X-Ray Crystallographic Study of 3-*O*-Acetyl-1,2:4,5-di-*O*-isopropylidene-α-D-glucoseptanose

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Summary In the title compound, the seven-membered ring has been shown to have a distorted chair conformation; one of the dioxolan rings has a distorted twist conformation and the other is close to an envelope conformation.

3-*O*-ACETYL-1,2:4,5-di-*O*-ISOPROPYLIDENE-α-D-GLUCOSEPTANOSE was prepared[1] by treating 1,2-*O*-isopropylidene-α-D-glucoseptanose[2] with acidified acetone, followed by acetylation. Crystallisation from benzene–light petroleum gave rectangular plates, m.p. 159—160°, $[\alpha]_D^{22}$ −50·2 (*c* 0·88, $CHCl_3$). The crystals belong to the orthorhombic space group, $P2_12_12_1$; $a = 13{\cdot}358(3)$, $b = 16{\cdot}506(3)$, $c = 6{\cdot}879(1)$ Å; $Z = 4$.

Intensity data were collected on a computer-controlled Siemens automatic diffractometer using Cu-K_α radiation. The unit cell constants were calculated from the observed values of selected high-angle reflections. A total of 1684 reflections were recorded.

The structure was solved by direct methods[3–5] which utilized the tangent refinement and other programmes developed in the *X*-ray crystallographic laboratory of this University by Dr. C. T. Grainger. The non-hydrogen atomic parameters were refined using full-matrix least-squares methods[6] and selected data (sin $\theta/\lambda > 0{\cdot}3$).

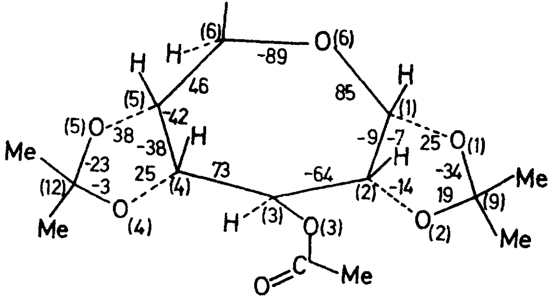

FIGURE 1

Hydrogen atoms were subsequently located from difference Fourier syntheses. Positional parameters for all atoms together with anisotropic thermal parameters for non-hydrogen atoms were then refined as above but using all data and fractional parameter shifts. The final R value is 0·034.

Bond angles (°) within the seven-membered ring are significantly greater than the tetrahedral value of 109·5° and have the following values (numbers in parentheses are standard deviations and refer to the least significant figure): C(1), 113·2(2); C(2), 115·9(2); C(3), 116·0(2); C(4), 115·9(2); C(5), 120·5(2); C(6), 114·1(2); and 0(6), 112·2(2).

Torsional angles (estimated standard deviation about 0·3°) about the ring bonds are given in Figure 1. A comparison of the values for the seven-membered ring with those computed[7] for the chair and twist–chair conformations in cycloheptane (see Table) shows that this ring is close to a chair conformation [cycloheptane plane of symmetry passing through C(5)]. The angular requirements for dioxolan ring formation[8] have resulted in a flattening of the septanose ring by movement of C(5) towards the plane of C(6), O(6), C(3), and C(4) with resultant decrease in the magnitude of torsional angles about C(4)–C(5) and C(5)–C(6). The small negative torsional angle about C(1)–C(2) shows that the conformation lies between the twist–chair [cycloheptane axis of symmetry passing through C(2)] and chair, being closer to the latter.

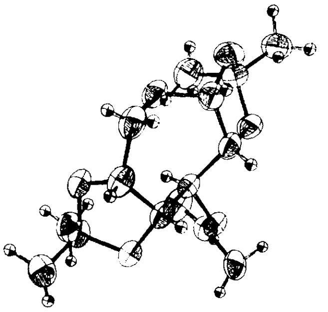

Figure 2. *Structure of* 3-*O*-*acetyl*-1,2:4,5-*di*-*O*-*isopropylidene*-α-D-*glucoseptanose*.

Table

Torsional angle values for cycloheptane

Bond	Chair[a]	Twist-chair[b]	Septanose
C(1)–C(2)	0	−39	−9
C(2)–C(3)	−66	−39	−64
C(3)–C(4)	84	88	73
C(4)–C(5)	−64	−72	−42
C(5)–C(6)	64	54	46
C(6)–O(6)	−84	−72	−89
O(6)–C(1)	66	88	85

[a] Cycloheptane plane of symmetry passing through C(5).
[b] Cycloheptane axis of symmetry passing through C(2).

Both dioxolan rings may be described as distorted twist forms, although the C(4)–C(5) ring is very close to the envelope conformation. In one ring, O(1) is displaced 0·16 Å on one side and C(9) is displaced 0·33 Å on the other side of the plane of C(1), C(2), and O(2). In the other ring, C(4) is displaced 0·07 Å on one side, and C(5) is displaced 0·53 Å on the other side of the plane of O(4), C(12), and O(5). From the best plane through C(4), O(4), C(12), and O(5), C(5) is displaced 0·58 Å.

Finally, in keeping with earlier observations,[8-10] the acetoxy-group is close to planar with the C=O group eclipsing O(3)–C(3) and rotated 4° out of eclipsing with the carbinol C-H group.

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