CCCXVII.—*An* X-*Ray Examination of Arabinose, Xylose, and Rhamnose.*

By Ernest Gordon Cox.

The results presented here are the first obtained in an investigation, which will be extended to include many sugars and their derivatives with the object of investigating closely by *X*-ray methods the structure of the sugar-ring in the monosaccharides and of determining as far as possible the manner in which these rings are linked in the polysaccharides.

The available data for the sugars have been reviewed by Astbury and Marwick (*Nature*, 1931, **127**, 12), who suggested that the six-atom sugar-ring has in the crystalline state approximately constant dimensions, being about 4½ by 5½ by 7½ Å.U., the first dimension being that normal to the ring. Unfortunately it is at present almost impossible to interpret such results as these in terms of the structure of the molecule. Considerations of space-filling alone are not enough to decide between the various possible structures, since our knowledge of atomic diameters in organic compounds is so scanty. We do not know with any certainty the diameter of the oxygen atom when singly bound to carbon, and still less do we know what the diameter of the hydrogen atom in these compounds may be. Consequently almost any of the possible models for a sugar molecule can be made to fit such figures as those quoted above. If, however, similar data were available for several series of closely related carbohydrates, it would be possible to find the effect of additional groups in various positions, and the size and mode of attachment of these groups might be inferred. For example, a study of the two series xylose–glucuronic acid–glucose and arabinose–galacturonic acid–galactose might be expected to throw light on the attachment of the CO·OH and CH_2·OH groups to the sugar-ring, particularly as there is a certain amount of information available as to the dimensions of the CO·OH group. It seems likely that in many cases such as this, where only one group is changed on going from one substance to the next, there is a comparatively small change in crystal structure. The small change in density of the sugars mentioned above, for instance, is significant :

Sugar	Arabinose.	Galactose.	Xylose.	Glucose.
Density	1·625	1·614	1·526	1·544

Clearly, before any useful comparisons of the kind suggested can be made, a greater amount of information must be collected, starting preferably with the simplest substances available. This paper, therefore, deals with the preliminary data for two pentoses, α-xylose and β-arabinose, and one methyl-pentose, rhamnose hydrate. The usefulness of the data for the latter is somewhat impaired by the presence in the crystal of one molecule of water of crystallisation, but it is intended later to investigate the anhydrous substance.

It is not suggested that a series of comparisons, however complete, will be sufficient to solve the problem of the structure of the sugar-ring. When some preliminary information has been derived from such comparisons, it will be profitable to study individual sugars closely; by means of accurate and extensive measurements of the intensities of *X*-ray reflections, very definite and valuable conclusions will undoubtedly be reached.

β-l-*Arabinose*.

This substance crystallises from aqueous alcohol in small needles, usually somewhat distorted and with a tendency to form radiated growths. It has been examined by Traube (*Z. Kryst. Min.*, 1895, **25**, 630), by Groth and Hintze (*Ber.*, 1873, **6**, 615), and by Wherry (*J. Amer. Chem. Soc.*, 1918, **40**, 1852). Although the combinations observed by these different workers were not quite the same, they agreed in describing arabinose as orthorhombic with axial ratios $a : b : c = 0{\cdot}668 : 1 : 0{\cdot}492$. (These axial ratios are the mean of those given in the literature, which were recorded with more figures than are significant. As apparently all the crystals measured were imperfect, the accuracy of the measurements was not high.) The class appeared to be bipyramidal, but since arabinose is optically active, it was considered to be undoubtedly bisphenoidal.

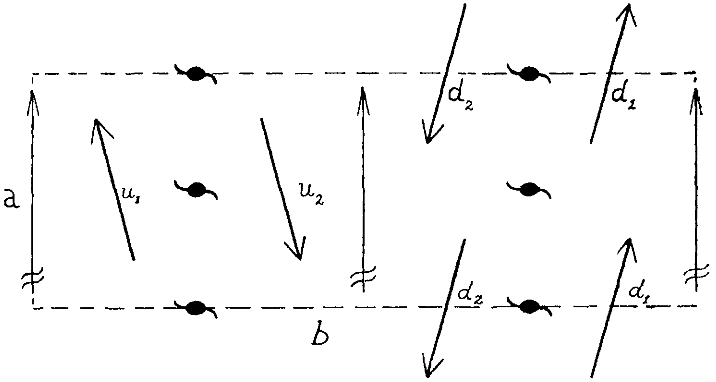
The crystals obtained by the writer had the same general appearance as those previously described, so no goniometric measurements were made upon them. An *X*-ray examination was carried out by the rotating-crystal method, using filtered K_α radiation from copper ($\lambda = 1{\cdot}539$ Å.U.). The dimensions of the unit cell were found to be $a = 6{\cdot}51$, $b = 19{\cdot}43$, $c = 4{\cdot}85$ Å.U. The axial ratios are thus $a : b : c = 0{\cdot}670 : 2 : 0{\cdot}499$, agreeing as well as can be expected with those given above. With four molecules to the unit cell, the density is found to be 1·625, as compared with the directly determined value of 1·627.

From a series of oscillation photographs it was found that there are no general halvings, but that the odd orders of (001), (010), and (100) are absent, as well as some chance halvings. The space-group of β-arabinose is therefore Q_4, orthorhombic bisphenoidal, based on the simple orthorhombic lattice (Astbury and Yardley, *Phil. Trans.*, 1924, *A*, **224**, 221). No other orthorhombic space-group has the same halvings. The four asymmetric molecules are derived from each other by the operations of three mutually perpendicular sets of digonal screw axes, as shown in Fig. 1, which represents a projection of the unit cell on (001). The molecules are indicated by the thick arrows, the letters u and d signifying that the heads of the arrows are to be taken as pointing up and down respectively; the arrows u_2 and d_2 represent molecules at a depth $c/2$ below u_1 and d_1 respectively. Not all the screw axes are shown; those which are shown parallel to the *a*-axis may be taken as lying at a depth midway between u_2 and d_2, or between u_1 and d_1.

The arrangement of molecules shown in Fig. 1 is not the only one consistent with the symmetry of Q_4, but in view of the considerable length of the *b*-axis it appears fairly certain that the molecules must be disposed somewhat as shown, more or less side by side along the *b*-axis. The space occupied by a molecule is thus 6·51 by 4·86 ($= \frac{1}{4} \times 19{\cdot}43$) by 4·85 Å.U., and presumably one of the last two represents the dimension perpendicular to the ring. As was pointed out in the introduction, however, this result by itself gives no help in eliminating any of the possible molecular models.

A consideration of the intensities of the reflections from some of the more important planes gives some indication of the manner in which the structure is built up. The (020) reflection is weak, and the (040) much stronger; this is what would be expected if the molecules are arranged along the *b*-axis as suggested above. Further, the reflection from (0180), allowance being made for its large glancing angle, is very strong, indicating that most of the scattering mass in the cell is arranged in layers parallel to (010) at intervals of 1·08 Å.U. (*i.e.*, 1/18 of 19·43). A structure which would give this effect can easily be obtained with the sugar-ring which is considered by Haworth ("The Constitution of the Sugars," p. 90, Fig. 1); it is similar to that proposed by Andress (*Z. physikal. Chem.*, 1929, 4, 431) to explain the *X*-ray results from cellulose. Thus, suppose that the five carbon atoms (of diameter 1·54 Å.U.) lie in a plane, the ring-oxygen atom being displaced out of it somewhat. Then, if the hydroxyl oxygen atoms (of diameter 1·40 Å.U. say) are placed so that the bonds between them and the carbons make angles of about 47° with the plane of the ring, their centres will lie in two planes on either side of the ring, at a distance of 1·08 Å.U. from it. Clearly, if four such molecules are arranged suitably parallel to (010), its eighteenth order will be very strong, since all the atoms except the

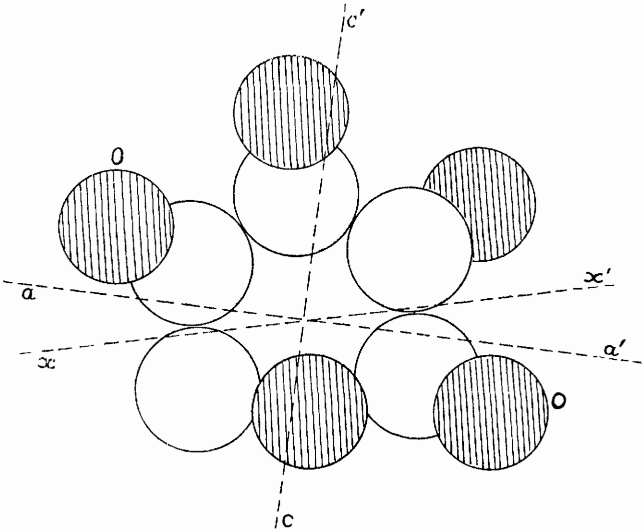
FIG. 1.



ring-oxygens will be in phase. Fig. 2 represents a molecule of β-arabinose on these lines, the oxygen atoms being shaded. Since the five carbon atoms are coplanar, this will be referred to for convenience as the flat-ring structure, but it should be made clear that there is no suggestion here that the oxygen atom is coplanar with the other members of the ring.

A further point of considerable interest is that the fourth order of (100) is absent. This means that the arrangement of scattering matter parallel to (100) is repeated at intervals of 0·81 Å.U. (*i.e.*, $\frac{1}{8}$ of 6·51). This requirement again can be satisfied by a flat-ring structure; referring to Fig. 2, if the molecule is oriented with the direction aa′ parallel to the *a*-axis, the structure-factor for (400) could easily be made zero. The length of the molecule in this direction is 6·2 Å.U., which would fit into the *a*-spacing quite well. The width of the molecule at right angles to this is 4·9 Å.U., which is slightly too great for the *c*-axis (4·85), but this slight discrepancy could be removed by adjustments which would not affect seriously the points already discussed. In this scheme there is no room for the hydroxyl oxygens in the direction of the *c*-axis, and not much along the *a*-axis, but they could be fitted in in the direction of the *b*-axis very well; for example, directly over (or under) the carbon atoms, in Fig. 2.

FIG. 2.



Thus it may be said that a fair agreement with some of the main experimental facts can be obtained by assuming a structure in which the molecules of β-arabinose contain five coplanar carbon atoms each, and are arranged with their rings parallel to the (010) face of the unit cell. This is at present only a suggestion, but so far no structure has been found which agrees as well with the experimental results. Assuming provisionally that the structure is approximately as suggested, one or two interesting points arise. In the first place, it can be seen that along the *a*-axis the molecules are arranged so that number one carbon atom in any molecule is nearest to number four in the next; this is reminiscent of cellobiose and cellulose, in which the glucose residues are considered to be connected by 1 : 4 linkages. Secondly, we may reasonably assume, although it is at present incapable of proof, that the direction of the bond between a carbon atom and its attached hydrogen atom is inclined to the plane of the ring at about the same angle as is the valency-direction between carbon and oxygen; then, with the model proposed above, the angle between these two directions will be in the neighbourhood of 95°, which, although somewhat smaller than the value to be expected in such a case, is qualitatively in accord with the view that the formation of a plane ring with valency angles of about 120° results in an external valency angle which is less than the tetrahedral angle. Thirdly, it may be noted that the adoption of a planar sugar-ring has advantages from the stereochemical point of view in that there are only two possibilities for the structure of a given pentose; the ring oxygen atom may be above the plane of the ring as in Fig. 2, or it may be below it (the reducing group being in both cases above). From many points of view there would not be a great deal of difference between these two arrangements. On the other hand, with a strainless ring, in which the tetrahedral angle is everywhere conserved, there are eight possible forms for, say, β-arabinose. Another difficulty which arises is that for half of the possible number of pairs of structures for the α- and β-forms of a pentose, including the cases which are usually regarded as most probable, the relative positions of the hydroxyls on the first and second carbon atoms are exactly the same in the two forms. This difficulty does not exist for the flat-ring structure.

α-d-*Xylose*.

The literature of xylose is in a somewhat confused state. Pionchon (*Compt. rend.*, 1897, **124**, 1523) described it as occurring in beautiful white monoclinic needles with axial ratios $a : b : c =$ 1·6696 : 1 : 1·9896 (the angle β was not given). Wherry (*loc. cit.*) described it as monoclinic with axial ratios $a : b : c =$ 1·655 : 1 : 1·766 ; β = 117°05′. Fig. 3 shows the type of crystal which he observed, the forms being *m*{110}, *c*{001}, and *d*{101}. Crystals obtained by the writer from water, aqueous alcohol, and pyridine all had the same general appearance as this, but a preliminary examination gave the impression that the faces *c* and *d* belonged to the same form, and consequently that the crystals were orthorhombic. A Laue photograph taken with the *X*-ray beam parallel to Wherry's *b*-axis showed definitely orthorhombic symmetry, *i.e.*, two planes of symmetry at right angles. The same result was obtained from a photograph taken with the beam perpendicular to his (100). These facts were sufficient to show that α-xylose is orthorhombic, but for the sake of completeness some goniometric observations were made. In the following, the *a*- and *b*-axes correspond to the *b*- and *a*-axes respectively of Wherry; this interchange was made in order to bring xylose in line with arabinose. The *c*-axis is parallel to the direction of elongation of the crystals.

FIG. 4.

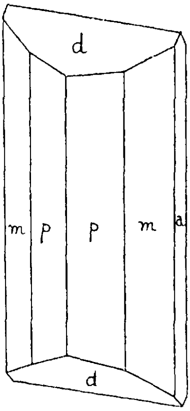
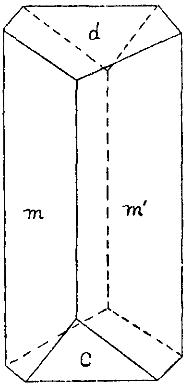


FIG. 3.



The most suitable crystals were obtained from about 90% alcohol by slow evaporation; those from water were almost as good, but were not formed so readily. Pyridine solutions did not yield very good crystals on account of their high concentration. It was observed that the crystals grown in pyridine, while still in the liquid, were almost perfect, showing none of the distortion usually observed on the other specimens, but since the mother-liquor was so syrupy, they could not be removed and dried without spoiling the faces. All the crystals measured were distorted, the faces being curved, and doubly terminated examples were rare on account of a pronounced tendency towards radiated formations. In addition to the forms observed by Wherry, *viz.*, *m*{210} and *d*{011}, *a*{100} and *p*{110} were measured. Fig. 4 represents a fairly typical crystal, although the relative development of *m* and *p* varied considerably, and frequently faces of the same form were very different in size. The results of the goniometric investigation are given in the following table; owing to the distortion of the faces, the angular measurements are not accurate to more than 15′.

α-*d*-Xylose: orthorhombic, apparently bipyramidal, but without doubt bisphenoidal.

$$a : b : c = 1{\cdot}354 : 1 : 0{\cdot}608.$$

		Observed.	Calculated.
$d : d' = (011) : (011)$	....	62° 35′	—
$p : a = (110) : (100)$	....	53 33	—
$m : a = (210) : (100)$	....	34 16	34° 06′
$d : p' = (011) : (110)$	....	64 34	65 18

It is difficult to reconcile the results of Wherry with these; the only explanation seems to be that the crystals he used were very distorted, possibly exhibiting vicinal faces. It is just possible that his crystals, through some accidental conditions of growth, exhibited the faces (011), (011), (034) and (034) instead of the complete form {011}; this would agree approximately with his measurements. Such cases of very unequal development appear to be not unknown among the sugars and their derivatives; for example, some crystals of monoacetyl γ-methylrhamnoside examined by the writer appeared to be quite definitely monoclinic domatic, although an *X*-ray investigation showed that they were actually orthorhombic.

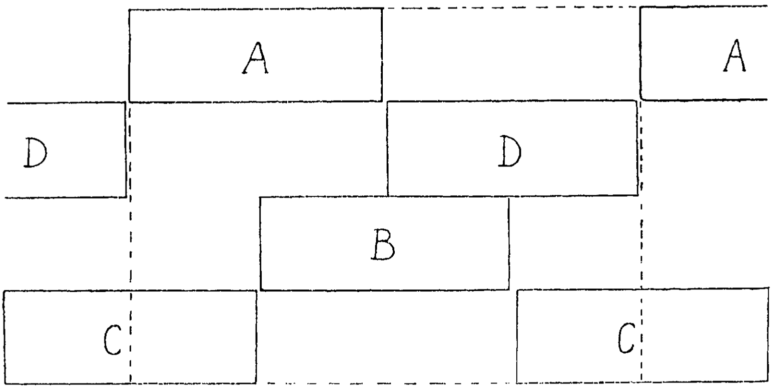
By means of *X*-ray rotation photographs, the dimensions of the unit cell of α-*d*-xylose were found to be $a = 12{\cdot}64$, $b = 9{\cdot}20$, $c = 5{\cdot}62$ Å.U. The axial ratios are thus $a : b : c = 1{\cdot}374 : 1 : 0{\cdot}609$, which are not in such good agreement with those obtained goniometrically as might be expected; the inference is that some of the angular measurements were in error by more nearly 30′ than 15′. With four molecules per cell, the density is 1·526, as compared with the directly determined value of 1·525 (Wherry, *loc. cit.*).

A series of oscillation photographs showed that the halvings for xylose are the same as for arabinose; thus the space-group of xylose also is Q_4, orthorhombic bisphenoidal, the symmetry of which is shown in Fig. 1.

It will be seen that the cell-dimensions for xylose and arabinose correspond fairly closely, the biggest alteration being in the *c*-axis. In the case of xylose, however, it seems fairly certain straightaway that the molecules must lie with the planes of their rings approximately parallel to the *b*-plane, since the length of the *b*-axis, 9·20, is too great to be a dimension of one molecule, and too small to be double any dimension except the one perpendicular to the plane of the ring. The space occupied by one molecule is evidently 6·32 × 5·62 × 4·60 Å.U.

It is more difficult here than with arabinose to decide on a probable arrangement for the molecules. A structure which is roughly in agreement with some of the outstanding experimental results is shown in Fig. 5, which gives a view along the *c*-axis. The molecules are represented diagrammatically only; the planes of the rings are parallel to (010). The level of the molecules A and B are probably about the same, while C and D are at a depth $\frac{1}{2}c$ below A and B respectively. This arrangement of the molecules would agree with the facts that for both (010) and (100) the fourth order is very much stronger than the second order, while for (001) this is not the case. Further it would, with very slight adjustment, make (110) and (220) strong, but (210) weak, as is found to be so. A molecule built up in the same way as that proposed for arabinose would fit this arrangement fairly well if the direction xx′ in Fig. 2 is taken parallel to the *a*-axis. (Fig. 2 can be made to represent α-xylose by placing the oxygen atoms marked O below the plane of the ring instead of above it.) In this structure we should still get the juxtaposition of atoms one and four in neighbouring rings; number one atom in molecule A would be close to number four in molecule D, but instead of the molecules being in straight lines as in arabinose, they would form a zig-zag arrangement. It is not suggested that the forces between molecules A and D, for example, are different in their nature from those between B and D; the similarity to cellulose, even if it exists, is probably not very significant, although it is interesting to note that it has now been shown chemically that a similar 1 : 4-linkage occurs in xylan.

FIG. 5.



The dimensions of the unit cell of α-*d*-glucose (Hengstenberg and Mark, *Z. Krist.*, 1929, **72**, 301) show a fairly close parallelism with those of xylose, as is shown below;

Xylose.	Glucose.
$a = 12{\cdot}64\ (= 2 \times 6{\cdot}32)$	$b = 14{\cdot}89\ (= 2 \times 7{\cdot}44)$
$b = 9{\cdot}20\ (= 2 \times 4{\cdot}60)$	$c = 4{\cdot}99$
$c = 5{\cdot}62$	$a = 10{\cdot}40\ (= 2 \times 5{\cdot}20)$

Thus the chief effect of the addition of the $CH_2{\cdot}OH$ group is to increase the *a*-axis by 1·12 Å.U.; evidently the *b*-axis in glucose corresponds to the width of the ring in the direction of the side-group, which is not much different from the direction of the corresponding axis (the *a*-axis) proposed above for xylose. As the other two dimensions are not greatly changed, it seems probable that the two structures are not very different.

It must be emphasised that the structures proposed here for arabinose and xylose can be regarded only as very rough approximations to the truth; even if the suggested structures agreed with a very great amount of experimental evidence, it would require an extensive investigation to show that there were no structures which gave a better agreement. As was pointed out in the introduction, such a detailed study is not considered advisable at present. The arrangements of the molecules shown in Figs. 1 and 5 are probably fairly close to the actual structures, and may be regarded with some degree of confidence, but all that can be said for the particular molecular model put forward is, that of the more obvious possibilities this one appears, on a preliminary examination, to fit rather better than the others.

d-*Rhamnose Hydrate.*

This substance, since it crystallises easily in large well-formed crystals, has been the subject of numerous investigations, which are summarised in Groth's "Chemische Kristallographie," vol. III, p. 435. It is monoclinic sphenoidal with axial ratios $a:b:c = 0{\cdot}9998:1:0{\cdot}8435$; $\beta = 95°25'$. Crystals obtained by the writer from water and aqueous alcohol had the same appearance as those previously described, but some which crystallised very slowly from acetone showed quite different development, being tabular on (100). They were similar to, although not identical with, some observed by Websky (*Z. Kryst. Min.*, 1887, **12**, 187).

By means of *X*-ray rotation photographs, the dimensions of the unit cell were found to be $a = 7{\cdot}96$, $b = 7{\cdot}95$, $c = 6{\cdot}71$ Å.U. The axial ratios calculated from these values are $a:b:c = 1{\cdot}001:1:0{\cdot}8436$, which are practically the same as those determined goniometrically. Taking two molecules to the cell, the density works out to 1·44; that found directly is 1·47. This discrepancy is rather greater than can be accounted for by experimental error, and is being investigated.

A series of oscillation photographs showed that reflections from the odd orders of (010) are absent. This indicates that the space-group is C_2^2 (Astbury and Yardley, *loc. cit.*), which is characterised by a set of two-fold screw axes parallel to the *b*-axis. Thus the two asymmetric molecules are arranged so that their separation in the direction of the b-axis is $\frac{1}{2}b$.

Since we know nothing of the way in which the rhamnose and water molecules are related, we cannot very well decide upon the arrangement from the cell-dimensions alone. It has been thought best to defer consideration of the structure until the data for anhydrous rhamnose and some of its derivatives have been obtained.

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