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The Crystal and Molecular Structure of β-Arabinose

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The crystal and molecular structure of β-arabinose has been determined, mainly by means of the "multiplication rule". There is a *cis*-glycol grouping on C_1 and C_2, and the molecule has the structure 1*a*2*e*3*e*4*a*.

As the pyranose ring has the staggered "chair" form, there are according to Hassel[1] two possibilities for the molecular structure of each pyranose sugar, the one being formed from the other by conversion of the ring. For some sugars it is fairly evident which structure is the more stable one and to be expected in the crystalline state. In other cases, such as the present one, it would appear difficult to settle this question without determining the crystal structure. So far detailed structure analysis of two pyranose sugars, α-glucose and α-rhamnose monohydrate, have been reported in the literature (Beevers *et al.*[2,3]).

EXPERIMENTAL CRYSTAL DATA

A commercial sample of β-D-(−)-arabinose from Eastman Kodak Co. was used for the investigation. Good crystals were obtained by recrystallization from alcohol. They are needle-shaped and elongated along the *c*-axis. Weissenberg- and oscillation diagrams were taken about two axes, using filtered copper radiation. The crystals are ortorhombic, with unit cell dimensions $a = 6.50$ Å, $b = 19.41$ Å, and $c = 4.83$ Å (± 0.5 %). The values agree well with those given by Cox[4]. The density is 1.627 g/cm^3 and there are four molecules $C_5H_{10}O_5$ in the unit cell. The only systematic absences occur in the odd-order reflections $h00$, $0k0$ and $00l$, and the space group is therefore $P2_12_12_1$, as was also found by Cox[4].

The relative intensities were estimated visually from a series of Weissenberg photographs of the $hk0$ and $0kl$ zones. 93 of the 146 $hk0$ reflections and 100 of the 127 $0kl$ reflections accessible with Cu$K\alpha$ radiation were recorded with measurable intensity. The intensities were corrected for Lorentz and polarisation effects, but not for absorption, as small crystals of dimensions less than 0.2 mm were used. For the $0kl$ reflections a correction was also made for the "spot-shape" effect[5].

DETERMINATION OF THE STRUCTURE

Projections of the structure along the *c* and *a* axes were determined by Patterson projections, trial and error methods, the "multiplication rule", and

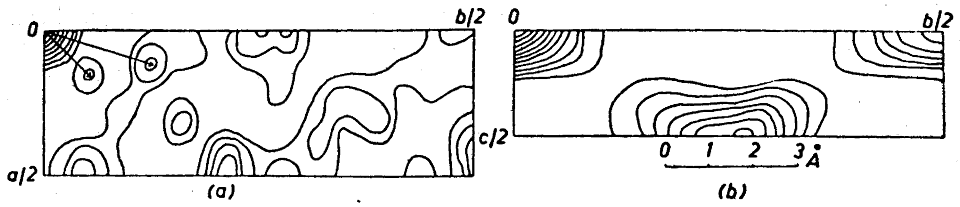
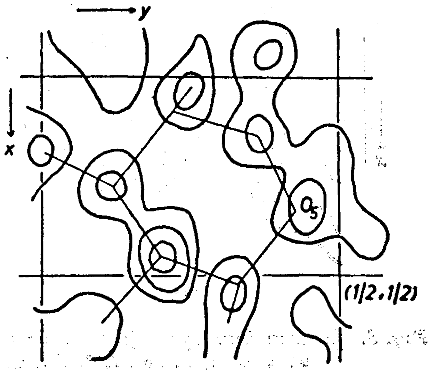


Fig. 1. Patterson projections on the (001) plane (a) and the (100) plane (b).

F_0 and (F_0—F_c) refinement. As the c axis is the shortest one, this projection was first determined.

The c-projection. The Patterson synthesis is reproduced in Fig. 1a. The orientation of the six-membered ring could be derived from the two intramolecular vectors shown in the figure. Following the procedure described by Beevers [2], two possible positions of the centre of the ring were found, but attempts at further interpretation were not successful. A number of reasonable structures were then postulated by studying selected reflections by Bragg-Lipson charts. However, all attempts at Fourier refinement of these structures failed. It was then tried to deduce the signs of the strongest reflections by inequalities and the "multiplication rule" [6,7]. The intensities were put on an approximately absolute scale by Wilson's method [8]. The reflection 1,17,0 was found to have a unitary structure factor (U) as high as 0.68, and 26 reflections had unitary structure factors greater than 0.30. Negative signs were chosen for 1,17,0 and 4,11,0 ($U = 0.52$) and the signs of the reflections 240 ($U = 0.38$), 0,18,0 ($U = 0.55$), 2,17,0 ($U = 0.44$) and 3,12,0 ($U = 0.45$) were denoted by a, b, c and d, respectively. Only two additional signs could be deduced from simple inequality relations, but the "multiplication rule" led to the determination of the probable signs of 18 more structure factors in terms of the letter symbols. Furthermore, the relations d = b and bc = —a were strongly indicated. Twenty of the reflections could be divided in four groups whose signs were expressed by —1, a, c and ac, respectively. Six other strong reflections for which the signs were given in terms of b and ab, were not con-

Fig. 2. The best electron density map obtained by permutation of the signs of groups of reflections. The postulated structure is shown.

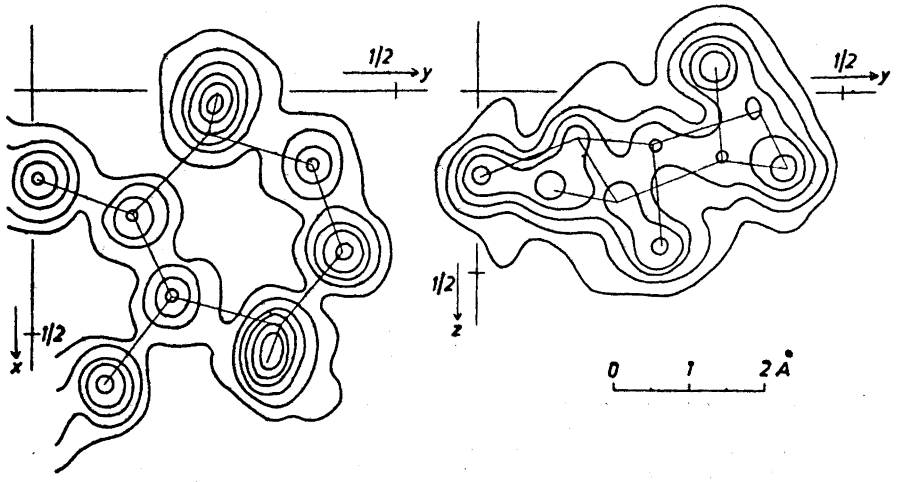


sidered in order to limit the number of permutations. The Fourier synthesis of the reflections within each group was then calculated, and the electron density maps corresponding to the four possible combinations of the signs of the groups were derived. In one of the maps (Fig. 2) a six-membered ring was indicated, although not very clearly. Fourier refinement of a structure postulated on this basis led eventually to the correct structure. Three (F_0—F_c) refinements were also carried out. The final structure factors showed that two of the reflections used to calculate the map in Fig. 2 had the wrong sign, and that the values used for the unitary structure factors were about 35 % too high. The reliability factor $R = (\Sigma|F_0-F_c|)/\Sigma|F_0|$ is 0.18, and the corresponding electron density map is shown in Fig. 3a. The contributions from the hydrogen atoms were not included in the structure factors. The atomic scattering factors employed are those given by Berghuis *et al.*[9] A temperature factor exp. ($-3.5\sin^2\Theta/\lambda^2$) was used.

The a-projection. The Patterson synthesis (Fig. 1b) gave little information,

Table 1. Atomic coordinates as fractions of the corresponding cell edge.

Atom	*x*	*y*	*z*
C_1	0.486	0.418	0.189
C_2	0.431	0.347	0.302
C_3	0.253	0.320	0.130
C_4	0.091	0.369	0.144
C_5	0.150	0.442	0.048
O_1	0.562	0.411	0.918
O_2	0.603	0.302	0.273
O_3	0.190	0.253	0.237
O_4	0.005	0.377	0.430
O_5	0.328	0.462	0.209



(a) (b)

Fig. 3. Electron density projections on the (001) plane (a) and the (100) plane (b). Contours at 2, 4, 6, . . . e . Å^{-2}. Calculated at 1/60 of *b* and 1/30 of *a* and *c*.

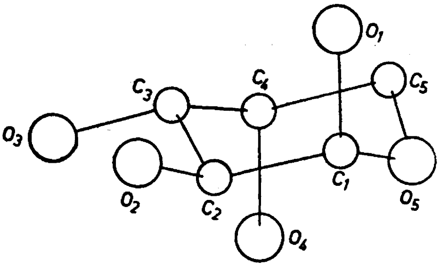


Fig. 4. The molecular structure of β-arabinose.

but confirmed that the "plane" of the molecule is nearly perpendicular to the c-axis. Approximate relative z coordinates were derived from the c-projection and known interatomic distances. The position of the molecule was deduced mainly by considering the possibilities for favourable hydrogen bond formation between neighbouring molecules. By Fourier and difference refinement satisfactory agreement between F_0 and F_c was finally obtained ($R = 0.16$). The electron density map is shown in Fig. 3b. In Table 1 the coordinates of the atoms are given.

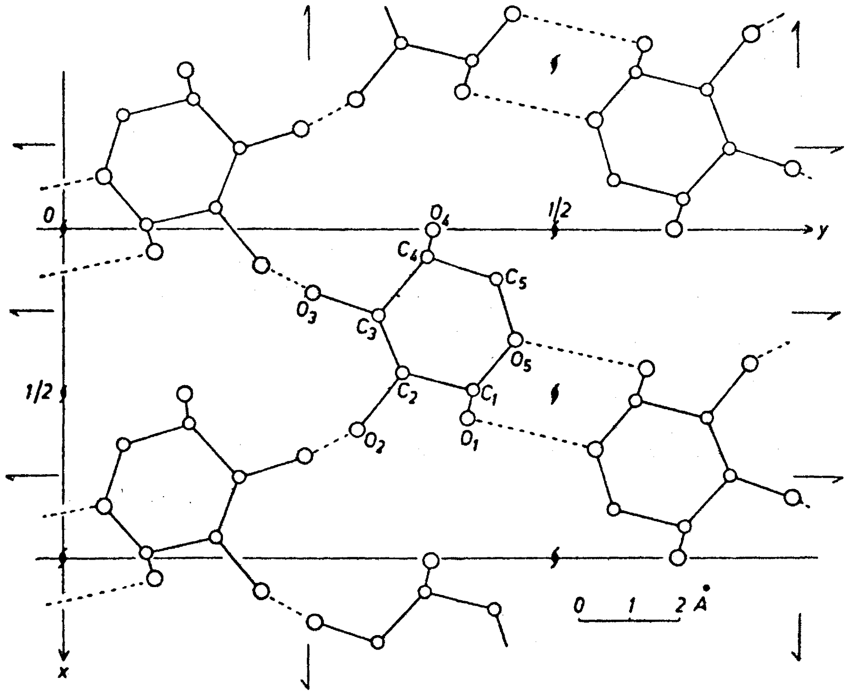


Fig. 5. The c-projection of the structure. Broken lines indicate hydrogen bonds.

DISCUSSION OF THE STRUCTURE

The electron density maps in Fig. 3 show that the molecule of β-arabinose has the structure given in Fig. 4. The ring has the staggered "chair" form, and the structure of the molecule is 1*a*2*e*3*e*4*a* (a = axial, e = equatorial). Thus β-arabinose has the "*cis*" configuration at atoms C_1 and C_2, as a study of its interaction with boric acid also indicates[10]. Its anomer α-arabinose consequently has the conformation 1*e*2*e*3*e*4*a* or 1*a*2*a*3*a*4*e*, probably the former.

The aim of the present investigation was to determine the molecular structure. Hydrogen atoms were neglected and the same temperature factor was used for all the atoms, although the (F_0—F_c) synthesis indicates considerable differences. No great accuracy can therefore be claimed in the bond lengths and bond angles derived from the coordinates in Table 1. Values between 1.48 Å and 1.59 Å were found for the C—C bonds whereas the C—O bonds vary in length between 1.38 Å and 1.46 Å, in agreement with the expected values of 1.54 Å and 1.42 Å, respectively. As was found also for α-glucose and α-rhamnose[2,3], C_1—O_1 appears to be somewhat shorter than the other C—O bonds. Possibly this bond has some double bond character, a point which may be of considerable interest for the understanding of the reactions of pyranose sugars. The molecules are linked together by a system of hydrogen bonds, as shown in Fig. 5. The atoms O_1, O_2, O_3 and O_5 take part in hydrogen bonds of lengths between 2.65 Å and 2.75 Å. Surprisingly, the distance from O_4 to the nearest oxygen atom in a neighbouring molecule is as great as 3.0 Å. In order to decide whether or not this corresponds to a weak hydrogen bond, it would appear necessary to determine the position of the corresponding hydrogen atom.

A further refinement of the structure will be carried out by one of us.

REFERENCES

1. Hassel, O. and Ottar, B. *Acta Chem. Scand.* **1** (1947) 929
2. McDonald, T. R. R. and Beevers, C. A. *Acta Cryst.* **5** (1952) 654.
3. McGeachin, H. McD. and Beevers, C. A. *Acta Cryst.* **10** (1957) 227.
4. Cox, E. G. *J. Chem. Soc.* **1931** 2313.
5. Broomhead, J. M. *Acta Cryst.* **1** (1948) 324.
6. Sayre, D. M. *Acta Cryst.* **5** (1952) 60.
7. Zachariasen, W. H. *Acta Cryst.* **5** (1952) 68.
8. Wilson, A. J. C. *Acta Cryst.* **2** (1949) 318.
9. Berghuis, J., *et al. Acta Cryst.* **8** (1955) 478.
10. Bøeseken, J. *Advances in Carbohydrate Chem.* **4** (1949) 189.

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