

**376.** *The Crystalline Structure of  $\alpha$ -Methylxyloside.*

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IN a previous communication (this vol., p. 138) it was shown that a close relation exists between the crystal lattices of  $\beta$ -methylxyloside and  $\alpha$ -xylose; it has now been found that there is a similar and even closer relation between the lattices of  $\alpha$ -methylxyloside and  $\alpha$ -xylose. The molecular arrangement in crystalline  $\alpha$ -methylxyloside has been determined with some degree of certainty, and further progress has been made toward the exact determination of the form of the pyranose sugar-ring.

A crystallographic investigation of  $\alpha$ -methylxyloside was made by Reuter (*Z. Krist.*, 1901, **35**, 388) who described it as monoclinic sphenoidal with axial ratios  $a : b : c = 1.277 : 1 : 0.802$ ;  $\beta = 111^\circ 46'$ , the crystals being combinations of  $a\{100\}$ ,  $c\{001\}$ ,  $q\{021\}$ , and

$\alpha\{\bar{1}\bar{1}\}$  elongated in the direction of the  $b$ -axis. The optical properties are given in Table II. The crystals used in the present investigation were obtained from a pure specimen available in this laboratory by recrystallisation from ethyl acetate; they were easily distinguishable from crystals of the  $\beta$ -isomeride, and corresponded with those described by Reuter, except that the form  $m\{10\bar{1}\}$  was usually equally developed with  $a$  and  $c$ . On account of the high solubility of the substance, and the consequent syrupy nature of the mother-liquor, it was not possible to obtain crystals with faces sufficiently good for accurate goniometric work, so Reuter's measurements could only be confirmed approximately.

An  $X$ -ray examination was carried out by the rotation method, using filtered copper  $K_\alpha$  radiation. The dimensions of the unit cell were found to be  $a = 11.28$ ,  $b = 6.72$ ,  $c = 11.02$  Å.U.  $\pm \frac{1}{2}\%$ , while the length of the  $[101]$  axis was determined as  $12.44$  Å.U., from which  $\beta = 112^\circ 12'$ . The axial ratios are  $a : b : c = 1.678 : 1 : 1.639$ , which apparently bear no resemblance to those of Reuter; if, however, the faces  $q$  and  $o$  are indexed  $(011)$  and  $(3\bar{4}2)$  respectively, his values become  $1.703 : 1 : 1.604$ , which are in as good agreement with the  $X$ -ray results as can be expected from crystals having such imperfect faces. (Reuter's material was crystallised from ethyl acetate, and the agreement between his observed and calculated angles is not good.) With four molecules to the unit cell, the calculated density is  $1.40$  g./c.c., while the value obtained by the flotation method is  $1.41$ . From two series of oscillation photographs it was found that the only absent reflexions were  $(0k0)$  for  $k$  odd. The space-group is consequently  $C_2^2$  ( $P2_1$ ). Since the only symmetry element in this space-group is a two-fold screw axis, two chemical molecules are associated to form the asymmetric crystal unit. In Table I the intensities (estimated by eye from the oscillation photographs, in arbitrary units) of the  $X$ -ray reflexions from some of the more important lattice planes are given.

TABLE I.

$hkl$	$I$	$hkl$	$I$	$hkl$	$I$	$hkl$	$I$	$hkl$	$I$
001	50	008	$2\frac{1}{2}$	600	5	404	10	$20\bar{2}$	80
002	60	009	2	700	$<\frac{1}{2}$	11 $\bar{1}$	100	$30\bar{3}$	4
003	60	020	60	800	$2\frac{1}{2}$	$22\bar{2}$	50	$40\bar{4}$	16
004	4	040	20	900	$<\frac{1}{2}$	$33\bar{3}$	50	$50\bar{5}$	5
005	$<\frac{1}{2}$	060	7	101	2	$44\bar{4}$	8	$60\bar{6}$	$\frac{1}{2}$
006	$<\frac{1}{2}$	100	20	202	25	$55\bar{5}$	12	707	5
007	$<\frac{1}{2}$	500	30	303	35	$10\bar{1}$	8	$80\bar{8}$	1

As in the case of  $\beta$ -methylxyloside, the  $a$  and  $c$  axes are nearly equal, so that a pseudo-orthorhombic cell can be derived by means

of the transformations  $x = [101]$ ,  $y = \frac{1}{2}[10\bar{1}]$ ,  $z = b$ . The result is shown below side by side with the corresponding values for  $\alpha$ -xylose and  $\beta$ -methylxyloside.

	$\alpha$ -Xylose.	$\alpha$ -Xyloside.	$\beta$ -Xyloside.
$x$ .....	12.64	12.44	13.0
$y$ .....	9.20	9.26	8.6
$z$ .....	5.60	6.72	6.89

The relation between these sets of figures is so close that it cannot be doubted that the three substances have essentially the same molecular orientation with respect to the axes, the difference between xylose itself and the xylosides being just the amount to be expected on the addition of the  $\text{CH}_3$  group. Further proof of the similarity of structure is afforded by the optical properties of the methylxylosides (Table II).

TABLE II.

	$\alpha$ -Xyloside.	$\beta$ -Xyloside.
Mean refractive index .....	1.52	1.52
Optic sign .....	—	—
$2E$ .....	$56^\circ$	app. $60^\circ$
Plane of optic axes .....	(010)	(010)
Direction of acute bisectrix .....	app. perp. to (10 $\bar{1}$ )	app. perp. to (10 $\bar{1}$ )

Finally the approximate intensities of the X-ray reflexions from the orders of (010), *i.e.*, the  $z$ -plane, may be compared :

Plane .....	020.	040.	060.
$\alpha$ -Xyloside .....	60	20	7
$\beta$ -Xyloside .....	60	14	5

This close and sustained agreement between the properties of the two methylxylosides leads inevitably to the conclusion that their structures differ only in minor details, such as would arise from changing the methoxyl group from one side of the ring to the other without altering the general molecular arrangement. In both cases the molecules must be arranged in the monoclinic cell with the planes of the rings parallel to (10 $\bar{1}$ ) (the  $y$ -plane of the pseudo-orthorhombic cell), and oriented with respect to the other two axes somewhat as shown in Fig. 1. (In this and the succeeding figures the oxygen atoms are shaded and the hydrogens omitted.) The same applies to  $\alpha$ -xylose except that, since the methyl group is replaced by hydrogen, the  $z$ -axis is about 1.2 Å.U. shorter. It may be noted that this interpretation makes the acute bisectrix in the two xylosides approximately perpendicular to the plane of the molecules, as might be expected, but actually too much weight should not be attached to this, since the birefringence is small (*ca.* 0.02), and no such correlation between optical properties and structure has so far been established for any other pyranose carbohydrates.

Since there is no doubt as to the reality of this connexion between the molecular dimensions in certain directions and the values on p. 2537, the differences between the figures for the three substances assume considerable significance. In the first place, it is clear that the difference between the results for the free sugar and those for the xylosides, which is so readily explained by the replacement of H by  $\text{CH}_3$ , could have no simple explanation if the ring-structure in the sugar differed from that in its derivatives. Although there is no reason for supposing that the simple pentoses have a different ring-form from the methylpentosides, the actual chemical proof

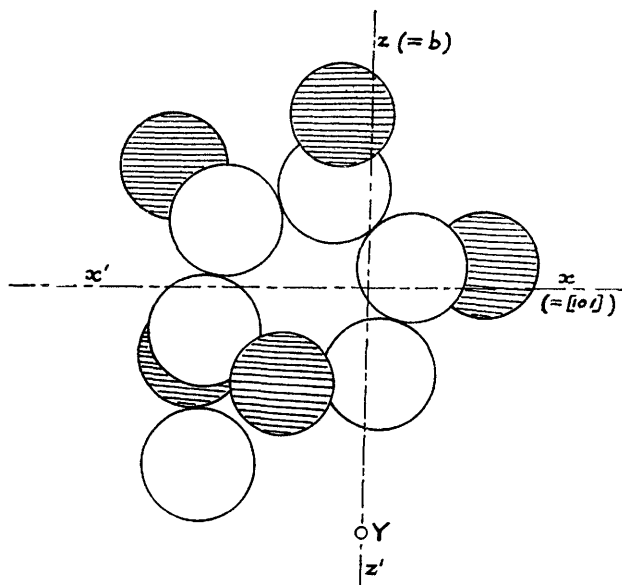


FIG. 1.

of structure usually applies strictly to the latter, and only by inference to the free sugars. It is therefore satisfactory that the crystallographic evidence leads to the same conclusion as the chemical. The fact that the ring-structure is of the pyranose type may be regarded as established beyond dispute, and will be assumed in the following discussion; it is highly improbable that the very good agreement which is thereby obtained could occur if this assumption were incorrect.

Of the two xylosides, the dimensions for the  $\alpha$ -form, as would be expected, are the more nearly related to those for  $\alpha$ -xylose. The  $\beta$ -methylxyloside molecule is longer and thinner than that of the  $\alpha$ -isomeride. This makes the possibility of an entirely flat pyranose ring remote, since with such a configuration, the valency directions

on each carbon atom would be symmetrical about the plane of the ring, and the reducing group would have precisely the same position with respect to it whether in an  $\alpha$ - or a  $\beta$ -position. On the other hand, the difference between the dimensions of the two forms is insufficient to admit of a strainless *trans*-ring, since in this case one of the valencies of the first carbon atom is normal to the mean plane of the ring, while the other is almost parallel to it; thus the lengths of the  $\alpha$ - and  $\beta$ -molecules should differ by about 1 Å.U. (Fig. 2) instead of the observed 0.2 Å.U. [The results for  $\alpha$ -methylmannopyranoside (Cox and Goodwin, this vol., p. 1844) are also unfavourable to the *trans*-strainless ring; the "thickness" of the

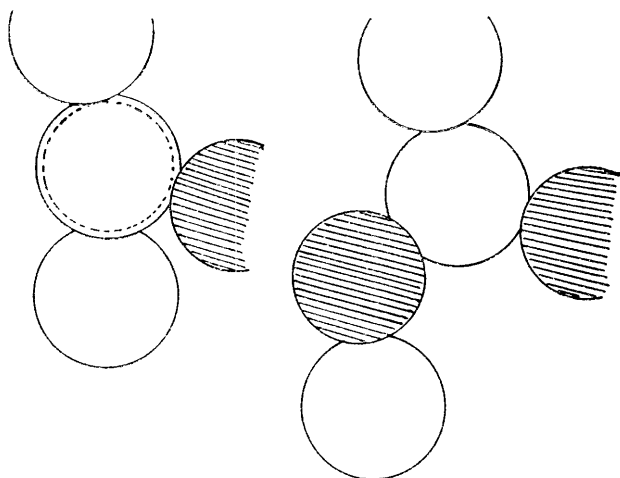


FIG. 2.

molecule of this substance is 4.62 Å.U., whereas with a *trans*-ring it should be at least 5 Å.U.]

If, however, the pyranose ring consists of five carbon atoms in a plane with the oxygen atom displaced out of it, then the extracyclic valency angles of the two carbon atoms adjacent to the oxygen are no longer bisected by the plane of the ring; the  $\alpha$ - and the  $\beta$ -form differ as shown in Fig. 3, one being shorter and thicker than the other by about the amounts required if the oxygen valency is assumed to be in the neighbourhood of  $110^\circ$ . Since it is the longer, it appears that the  $\beta$ -form is the one in which the reducing group is nearer the ring oxygen atom, but this may not apply to other sugars.

A similar result can be obtained with a *cis* ("boat-shaped") strainless ring, but since, as will be seen later, the plane ring gives a very satisfactory agreement in the matter of X-ray reflexion

intensities, it will not be discussed in detail, although at this stage it cannot be excluded definitely as the totally planar and *trans*-forms apparently can.

The value of accurate atomic models in discussions such as the preceding should need no emphasis; the full significance of the conventional projection formulæ, and the differences which arise from the adoption of the various forms of the pyranose ring, cannot be satisfactorily understood without their use. This point has been urged before (*e.g.*, Haworth, "Constitution of the Sugars," p. 1), but is apparently not yet sufficiently appreciated.

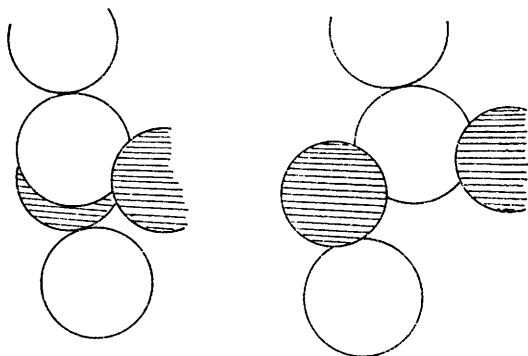


FIG. 3.

The determination of the exact molecular arrangement in  $\alpha$ -methylxyloside is somewhat complicated by the fact that two molecules are associated in the asymmetric crystal unit, so that symmetry considerations alone do not lead very far. However, the orientation of each molecule must be the same as that shown in Fig. 1, or differ from it only by a rotation of  $180^\circ$  about one of the pseudo-orthorhombic axes, so that the problem resolves itself largely into the determination of the relative positions of the centres of the molecules. Reference to Table I shows that the first- and third-order intensities of  $(10\bar{1})$  are very weak, indicating a pseudo-two-fold screw axis perpendicular to that plane, while since the second-order reflexion is much stronger than the fourth, the molecules must lie in pairs in the  $(20\bar{2})$  planes. Thus, denoting the four molecules by A, B, C, and D, A and B lie in the  $(10\bar{1})$  plane, C and D in a parallel plane distant by approximately half the  $(10\bar{1})$  spacing, while C is related to A, and D to B, by the pseudo-screw axis. Now the true two-fold screw axis (the *b*-axis) may relate C to B and D to A, or C to D and B to A. It can be shown that in the latter case, the odd-order intensities of  $(11\bar{1})$  should be relatively much weaker than the even-order, whereas if the former is the

correct arrangement, the intensities of  $\{11\bar{1}\}$  should fall off fairly smoothly with increasing glancing angle; the results given in Table I are clearly strongly in favour of this. Thus the molecular arrangement is as shown in Fig. 4, which represents a projection on (010), the figures indicating the depths of the molecules below this plane. It will be seen that there is also a pseudo-screw axis perpendicular to (101), but since its translation is equal to the spacing of this plane, no halving results.

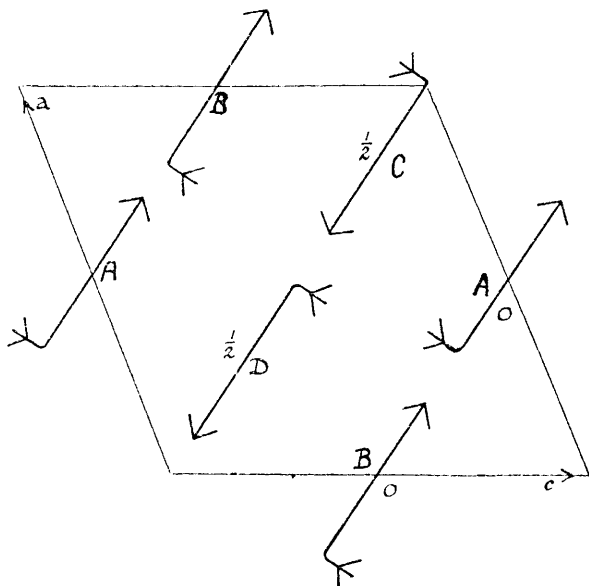


FIG. 4.

It remains now to determine the molecular arrangement somewhat more precisely. It will be assumed that the molecule contains a pyranose ring of five coplanar carbon atoms and an oxygen atom displaced about 0.8 Å.U. out of their plane, the extracyclic valency angle of the carbon atoms being about  $100^\circ$ . The best agreement with the experimental results is then obtained by supposing that the molecule A is arranged with respect to the  $x$  and  $z$  axes as shown in Fig. 1, and that the molecule C is derived from it by a rotation of  $180^\circ$  in its own plane about the point Y, followed by a translation of 5.0 Å.U. parallel to  $[10\bar{1}]$ . B is obtained from A by a rotation of  $180^\circ$  about  $xx'$  plus a translation of 6.2 Å.U. along it; the position of D is then fixed by symmetry considerations. This structure, which is shown in Fig. 5, gives good qualitative agreement with all the results of Table I. In the case of certain planes where

fewer parameters are involved the geometric structure factors ( $F$ ) have been calculated from the observed intensities and also from the structure shown in Fig. 5. The results (in arbitrary units) are compared in Table III. Since an average atomic scattering factor for carbon and oxygen was used in the calculations, this agreement may be regarded as very satisfactory. It seems fairly certain that the structure represented in Fig. 5 is at least a close approximation to the truth.

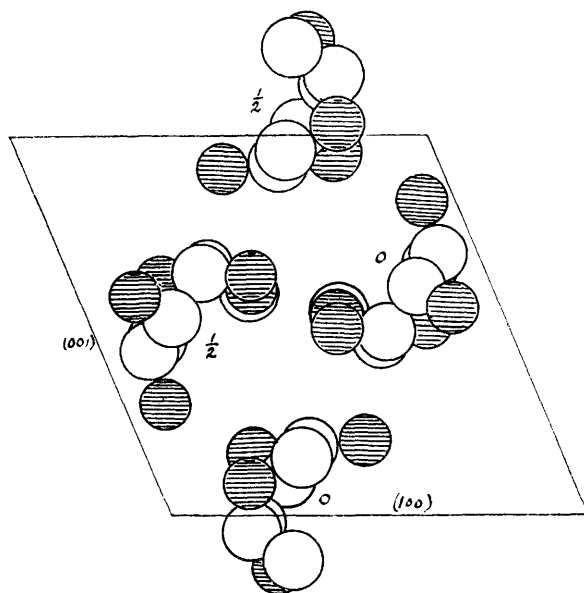


FIG. 5.

TABLE III.

$hkl$ .	$I$ (exp.).	$F$ (exp.).	$F$ (calc.).	$hkl$ .	$I$ (exp.).	$F$ (exp.).	$F$ (calc.).
020	60	8.0	8.3	202	25	5.5	5.0
040	20	11.2	11.0	303	35	10.9	14.0
060	7	12.0	10.0	404	10	9.4	10.0
101	2	0.8	0.4				

The author takes this opportunity of making a correction to an earlier paper (this vol., p. 138). Owing to an error in calculation, the goniometric axial ratios of  $\beta$ -methylxyloside were given as  $a : b : c = 1.040 : 1 : 1.022$ ; these ratios actually should have been  $1.134 : 1 : 1.115$ , in good agreement with the X-ray results.

#### Summary.

An X-ray examination of  $\alpha$ -methylxyloside has been made; it is found that its lattice is closely related to those of  $\alpha$ -xylose and



$\beta$ -methylxyloside. A detailed structure is proposed which is in good agreement with the experimental results, and arguments are brought forward against completely planar or *trans*-strainless forms of the pyranose ring.

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