

Conformations of Two D-Glucoseptanosides: An X-Ray Crystallographic Study of Ethyl 2,3:4,5-Di-O-isopropylidene-1-thio- β -D-glucoseptanoside and Methyl 2,3,4,5-Tetra-O-acetyl- β -D-glucoseptanoside

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Summary In ethyl 2,3:4,5-di-O-isopropylidene-1-thio- β -D-glucoseptanoside (I), the seven-membered ring has been shown to have a twist-chair conformation and the two dioxolan rings have twist conformations; in methyl 2,3,4,5-tetra-O-acetyl- β -D-glucoseptanoside (II), the seven-membered ring has a conformation between a chair and twist-chair.

ETHYL 2,3:4,5-DI-O-ISOPROPYLIDENE-1-THIO- β -D-GLUCOSEPTANOSIDE (I) was prepared¹ by demercaptalation of 2,3:4,5-di-O-isopropylidene-D-glucose diethyl dithioacetal.

Crystallization from aqueous alcohol gave rectangular plates, m.p. 66–67°, $[\alpha]_{25}^D - 156.0^\circ$ (c 1.19, CHCl_3).

The crystals have the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell of dimensions $a = 16.70(3)$, $b = 11.70(2)$, $c = 8.78(1)$ Å. The intensity data were collected on multiple film equi-inclination Weissenberg photographs taken around $[001]$, ($l = 0, 1, 2 \dots 6$) using $\text{Cu-K}\alpha$ radiation. A total of 1322 independent intensities were estimated by visual comparison with a calibration strip. The unit cell dimensions were obtained from precession photographs taken with $\text{Mo-K}\alpha$ radiation.

The structure was solved by combining partial structural

information obtained from a Patterson synthesis with the Tangent formula and refined by full-matrix least-squares procedures to a final discrepancy (R) factor of 0.103.

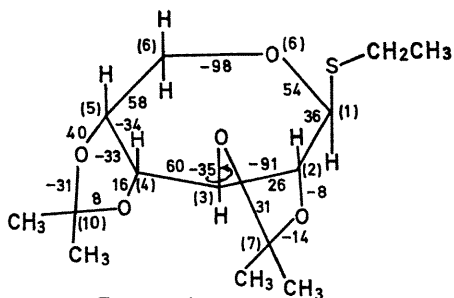


FIGURE 1

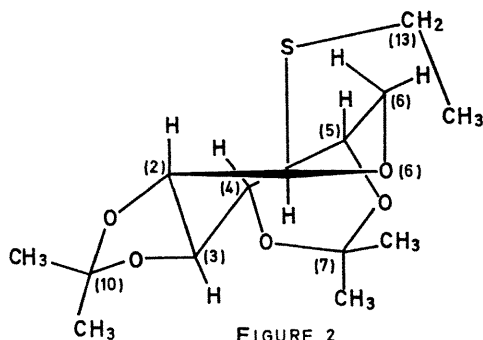


FIGURE 2

Torsional angles about the ring bonds are given in Figure 1. Examination of a model constructed using these values shows that the conformation of (I) is close to a twist-chair² in which the corresponding cycloheptane axis of symmetry passes through C(1). Figure 2 gives a diagrammatic representation of this conformation. Atoms C(3) and C(4) are displaced 0.99 Å and 0.31 Å, respectively, on one side, and atoms C(5) and C(6) are displaced 0.34 Å and 0.93 Å, respectively, on the other side of the least-squares plane through O(6), C(1), C(2), and the midpoint of the C(4)-C(5) bond. There is some deviation from an ideal twist chair as may be seen from the fact that C(4) is coplanar with O(6), C(1), and C(2) [C(3) is displaced 0.82 Å on one side and C(5) and C(6) are displaced 0.64 Å and 1.08 Å, respectively, on the other side of this plane] and that the torsional angles about bonds O(6)-C(1) and C(1)-C(2) are not equal (as would be the case in an ideal twist-chair conformation).

In contrast to the envelope conformations adopted by dioxolan rings in another glucoseptanose derivative,³ both dioxolan rings in (I) may be described as twist forms. In one ring, O(3) is displaced 0.33 Å on one side and C(3) is displaced 0.19 Å on the other side of the plane of C(2), O(2), and C(7) (Figure 3). In the other ring, O(5) is displaced 0.20 Å on one side, and C(5) is displaced 0.41 Å on the other side of the plane of C(4), O(4), and C(10) (Figure 4).

We note that in the previously determined structure and in (I) the projected bond angles O-C-C-O in the dioxolan rings are not greater than 33°, which is somewhat less than the angle (*ca.* 40°) deduced for 2,2-dimethyldioxolan on the basis of n.m.r. studies.⁴ The corresponding torsional angle

in a 2,2-dimethyldioxolan derivative has now been calculated from X-ray data⁵ as 25° [for the 5,6-*O*-isopropylidene group in 3-deoxy-3,4-*C*-(dichloromethylene)-1,2:5,6-di-*O*-isopropylidene- α -D-galactofuranose] and this angle is probably close to the value which corresponds to minimum strain in the dioxolan ring. The SET group is oriented antiperiplanar to C(2), the torsional angle C(13)-S-C(1)-C(2) being 177°.

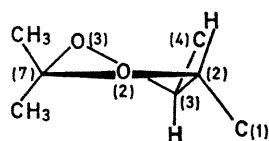


FIGURE 3

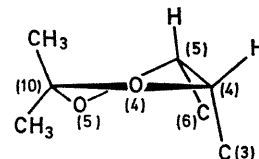


FIGURE 4

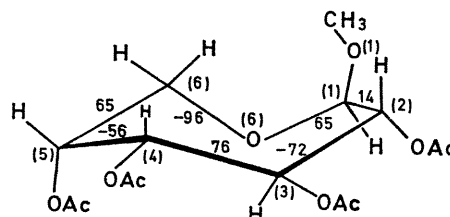


FIGURE 5

Methyl 2,3,4,5-tetra-*O*-acetyl- β -D-glucoseptanoside (II) was prepared by acetylation of methyl β -D-glucoseptanoside, obtained from its 2,3:4,5-di-*O*-isopropylidene derivative.⁶ It crystallized from aqueous alcohol as plates, m.p. 96–97°, [α]_D²⁰ -82.7° (*c* 1.08, CHCl₃). The crystals have the orthorhombic space group $P2_12_12_1$ with four molecules in a unit cell of dimensions $a = 8.819(1)$, $b = 12.211(2)$, and $c = 16.703(3)$ Å.

Intensity data and unit cell dimensions were obtained with a Siemens automatic single crystal diffractometer with Cu- $K\alpha$ radiation and nickel attenuators. Integrated intensities were recorded using the five-value method.⁷ A total of 1966 independent intensities were recorded with θ values less than 70°. The structure was solved using direct phasing methods and refined by full-matrix least-squares procedures to a final discrepancy (R) factor of 0.045.

Torsional angles about the ring bonds are given in Figure 5. The small value of the torsional angle about bond C(1)-C(2) shows that the conformation of (II) lies between a chair and twist chair, being closer to a chair in which the corresponding cycloheptane axis of symmetry passes through C(5). A diagrammatic representation is given in Figure 5. Atom C(5) is displaced 0.65 Å on one side and C(1) and C(2) are displaced 1.00 Å and 1.21 Å, respectively, on the other side of the least-squares plane through C(3), C(4), C(6), and O(6).

A comparison of the conformations of these two septanosides shows that they may both be derived from the chair conformation [cycloheptane axis of symmetry passing through C(5)] by torsion about C(1)-C(2), the extent of this torsion being less in (II) than in (I).

As with the earlier reported case of methyl 1,2,3,5-tetra-*O*-acetyl- β -D-galactofuranuronate,⁸ for each of the acetoxy groups the five atoms in the C-O-(CO)-C grouping are close

to coplanarity with the carbonyl group eclipsing the O-C group (an *s-cis* conformation) and these groups are oriented such that the carbonyl group is rotated -3° , -23° , -14° , and $+13^\circ$ out of eclipsing with the carbinol C-H group for the C(2), C(3), C(4), and C(5) acetoxy-groups, respectively.

The methoxy methyl group is oriented antiperiplanar to C(2), the torsional angle about bond O(1)-C(1) being 171° with respect to C(2).

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² For a detailed discussion on the conformations of cycloheptane, see J. B. Henrickson, *J. Amer. Chem. Soc.*, 1967, **89**, 7036 and previous papers.

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