17. *An X-Ray Examination of β-Methylxyloside.*

By ERNEST GORDON COX.

IN continuation of the investigation of the sugars and their derivatives (J., 1931, 2313), a derivative of xylose, β-methylxyloside, has been examined. This substance had apparently not been investigated crystallographically.

Moderately good crystals were readily obtained by crystallisation from alcohol. On a preliminary examination they appeared to exhibit no symmetry, a typical crystal being shown in Fig. 1. Some crystals, however, were found possessing a two-fold axis of symmetry, indicating that the substance is actually monoclinic sphenoidal. This was confirmed by a Laue photograph which showed a plane of symmetry, characteristic of the monoclinic system. Most of the crystals examined exhibited some single faces instead of complete forms, but the forms $c\{001\}$, $s\{0\bar{1}1\}$, $p\{110\}$, and $p'\{1\bar{1}0\}$ were complete in nearly all cases, with p and p' predominating, terminated by c. Individual faces $r(101)$, $r'(10\bar{1})$ were frequently observed, while faces which appeared to be (552) and $(37\bar{2})$ each occurred once. All the faces were often distorted, so the accuracy of the goniometric measurements, which are summarised below, was not extremely high.

β-*d*-Methylxyloside; monoclinic sphenoidal.

$a : b : c = 1{\cdot}040 : 1 : 1{\cdot}022$; $\beta = 113° 25'$.

	Calc.	Obs.
$p : p' = (110) : (1\bar{1}0)$	—	92° 15′
$c : p = (001) : (110)$	—	74 01
$c : s = (001) : (0\bar{1}1)$	—	45 38
$s_1 : p = (0\bar{1}\bar{1}) : (110)$	71° 10′	70 59
$s : p = (01\bar{1}) : (110)$	44 56	44 54
$r : p = (10\bar{1}) : (110)$	69 18	68 46

As the crystals were only moderately good, it was not possible to determine the optical properties very accurately. The mean refractive index is approximately 1·51. The plane of the optic axes is (010), one of the axes being nearly parallel to the *c*-axis. The apparent optic axial angle in air is about 60°.

FIG. 1.

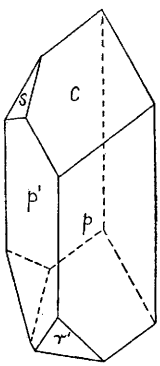
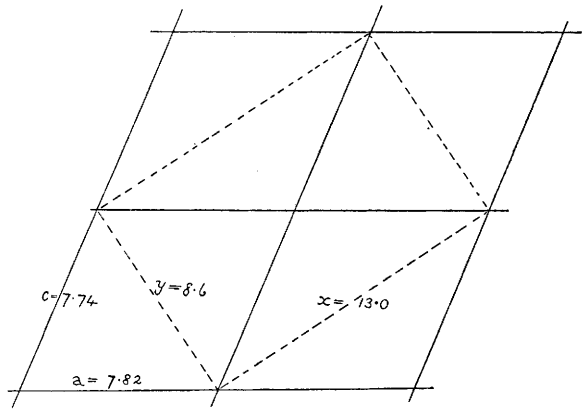


FIG. 2.



An *X*-ray examination was carried out by the rotating crystal method, using filtered copper K_α radiation. In order to avoid any dependence on the goniometric measurements, the angle β, as well as the linear dimensions of the cell, was determined by *X*-ray methods. The lengths of the (001), (010), (100), and (111) axes were determined, and the angle β calculated from them. The results are as follows: $a = 7{\cdot}82$, $b = 6{\cdot}89$, $c = 7{\cdot}74$ Å.U., and $\beta = 113° 10'$. The axial ratios are thus $a : b : c = 1{\cdot}135 : 1 : 1{\cdot}123$, in very poor agreement with the goniometric results. It is difficult to see why the goniometric results should be in error, since the agreement shown in the angular measurements given above is reasonably good, but the most probable explanation is that some of the faces observed are vicinal faces of high indices; thus if *p* is renamed (10,11,0) and *s* (0,$\bar{1}\bar{1}$,10) then the axial ratios are $a : b : c = 1{\cdot}144 : 1 : 1{\cdot}123$, which is in good agreement with the *X*-ray results.

Such vicinal faces might be caused by the presence in the alcohol from which the crystals were grown of a trace of some asymmetric impurity, or merely by too rapid growth. The *X*-ray measurements were repeated on several crystals, in all cases the ones which had been used for goniometric work, and as an additional check the length of the (110) axis was measured and was found to agree perfectly with the value calculated from *a* and *b*.

On the basis of two molecules to the cell, the density is calculated to be 1·412: by direct experiment it is app. 1·40. From a series of oscillation photographs about the *c*-axis, it was found that the odd orders of (010) are absent; the space-group is thus C_2^2.

The space-groups of practically all the carbohydrates and glucosides so far examined are either C_2^2 or Q_4, which are the only space-groups in the monoclinic and the orthorhombic system respectively which have no symmetry elements other than two-fold screw-axes. It would be of considerable interest to investigate the optical rotation of some of these substances in the crystalline state; the spiral arrangement due to the screw-axes would presumably give rise to a rotation independent of the molecular rotation, and by a comparison of a number of carbohydrates in which the molecular arrangement was known approximately from *X*-ray work, it might be possible to separate the rotatory effects of lattice structure and molecule.

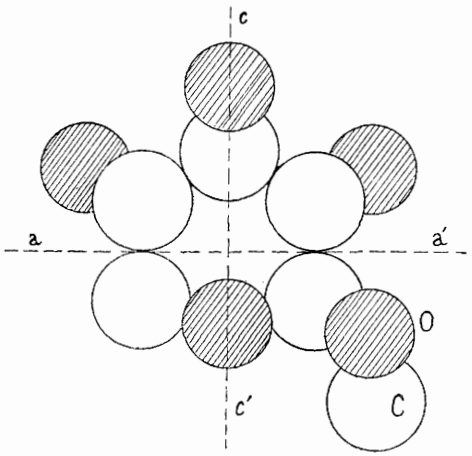
It is proposed not to discuss the structure of β-methylxyloside in detail at present, but to await the results for α-methylxyloside, which is now being examined. There is, however, a very interesting relation between the cell-dimensions of α-xylose (Cox, *loc. cit.*) and of β-methylxyloside. Fig. 2 is a projection of four unit cells of β-methylxyloside on (010); by drawing the diagonals as shown by the dotted lines, the projection of a cell containing four molecules is obtained (supposing *b* to be the same). Since *a* and *c* are nearly equal, this cell is practically rectangular. Calling its dimension normal to the paper *z* (= *b* of β-methylxyloside), we have the following comparison:

New cell.	α-Xylose.
$x = 13{\cdot}0$	$a = 12{\cdot}64$
$y = 8{\cdot}6$	$b = 9{\cdot}20$
$z = 6{\cdot}89$	$c = 5{\cdot}60$

It is seen that the first two dimensions are about the same, but that the *c*-axis of xylose has been increased by 1·3 Å.U. Now, Fig. 3 shows a molecule of β-methylxyloside, the oxygen atoms being shaded and the hydrogen atoms left out for clearness. α-Xylose can be obtained by leaving out the atom C and putting the atom O below the plane of the ring instead of above it. This

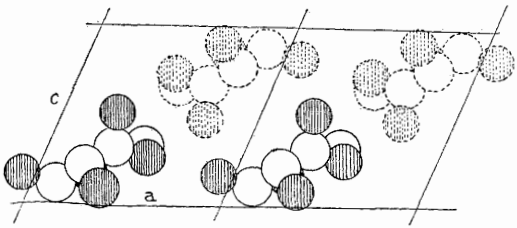
particular structure with five coplanar carbon atoms is similar to the one suggested for arabinose (Cox, *loc. cit.*). It is clear that changing the position of O does not alter the thickness of the ring, while the atom C can take up a position as shown without increasing the thickness; in this position, however, the width of the ring in

FIG. 3.



the direction *aa'* will be increased slightly, and the length in the direction *cc'* will be increased by somewhat less than the diameter of a carbon atom, *i.e.*, about 1·3 Å.U. Actually the *c*-axis has increased by 1·3 Å.U., and the *a*-axis by 0·4 Å.U. It was suggested that in α-xylose the directions *aa'* and *cc'* were the directions of *a* and *c* respectively, and it is at once evident that the increases in *a*

FIG. 4.



and *c* on going from xylose to β-methylxyloside are just those which are necessary if the molecule of Fig. 3 is oriented in the dotted cell of Fig. 2 as the molecules appear to be in the xylose cell. If this picture is correct, the thickness of the ring has been reduced from 4·6 Å.U. to 4·3 Å.U. This may mean merely that the rings are more closely packed in this direction in the xyloside,

but in any case, if 4·3 Å.U. does represent the thickness of the ring, it seems to indicate that the carbon atoms in the ring must be coplanar or very nearly so. It should be noted that the oxygen atom in the ring may be as much as 1 Å.U. out of the plane of the carbon atoms without affecting the thickness of the molecule. Fig. 4 gives a view of the suggested arrangement of the molecules in β-methylxyloside, viewed along the *b*-axis. The dotted molecules are at a distance $\frac{1}{2}b$ below the others. Since *a* and *c* are practically equal, the foregoing remarks would apply equally well if *a* and *c* in Figs. 2 and 4 were interchanged; a careful study of intensities of *X*-ray reflections will be necessary to decide which of the two alternatives is correct.

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