270 nm (log ε 4.07 and 2.80 respectively); n.m.r. δ 1.78 and 1.95 (each 3 H, broadened s, $W_{1/2}$ 3.0 Hz, 3-CCH_3 and 2-CCH_3 respectively), 3.52 (3 H, s, $W_{1/2}$ 1.5 Hz, -OCH_3), 2.47 (1 H, m, -OH), 3.95 (2 H, d, *J* 4.0 Hz, -CH_2), 4.38 (1 H, t, *J* 4.0 Hz, H-5), and 4.93 (1 H, s, H-1).

Anal. Calc. for $C_9H_{14}O_4$: C, 58.05; H, 7.58; O, 34.37. Found: C, 57.78; H, 7.51; O, 34.2.

X-Ray crystallographic analysis of compound **4**. — Crystals of compound **4** were grown from chloroform–hexane and a crystal of ~0.12 × 0.12 × 0.25 mm was used in the analysis.

The crystal data are summarised in Table II. The intensity data were measured with a Hilger–Watts diffractometer (Ni-filtered Cu$K\alpha$ radiation, $\theta - 2\theta$ scans, pulse-height discrimination), and were corrected for absorption. Of the 1517 independent reflections for $\theta < 57°$, 1208 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure[9] and was refined by full-matrix least squares. One reflection which was strogly affected by extinction

TABLE II

CRYSTAL DATA

Formula	$C_{18}H_{26}O_6S$
Formula weight	370.46
Space group	$P2_12_12_1$
a	8.498(5) Å
b	13.016(4) Å
c	17.472(5(Å
Z	4
d_{calc}	1.273 g.cm^{-3}
μ (CuKα)	17.1 cm^{-1}

was excluded from the final refinement and difference map. In the final refinement, anisotropic thermal parameters were used for the nonhydrogen atoms. The hydrogen atoms were included in the structure-factor calculations but their parameters were not refined. The final discrepancy indices were $R = 0.037$ and w$R = 0.037$ for the remaining 1207 observed relections. The final difference-map has no peaks greater than $\pm$ 0.2 eÅ^{-3}.

The absolute configuration of compound **4** is based on the anomalous scattering of the sulphur atom and was established by refining data to consider both enantiomers. The final, weighted *R* values were 0.0366 for the configuration depicted and 0.0436 for its antipode. Thus, by Hamilton's test[10], the configuration shown corresponds to the absolute configuration*.

ACKNOWLEDGMENT

We thank Dr. P. S. Manchand for his interest in this work.

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*Final anisotropic thermal parameters, bond lengths, bond angles, torsion angles, and final structure-factors for compound **4** are listed in Tables 3–7, respectively, and can be obtained from Elsevier Science Publishers B.V , BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/256/*Carbohydr. Res* , 119 (1983) 85–93.