Preliminary communication

An X-ray crystallographic study of β-D-mannofuranose$\cdot CaCl_2 \cdot 4H_2O$

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Two crystalline adducts of D-mannose with calcium chloride were prepared by J.K. Dale[1], and he showed that, in one of these, namely, D-mannose$\cdot CaCl_2 \cdot 2H_2O$ (m.p. 159–160°), the sugar moiety is β-D-mannopyranose. The ring form and anomeric configuration of the D-mannose in the other compound, namely, D-mannose$\cdot CaCl_2 \cdot 4H_2O$ (m.p. 101–102°), named the "first isomer" by Dale, has not been determined definitely, although bromine-oxidation studies[2] pointed to a furanose structure. We have determined the structure of the first isomer by X-ray diffraction, which has verified presence of the furanose form of D-mannose.

The compound (m.p. 104–106°, cap. tube) crystallizes in space group $P2_12_12_1$ with a unit cell of dimensions a = 13.844(3), b = 14.529(3), and c = 7.609(2) Å, containing four molecules.

A prismatic crystal having approximate dimensions of 0.15 × 0.23 × 0.40 mm was used for collection of data. Integrated intensities for reflections with θ up to 70° were measured with a Siemens, computer-controlled, AED, four-circle diffractometer by using CuKα radiation and a θ–2θ scan technique. Lorentz, polarization, and absorption corrections were applied, and the structure was solved by Patterson and Fourier methods. Refinement was made by full-matrix, least squares, using anisotropic temperature-factors and isotropic extinction-corrections[3]. A final, conventional, R factor of 0.031 was obtained.

The structure is depicted in Fig. 1. The furanose sugar has the β-D configuration at C-1, and the torsional angles, given in Table I, indicate an envelope conformation, with C-2 displaced 0.59 Å from the least-squares plane passing through the other four atoms (the E_2 conformation[4]). We note that the arrangement of hydroxyl groups on C-1, C-2, and C-3 is very similar to the *a-e-a* arrangement that has been found to favor complexing in six-membered rings[5].

Each calcium ion is shared by two sugar molecules, co-ordinating through O-1, O-2, and O-3 of one molecule and O-4 and O-5 of the other. In addition, three of the water molecules are co-ordinated to calcium through their oxygen atoms, labeled W1(O), W2(O), and W3(O), giving a total of eight co-ordinating oxygen atoms, for each

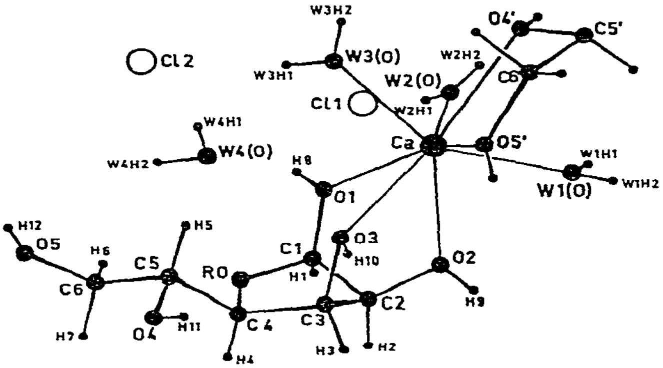

Fig. 1. Structure of β-D-mannofuranose·$CaCl_2$·$4H_2O$.

TABLE I

TORSIONAL ANGLES IN THE FURANOSE RING

	Angle (degrees)
RO–C-1	+21.2(4)
C-1–C-2	−36.8(4)
C-2–C-3	+37.5(3)
C-3–C-4	−25.3(3)
C-4–RO	+2.8(4)

calcium ion. The arrangement of these oxygen atoms about a calcium ion cannot be described readily in terms of the usual co-ordination polyhedra. Eight-fold co-ordination has been observed for calcium in the calcium salts of several polyhydroxy carboxylic acids[6].

The sharing of the calcium ions between sugar molecules results in zigzag chains running parallel to the *b* axis, and these are joined together into sheets normal to the *a* axis by hydrogen-bonding between the ring-oxygen atom (RO) and the water molecule (W1) associated with the nearest calcium ion in the *c* direction.

Chloride ions and the fourth molecule of water, W4, lie in planes between these sheets, and are extensively hydrogen-bonded to the hydroxyl groups and water molecules contained therein.

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