# An Unusual Case of Acetal Formation; 1,2:4,6- and 2,3:4,6-Di-*O*-isopropylidene-5-thio-α-D-glucopyranoses and the *X*-Ray Crystal Structure of the Latter Compound

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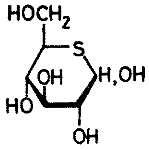
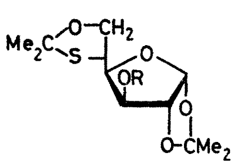
*Summary* Treatment of 5-thio-D-glucose with acetone and 2,2-dimethoxypropane in the presence of acid gives 2,3:4,6-di-*O*-isopropylidene-5-thio-α-D-glucopyranose whose structure has been confirmed by *X*-ray crystallography; the isomeric 1,2:4,6-di-*O*-isopropylidene-5-thio-α-D-glucopyranose has been obtained by an indirect route.

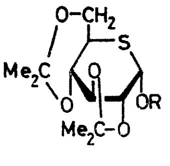
IN earlier communications[1] the reactions of 5-thio-D-ribose and 5-thio-D-xylose with acetone or 2,2-dimethoxypropane to give the unusual pyranoid 1,2:3,4-diacetals were described. We now report on the isopropylidenation of 5-thio-D-glucose (**1**).



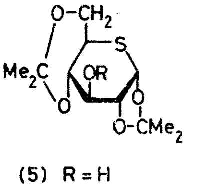
(1)



(2) R = H
(7) R = Ts



(3) R = Me
(4) R = H



(5) R = H
(6) R = Ts

Ts = *p*-$MeC_6H_4SO_2$

Treatment of the thiosugar (**1**) with acetone in the presence of acid gave the furanoid 1,2:5,6-diacetal (**2**)[2] in contrast to the earlier pentose cases[1] where the products retained sulphur in the pyranoid ring. However, when the thiosugar (**1**) reacted briefly with acetone containing 2,2-dimethoxypropane a different and highly crystalline diacetal was formed.

This new diacetal gave a positive test with sodium nitroprusside indicating a free, or potentially free, thiol group. Its n.m.r. spectrum showed a broad, low-field singlet for the anomeric hydrogen which sharpened to a narrow doublet ($J_{1,2}$ *ca.* 1 Hz) on deuterium exchange. The n.m.r. spectrum also showed a strong resemblance to that of methyl 2,3:4,6-di-*O*-isopropylidene-5-thio-α-D-glucopyranoside (**3**) obtained by treating methyl 4,6-*O*-isopropylidene-5-thio-α-D-glucopyranoside[2] with acetone and 2,2-dimethoxypropane. These results are in accordance with the new diacetal being 2,3:4,6-di-*O*-isopropylidene-5-thio-α-D-glucopyranose (**4**). This structure was confirmed by *X*-ray crystallography.

*Crystal data:* $C_{12}H_{20}O_5S$, $M = 276{\cdot}4$, monoclinic, $a = 5{\cdot}949$ (1), $b = 13{\cdot}082$ (4), $c = 9{\cdot}028$ (2) Å, $\beta = 94{\cdot}71$ (1)°, $U = 700{\cdot}2$ Å$^3$, $D_c = 1{\cdot}31$ g cm$^{-3}$, $Z = 2$, $D_m = 1{\cdot}30$, space group $P2_1$. The structure was solved by direct methods from 1326 independent reflexions with $I > 0$, measured on a Hilger-Watts Y290 diffractometer with Mo-$K_\alpha$ radiation

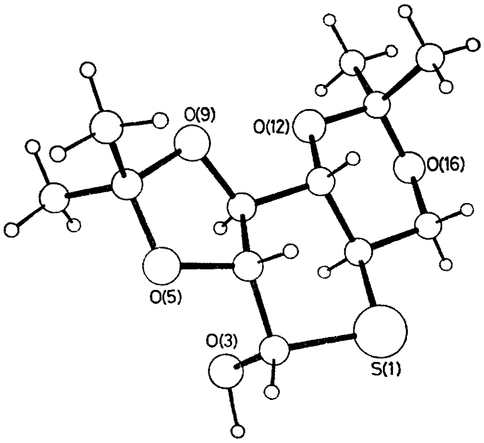


FIGURE. Structure of 2,3:4,6-di-*O*-isopropylidene-5-thio-α-D-glucopyranose (4).

($\lambda = 0{\cdot}71069$ Å), and refined to $R = 6{\cdot}83\%$. The molecular structure is shown in the Figure.†

The isomeric 1,2:4,6-diacetal (**5**) was synthesised independently by first treating 5-thio-3-*O*-*p*-tolylsulphonyl-D-glucose[2] with acetone and 2,2-dimethoxypropane in the presence of acid to give the sulphonate (**6**) whose n.m.r. spectrum showed the H-3 signal as a low-field doublet of doublets ($J_{2,3}$ 7·2; $J_{3,4}$ 9·6 Hz); cleavage of the sulphonate ester with sodium methoxide gave the diacetal (**5**), which was not detected as a product in either of the above isopropylidenation reactions of 5-thio-D-glucose. When either of the pyranoid diacetals (**4**) or (**5**) was left in acidified acetone no interconversion was observed; instead both were isomerised into the furanoid diacetal (**2**). The sulphonate (**6**) was similarly converted into the furanoid isomer (**7**).

The formation of the diacetal (**4**), possessing a *trans*-fused 1,3-dioxolan ring system, in preference to the *cis*-fused isomer (**5**) is unusual though previous examples have been reported in septanoses[3] and 1,6-thioanhydro hexitols[4] where fusion to a seven-membered ring occurs. Inspection of models, and in the case of (**4**) the *X*-ray study, suggests that the $^4C_1$ chair conformation of (**4**) is less distorted than that of (**5**).

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] N. A. Hughes and C. J. Wood, *J.C.S. Chem. Comm.*, 1975, 294; *Carbohydrate Res.*, 1976, **49**, 225.
[2] Preceding communication.
[3] J. D. Stevens, *Austral. J. Chem.*, 1975, **28**, 525.
[4] J. Kuszmann, P. Sohar, and G. Horvath, *Carbohydrate Res.*, 1976, **50**, 45.