Preliminary communication

An X-ray crystallographic study of methyl β-D-ribopyranoside

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As part of a study aimed at the comparison of X-ray and neutron diffraction* results for a light-atom compound, the crystal structure of methyl β-D-ribopyranoside (1) has been determined.

Methyl β-D-ribopyranoside[1], prepared by debenzoylation of its tribenzoate[2], crystallized from methanol–ethyl acetate–petroleum ether as thick plates, m.p. 81–82°. Systematic absences among the reflections on Weissenberg photographs indicated that the space group was $P2_12_12_1$. The unit-cell dimensions and final intensity-data were measured on a 4-circle, Siemens, automatic, single-crystal diffractometer by using CuKα radiation and nickel attenuators. The unit-cell constants calculated from the least-squares fit of selected, high-angle reflections were** $a = 5.753$ (5), $b = 19.986$ (5), and $c = 6.413$ (5) Å. The integrated intensities of 865 reflections ($\theta < 70°$) were recorded by using the five-value method[4], and were corrected for Lorentz, polarization, and absorption factors. All non-hydrogen atom positions were located by using the new, automatic, symbolic, tangent, refinement method, SYMTAN[5]. Refinement with isotropic and anisotropic temperature-factors lowered the residual (R) to 10.7%. At this point, the twelve hydrogen atoms were located in a Fourier difference map. Further refinement led to a final R of 5.0%.

Some bond angles, bond lengths, and torsional angles about the ring bonds (average standard deviations of 0.2°, 0.003 Å, and 0.3°, respectively) are given in the diagrammatic representation in Fig. 1. The molecule exists in the $^1C_4$ (D) conformation, which is the conformation found earlier[6] for the anomeric thio analogue, namely, methyl 1-thio-α-D-ribopyranoside (2). Just as in crystals of 2, there is intramolecular hydrogen-bonding involving O-2–H-7 and O-4, as well as intermolecular hydrogen-bonding involving O-3–H-8 of one molecule and O-2′ of another molecule; O-2 is, therefore, both a donor and an acceptor in hydrogen-bond formation. The oxygen–oxygen distances involved in these hydrogen bonds are 2.763 Å for O-2–O-4, and 2.839 Å for O-3–O-2′.

*Details of this X-ray crystallographic study will be published by one of us (V. J. J.) elsewhere, and the neutron diffraction study, for which all data have been collected, will be published by V. J. James and F. H. Moore.

**These values agree well with those reported[3] for this compound.

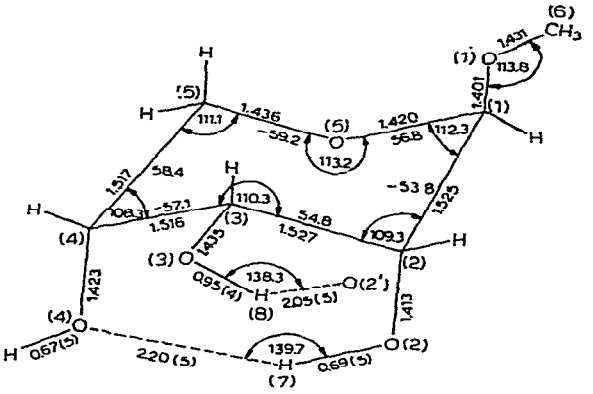

Fig. 1. Diagrammatic representation of the structure of crystalline methyl β-D-ribopyranoside, showing hydrogen bonding, bond angles, bond lengths, and torsional angles.

The best, four-atom, least-squares plane for the ring atoms involves C-2, C-3, C-5, and O-5, from which C-1 and C-4 are displaced by 0.62 and 0.70 Å, respectively. In common with a number of glycoside structures previously reported[6,7], C-6 is oriented antiperiplanar to C-2, the torsional angle C-6–O-1–C-1–C-2 being +168.8°. Calculations[8] using group-interaction energies have shown that the energy difference between the two chair conformations of 1 is very small, and, consequently, the possibility of a strong, intramolecular hydrogen-bond is undoubtedly an important factor favoring the $^1C_4$ (D) conformation in the crystal structure.

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