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Refinement of the Crystal Structure of β-Arabinose

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The crystal and molecular structure of β-arabinose has been determined more accurately by means of $(F_o - F_c)$ synthesis in a-axis and c-axis projections. The hydrogen atoms have been located and included in the calculations, and corrections have been made for individual and anisotropic thermal vibrations of carbon and oxygen atoms.

The mean length of C—C bonds is 1.535 Å, and the mean length of C—O bonds, excluding $C_1—O_1$, is 1.434 Å. The bond $C_1—O_1$ is 1.382 ± 0.012 Å, and deviates significantly from the mean value.

The mean value of the angles in the pyranose ring (excluding $C_1—O_5—C_5$) is 109.5°, equal to the tetrahedral angle. The angle $C_1—O_5—C_5 = 112.7 \pm 0.6°$ deviates significantly from the mean value, and so does the angle $O_5—C_1—O_1 = 113.0 \pm 0.7°$.

All the oxygen atoms and hydroxyl hydrogen atoms are engaged in hydrogen bonds, one of which is found to be as long as 3.035 ± 0.008 Å. O_2 takes part in three hydrogen bonds and has roughly tetrahedral surroundings.

The approximate crystal structure of β-arabinose has been determined earlier by means of the a-axis and c-axis projections [1]. It was, however, found desirable to try to obtain more information on details in the structure, particularly because the general interest in sugar structures in recent years seems to be focused on structural details. In order to know accurately the hydrogen bonding system in the crystal, it would be necessary to locate the hydrogen atoms. Regarding the angle $C_1—O_5—C_5$ in the pyranose ring, there seems to be some disagreement in the literature [2,3], and it was hoped that a new detailed structure determination of a pyranose sugar might give more reliable information about this angle. In the same way it would be valuable to have an accurate determination of the length of the bond $C_1—O_1$, which in sugars is usually reported to be shorter than the normal C—O single bond [2,3]. The apparent reactivity of O_1 might be related to such a shortened bond, and this might therefore be a point of interest for the study of the chemical reactions of pyranoses.

Two short axes and the space group $P2_12_12_1$ make β-arabinose suitable for two-dimensional refinement.

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CRYSTAL DATA

The X-ray data on which the preliminary structure determination was based [1], did not seem good enough for a more accurate structure analysis. A new series of X-ray photographs were therefore taken, using Cu*Kα* radiation. The crystals had cross-sections of about 0.1 × 0.1 mm. The unit cell dimensions were redetermined from high order reflections on Weissenberg photographs, using a crystal coated with KCl powder. As lattice parameter of KCl the value 6.293 Å was used [4].

The following axial lengths were derived:

$a = 6.535 \pm 0.007$ Å, $b = 19.467 \pm 0.020$ Å, $c = 4.841 \pm 0.005$ Å

The relative intensities of the reflections were corrected for "spot shape" effect [5].

The carbon and oxygen contributions to the calculated structure factors were based on the atomic scattering curves of Berghuis *et al.*[6], and the hydrogen contributions were based on the curve of Viervoll and Øgrim [7].

REFINEMENT OF THE STRUCTURE

The c-axis projection. About twenty successive $(F_o—F_c)$ refinements were carried out in order to bring the discrepancy factor $R_{hk0} = (\Sigma|F_o—F_c|)/\Sigma|F_o|$ from 0.30 to the final value 0.055. After the twelfth step, nine of the hydrogen atoms were projected from a molecular model on to the difference map, Fig. 1a,

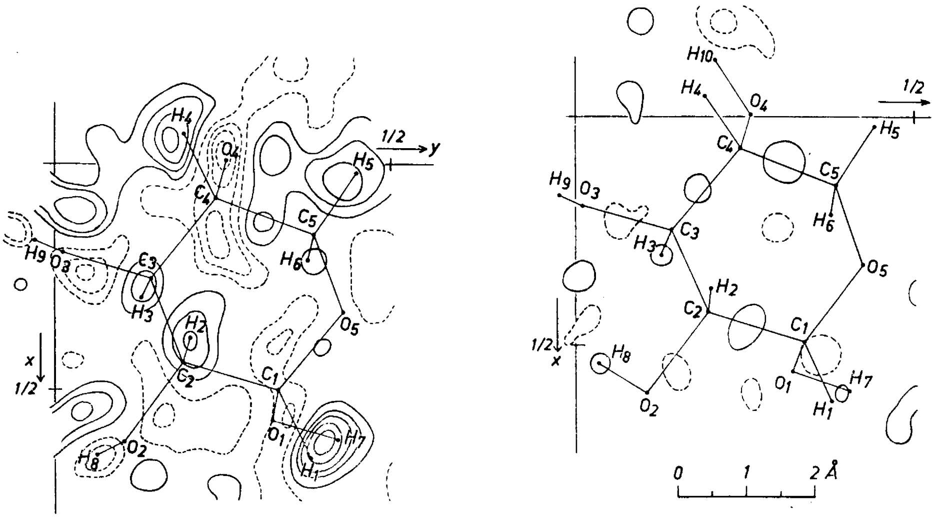

Fig. 1. (a) The twelfth difference projection of β-arabinose along the *c* axis, with hydrogen atoms *not* subtracted, and (b) the final difference projection along the same axis, with hydrogen atoms subtracted. Contour lines at intervals of 0.2 e·Å^{-2}, with negative lines dashed. The zero line is omitted. The maxima in the middle of $C_1—C_2$, $C_3—C_4$ and $C_4—C_5$ indicate asymmetry in the electron clouds due to the bonding electrons.

using a model with C—H = 1.09 Å and O—H = 0.96 Å. Fig. 1a shows that the six hydrogen atoms bound to carbon could be placed in positive areas on the map. Assuming H_7, H_8 and H_9 to be engaged in hydrogen bonding and lying near the straight line between adjacent oxygens, H_7 could be placed in a positive area, but H_8 and H_9 had to be placed in a negative. The negative area might however be due to anisotropic thermal vibrations of O_3. It was possible to place H_{10} in a positive area on the connecting line O_4....O_2, in agreement with the assumption that it should be engaged in a hydrogen bond. The distance O_4....O_2 (Fig. 4) did however seem rather long, about 3.0 Å, and might not correspond to a hydrogen bond. Even if it was assumed that the other positive areas in the neighbourhood of O_4 (Fig. 1a) were due to anisotropic vibrations of this atom, it was thought better to wait for the correct position of H_{10} to reveal itself during the further refinement. H_{10} was therefore not included in the first calculations, during which corrections were made for the thermal parameters of the heavy atoms only. For atoms with anisotropic thermal vibration the following formula was used, where ψ is the angle between the direction of maximum vibration and the b-axis, and φ is the angle between the normal of the reflecting plane and the direction of maximum vibration: $F = f_o \cdot A \exp[-(B + \Delta B \cos^2\varphi) \sin^2\Theta/\lambda^2] + f_o \cdot D \exp[-(B + \Delta B \cos^2(180° - 2\psi \pm \varphi))\sin^2\Theta/\lambda^2]$.

Positive sign before φ for $0° < \psi < 90°$ and negative sign for $90° < \psi < 180°$ A and D means:

$$\begin{aligned} h + k \text{ equal,} \quad A &= 2\cos 2\pi hx \cos 2\pi ky - 2\sin 2\pi hx \sin 2\pi ky \\ D &= 2\cos 2\pi hx \cos 2\pi ky + 2\sin 2\pi hx \sin 2\pi ky \\ h + k \text{ odd,} \quad A &= +2\cos 2\pi hx \cos 2\pi ky - 2\sin 2\pi hx \sin 2\pi ky \\ D &= -2\cos 2\pi hx \cos 2\pi ky - 2\sin 2\pi hx \sin 2\pi ky \end{aligned}$$

When it became evident from the difference map that sufficient corrections had been made for the vibrations of the atoms, H_{10} had appeared as a maximum of height 0.4 $e \cdot Å^{-2}$, on the line O_4....O_2'. H_8 was now situated in a minimum, -0.3 $e \cdot Å^{-2}$, and was moved to a maximum, 0.6 $e \cdot Å^{-2}$, at a distance of about 0.5 Å from the line O_2.....O_3'. The insertion of H_{10} and the shift of H_8 seemed to cause a better agreement between F_c and F_o, and the discrepancy factor became slightly smaller. During the whole refinement process, the hydrogen coordinates were changed only three times. All coordinates were finally adjusted [8] on the basis of gradients still present at some atomic positions in the last difference map.

Table 1. Reflections affected by secondary extinction.

Reflection	$\|F_c\|$	$\|F_o\|$	$\|F_o\|$ corrected
040	37.2	30.4	34.6
060	29.5	25.3	27.0
110	26.0	23.1	25.2
120	36.1	32.4	36.8
170	43.3	38.4	42.0
180	36.2	34.6	37.0
210	42.8	40.8	45.6
240	69.6	59.4	71.2

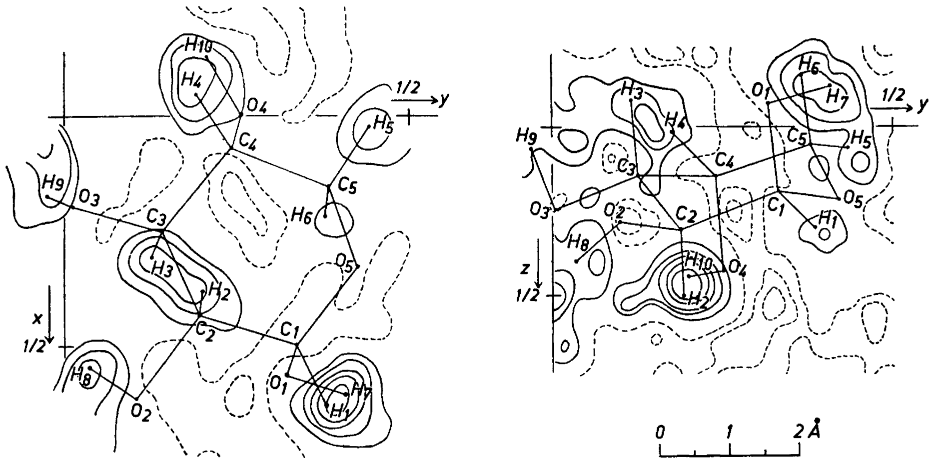

Fig. 2. The final difference projections of β-arabinose (a) along the *c* axis and (b) along the *a* axis, with hydrogen atoms *not* subtracted. Contour lines at intervals of 0.2 e·Å^{-2}, with negative lines dashed. The zero line is omitted.

In the course of the refinement process it was found that F_o values for the largest structure factors were systematically too low as compared with F_c. This might be due to secondary extinction, and the relevant reflections were for a few refinement cycles omitted from the calculations. Corrections for secondary extinction were then made according to the formula of Lipson [9], and the corrected reflections were again included in the synthesis.

The a-axis projection. Eight succesive refinements were carried out before R_{0kl} had dropped to 0.144. At this point the difference map showed positive areas for all hydrogen atoms in positions which agreed with the y coordinates found in the c-axis projection, and the hydrogen atoms were accordingly included in the calculations. Corrections were made for individual and anisotropic

Table 2. Individual and anisotropic temperature factors and the angle ψ between the direction of maximum vibration and the b-axis.

	c-axis projection			*a*-axis projection		
Atom	ψ(°)	B(Å^2)	ΔB(Å^2)	ψ(°)	B(Å^2)	ΔB(Å^2)
C_1		3.2			3.0	
C_2		3.0			3.0	
C_3		3.0			3.0	
C_4		3.5			4.0	
C_5		3.5			4.5	
O_1	0	3.5	0.5		3.2	
O_2		4.0		135	2.3	1.2
O_3	63	3.0	4.0		3.2	
O_4	0	3.7	3.5	35	4.0	2.6
O_5		3.2		74	2.0	2.0
H_{1-10}		3.5			3.5	

Table 3. Atomic coordinates, in fractions of corresponding cell edges. The y coordinates are mean values of y coordinates from the a- and c-axis projections.

Atom	x	y	z
C_1	0.493	0.4172	0.188
C_2	0.431	0.3469	0.2985
C_3	0.251	0.3198	0.131
C_4	0.0695	0.3712	0.149
C_5	0.150	0.4414	0.053
O_1	0.5625	0.4099	−0.080
O_2	0.6075	0.3019	0.271
O_3	0.191	0.2545	0.237
O_4	−0.004	0.3781	0.426
O_5	0.325	0.4632	0.211
H_1	0.628	0.442	0.290
H_2	0.376	0.347	0.500
H_3	0.303	0.311	−0.078
H_4	−0.043	0.343	0.007
H_5	0.024	0.472	0.064
H_6	0.220	0.439	−0.149
H_7	0.600	0.454	−0.120
H_8	0.539	0.267	0.392
H_9	0.173	0.237	0.067
H_{10}	−0.125	0.352	0.444

thermal vibrations of carbon and oxygen atoms. After four cycles the discrepancy factor was reduced to the final value of $R_{0kl} = 0.067$. As in the c-axis projection the atomic coordinates were finally adjusted on the basis of the final difference map.

DISCUSSION OF RESULTS

Accuracy. The standard deviation in electron density, evaluated as the root-mean-square of the figures in the difference maps, is 0.13 $e \cdot Å^{-2}$ in the c-axis projection and 0.16 $e \cdot Å^{-2}$ in the a-axis projection. The standard deviation in atomic coordinates was estimated from the gradients and the curvatures of the electron density peaks [10]. The curvatures 67.2 $e \cdot Å^{-4}$ and 83.6 $e \cdot Å^{-4}$ which were used for C and O, respectively, are the mean values of well resolved carbon and oxygen peaks in the c-axis projection. For the hydrogen atoms a curvature of 10 $e \cdot Å^{-4}$ was used as a rough estimate.

Table 4. Standard deviation in atomic coordinates.

		c-axis projection	a-axis projection
O	$\sigma(x)$	0.005 Å	
	$\sigma(y)$	0.006 Å	
	$\sigma(z)$		0.007 Å
C	$\sigma(x)$	0.006 Å	
	$\sigma(y)$	0.007 Å	
	$\sigma(z)$		0.009 Å
H	$\sigma(x)$	0.04 Å	
	$\sigma(y)$	0.05 Å	
	$\sigma(z)$		0.06 Å

Table 5. Bond lengths in β-arabinose.

	Length(Å)	Standard deviation(Å)		Length(Å)	Standard deviation(Å)
C_1-C_2	1.524	0.009	C_1-H_1	1.13	0.05
C_2-C_3	1.523	0.009	C_2-H_2	1.04	0.06
C_3-C_4	1.554	0.009	C_3-H_3	1.08	0.06
C_4-C_5	1.537	0.010	C_4-H_4	1.15	0.05
C_1-O_1	1.382	0.012	C_5-H_5	1.02	0.05
C_2-O_2	1.454	0.008	C_5-H_6	1.08	0.06
C_3-O_3	1.426	0.009	O_1-H_7	0.91	0.05
C_4-O_4	1.431	0.012	O_2-H_8	1.00	0.05
C_5-O_5	1.440	0.008	O_3-H_9	0.90	0.06
C_1-O_5	1.421	0.008	O_4-H_{10}	0.94	0.05

On account of overlapping, the errors in calculated bond lengths (Table 5) and bond angles (Table 6) may be larger than should be expected from the calculated standard deviations. However, the correspondence between the two independently determined sets of y coordinates, one from each zone, indicates that the estimates are of reasonable order of magnitude. The average difference between independently determined y coordinates are 0.006 Å for C and 0.008 Å for O atoms, and with respect to the overlapped atoms the y-differences are 0.002 Å, 0.006 Å and 0.002 Å for C_1, O_1, and O_4, and none for C_4. The standard deviations in bond lengths, calculated on the basis of the values in Table 5, are 0.012 Å for C—C (1.535 Å), and C—O (1.434 Å) bonds, and 0.04 Å for C—H (1.08 Å) and O—H (0.94 Å) bonds.

Bond lengths. The approximate molecular structure of β-arabinose has been described elsewhere [1]. Bond lengths and bond angles as derived from the present refinement and listed in Tables 5 and 6, may now be compared with those from other sugar investigations, of which the structure analysis

Table 6. Bond angles in β-arabinose.

	Angle(°)	Standard deviation(°)		Angle(°)
$C_1-C_2-C_3$	109.2	0.6	$O_5-C_1-H_1$	107
$C_2-C_3-C_4$	109.7	0.6	$O_1-C_1-H_1$	101
$C_3-C_4-C_5$	107.1	0.6	$C_2-C_1-H_1$	116
$C_4-C_5-O_5$	111.9	0.6	$C_1-C_2-H_2$	115
$C_5-O_5-C_1$	112.7	0.6	$C_3-C_2-H_2$	104
$O_5-C_1-C_2$	109.5	0.6	$O_2-C_2-H_2$	111
$O_5-C_1-O_1$	113.0	0.7	$C_2-C_3-H_3$	108
$C_2-C_1-O_1$	108.9	0.7	$C_4-C_3-H_3$	113
$C_1-C_2-O_2$	107.3	0.6	$O_3-C_3-H_3$	106
$C_3-C_2-O_2$	110.8	0.6	$C_3-C_4-H_4$	98
$C_2-C_3-O_3$	109.3	0.6	$C_5-C_4-H_4$	118
$C_4-C_3-O_3$	110.1	0.6	$O_4-C_4-H_4$	113
$C_3-C_4-O_4$	111.7	0.7	$C_4-C_5-H_5$	103
$C_5-C_4-O_4$	108.3	0.7	$O_5-C_5-H_5$	116
$C_1-O_1-H_7$	101		$C_4-C_5-H_6$	112
$C_2-O_2-H_8$	90		$O_5-C_5-H_6$	99
$C_3-O_3-H_9$	93		$H_5-C_5-H_6$	115
$C_4-O_4-H_{10}$	109			

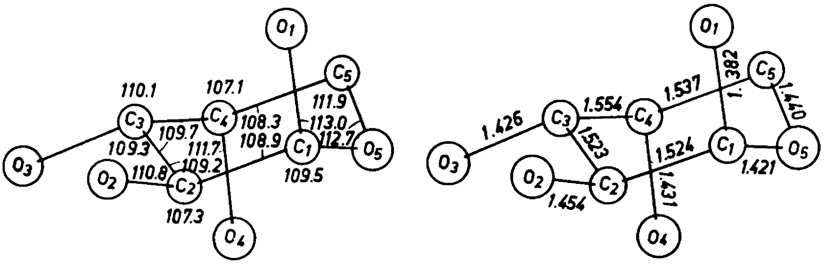

Fig. 3. Bond angles (°, left) and bond lengths (Å, right) in the β-arabinose molecule.

of α-rhamnose monohydrate [3] is presumably the most accurate. In β-arabinose the mean of C—C bonds is 1.535 Å. No individual C—C bond differs significantly from this mean value which agrees with the corresponding value for α-rhamnose, 1.532 Å. The mean value of C—O bonds, excluding C_1—O_1, is 1.434 Å in β-arabinose, exactly the same as in α-rhamnose. The bond C_1—O_1 is found to be 1.382 Å in β-arabinose and 1.376 Å in α-rhamnose, and both values differ significantly from the mean value 1.434 Å. According to Pauling [11] a C—O bond of 1.38 Å should correspond to 9% double bond character.

A detailed discussion of C—H and O—H bond lengths is hardly warranted in view of the uncertainty in the coordinates of the hydrogen atoms. The mean values of the six C—H and four O—H bonds should, however, be fairly accurate, and permit a comparison with C—H and O—H bonds reported in other X-ray investigations. In some recent X-ray analyses C—H bond lengths have been found shorter than would be expected from the currently accepted values [12,13], which are 1.09—1.11 Å for sp^3-hybridized and 1.07—1.09 Å for sp^2-hybridized carbon. Thus Tomiie *et al.*[14] reported a C(sp^2)-H bond of 0.94 Å in diformylhydrazine, and Marsh [15] found a C(sp^3)-H distance of 0.91 Å in glycine. In salicylic acid a C(sp^2)-H distance of 0.89 Å has been reported by Cochran. [16] Bommel and Bijvoet [17] found C(sp^3)-H bonds of 1.00—1.02 Å in ammonium hydrogen D-tartrate. The mentioned bond lengths appear to be significantly shorter than the normal C—H bond lengths, and the authors assume the shortening to be caused by a displacement of the electron cloud in the hydrogen atom towards the adjacent atom. The maximum of electron density might therefore be located nearer to this atom and give a shortened "bond" as result. The theoretical treatment by Cochran [18] of the electron distribution in the benzene molecule, indicates that the displacement of the maximum in the hydrogen electron cloud ought not be as drastic as found in salicylic acid. The calculated displacement in benzene was about 0.03 Å. In α-pyridone Penfold [19] found the mean value of C(sp^2)-H bond lengths to be 1.04 Å, in agreement with Cochran's theoretical results. For β-arabinose the mean length of C(sp^3)—H bonds is found to be 1.08 Å, and thus there seems to be only slight displacement of the maximum in the hydrogen electron cloud in agreement with Cochran's calculted shortening in benzene, and with α-pyridone.

McDonald[20] has derived a theoretical expression for the relation between electron distribution and temperature factor in a hydrogen peak. A rough estimate of the electron density at the hydrogen positions in β-arabinose gave as a mean 0.7 $e \cdot Å^{-2}$ at a temperature factor $B = 3.5$ $Å^2$ which agrees with McDonald's results. The mean length of O—H bonds in β-arabinose is 0.94 Å and agrees with those found by Cochran for salicylic acid, but it seems that a higher value might have been expected since the hydrogen atoms are engaged in hydrogen bonding[17].

Bond angles. Taking a difference of more than three times the standard deviation as real, it appears from Table 6 that some of the angles in β-arabinose deviate significantly from the tetrahedral angle. Among these are $C_5—O_5—C_1 = 112.7°$, $C_3—C_4—C_5 = 107.1°$ and $C_4—C_5—O_5 = 111.9°$ which belong to the pyranose ring. The mean value of the ring angles, excluding $C_5—O_5—C_1$, is 109.5°. The hetero atom O_5 seems to have caused a change in the angles $C_3—C_4—C_5$ and $C_4—C_5—O_5$. This seems likely because they are situated in the apparently most flexible part of the ring on account of absence of a hydroxyl group on C_5. However, O_5 might also have been expected to cause a change in the angles $C_1—C_2—C_3$ and $O_5—C_1—C_2$. Since the deviation of the angles $C_1—C_2—C_3$ and $C_3—C_4—C_5$ from their mean 108.2° and the deviations of the angles $C_4—C_5—O_5$ and $O_5—C_1—C_2$ from their mean 110.7° are not significant, a structure in which O_5 has caused deviations from the "ideal" chair form on both sides of the pyranose ring may be possible. The angle $C_1—O_5—C_5$ is in the literature reported to be 120° in α-rhamnose[3] and 111° for α-glucose[2]. In α-rhamnose the angle differs significantly from the tetrahedral angle, but the value appears surprisingly large.

The angles which include a hydroxyl oxygen atom $O_5—C_1—O_1 = 113.0°$, $C_1—C_2—O_2 = 107.3°$ and $C_3—C_4—O_4 = 111.7°$ appear to differ significantly from the tetrahedral value. The deviations may be due to repulsion between adjacent oxygen atoms, and this seems to agree with the fact that the greatest deviation is found in the angle $O_5—C_1—O_1$ where the repulsion on account of the O—O distance is presumably greatest. Exluding $O_5—C_1—O_1$, the mean value of the other angles including hydroxyl oxygen atom is 109.5°. The standard deviation in O—C—H and C—C—H angles, calculated on the basis of their deviations from 109.5°, was found to be 6°, which agrees with the values derived from the standard deviation of the atomic coordinates. This seems to confirm that the standard deviations in hydrogen coordinates have been correctly estimated. The mean value of the four C—O—H angles is 98°. A smaller than tetrahedral angle may here be expected on account of lone pair repulsion[21].

Hydrogen bonds. The intermolecular O—O distances, given in Table 7, correspond to hydrogen bonds. The distance $O_4.....O_2' = 3.035$ Å is rather long, but as H_8 is located near the connecting line it is probably engaged in a hydrogen bond between these atoms. Next to the O—O distances listed in Table 7, the closest approach of any two oxygen in the structure is 3.55 Å.

The environment of O_2 makes an interesting feature in the crystal structure, as O_2 is engaged in three hydrogen bonds. These bonds and $O_2—C_2$ are arranged in a roughly tetrahedral manner (Fig. 5). The fact that H_8 is displaced from the straight line connecting O_2 and O_3 makes for a better tetrahedral

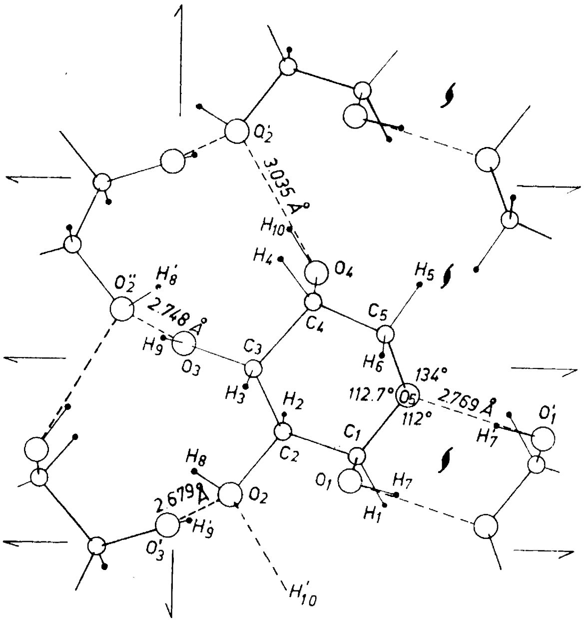

Fig. 4. The *c*-projection of the crystal structure of *β*-arabinose. Dashed lines indicate hydrogen bonds.

coordination, and supports the contention that O_2 is engaged in three hydrogen bonds.

O_3 takes part in two hydrogen bonds, O_1, O_4, and O_5 in one. O_3—C_3, O_3—H_9, and O_3....H_8' lie nearly in a plane as the sum of the angles at O_3 is

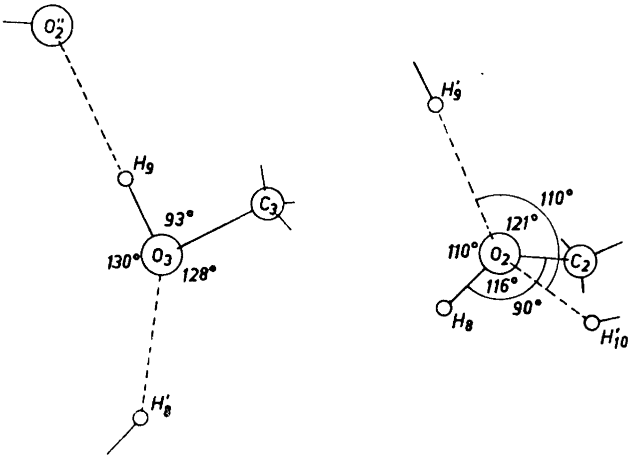

Fig. 5. Details in the crystal structure of *β*-arabinose at O_2 and O_3.

Table 7. Intermolecular O—O distances corresponding to hydrogen bonds, and angles at O atoms.

	Length(Å)	Standard deviation(Å)
$O_2...O_3'$	2.679	0.010
$O_3...O_2''$	2.748	0.010
$O_4...O_2'$	3.035	0.008
$O_5...O_1'$	2.769	0.009

Angles at O_2

	Angle(°)
$H_8-O_2..H_{10}'$	116
$H_8-O_2..H_9'$	110
$H_8-O_2-C_2$	90
$H_{10}'..O_2-C_2$	110
$H_9'..O_2..H_{10}'$	110
$H_9'..O_2-C_2$	121

Angles at O_3

	Angle(°)
$H_8'..O_3-C_3$	128
$H_8'..O_3-H_9$	130
$H_9-O_3-C_3$	93

Angles at O_5

	Angle(°)
$C_5-O_5..H_7'$	134
$C_1-O_5..H_7'$	112
$C_5-O_5-C_1$	112,7

351° (Fig. 5), and the same holds for O_5—C_5, O_5—C_1 and $O_5....H_7'$, as the sum of the angles at O_5 is 359° (Fig. 4). The direction of maximum thermal vibration of O_3 and O_5 is perpendicular to these planes. As regards O_1, O_2 and O_4 the direction of maximum vibration is about perpendicular to the C—O bonds. Thus the molecules are linked together in a three-dimensional array by hydrogen bonds in which all the available hydrogen and oxygen atoms take part.

The optical analogy between galactose and arabinose once made it difficult to designate the arabinose anomeres according to Hudson's rules [22]. The difficulty seems to have been due to the incompleteness of experimental evidence regarding the chair-formed pyranose ring and the conversion forms.

In 1909 Hudson set forth his well-known rules [23]. These were based on the suggestion that the principle of optical superposition holds for the sugars. Consequently the interest was focused on the configurations of the sugars. A relation between molecular configuration and the optical properties expressed in the α- and β-designations was sought for [22,24–26]. In 1933 the term "anomeres" was introduced by Riiber and Sørensen [25] as the class name for α- and β-forms of reducing sugars and their glycosides. Criticism was made to Hudson's rules, especially with respect to arabinose [25]. In 1947 Hassel and Ottar advanced the assumption that the six-membered pyranose ring is chair formed [27]. Each pyranose sugar should then theoretically have two chair forms, one being formed from the other by conversion of the ring, and a new problem arose concerning the relative stability of the two conversion forms. This problem was first attacked by Hassel and Ottar, who introduced what has been called the "Hassel-Ottar effect" [27], and the problem has later been approached from several different viewpoints [28].

If one adopts Reeves' symbols [29] C1 and 1C for the two possible chair forms of D-sugars, it appears that the configuration of substituents 1—5 (other than hydrogen atoms) is 1*a*5*e* and 1*e*5*a* for C1 and 1C α-D-aldohexoses, and likewise the β-forms have the configurations 1*e*5*e* and 1*a*5*a* for C1 and 1C, respectively. For aldopentoses exactly the same holds for 1—4 hydroxyl groups. α- and β-forms are consequently related to the configuration, as in fact anticipated by Hudson.

The present work has shown that the usual crystalline form of arabinose, which according to Hudson's rules is designated β-arabinose, has the configuration 1*a*2*e*3*e*4*a*. β-L-Arabinose must thus have the conversion form C1 which is the same as for α-D-galactose. Since the 1,2,3,4 hydroxyl groups in β-L-arabinose and α-D-galactose have the same configuration, the analogy in optical properties between the two sugars is explained.

Structure of β-arabinose and other pyranoses in relation to molecular criterions. For the eight aldohexoses and four aldopentoses some desirable information concerning the configuration is still missing. Half a century of research in sugar chemistry has not yet led to unambigous configurations for α- and β-forms for all [28].

Apart from the altroses, taloses and lyxoses, the expected configuration of an aldohexose or aldopentose in crystalline form follows from Reeves' investigations [29], and the molecular configurations of α-glucose [2], α-rhamnose [2], α-xylose [30] and β-arabinose, the only ones which so far have been determined by X-ray crystallographic methods, agree with Reeves' results. Reeves supposes that altroses and lyxoses exist in both conversion forms in aqueous solution, and this has later received support from work by Whiffen [31]. Mill's arguments against Reeves' "Δ 2 effect" are interesting, but do not seem to have any influence on Reeves' stability scheme. On the basis of the relative stability of α- and β-pyranosides to acid, Edward [33] discussed the problem that it is the *less* stable glucose anomer, α-glucose, which crystallizes from aqueous solution. This is explained by Edward as due to dipole-dipole interaction between the polar group on C_1 and the lone pair electrons on the ring oxygen. An axial alkoxyl group on C_1 is, according to Edward, more stable than an equatorial alkoxyl group on C_1. As to the pure pyranoses Edward believed that better opportunities for hydrogen bonding from equatorial C_1-hydroxyl group to the solvent may overcome the mentioned effect, and thus favour the anomer which has an equatorial hydroxyl group on C_1.

The distance from the oxygen atom on C_1 to the ring oxygen atom is probably independent of *e* or *a* position of the former. The difference in repulsive force between the oxygen atoms in the two configurations should therefore be mainly due to the change in relative orientation of dipoles. The direction of the dipole resulting from C_1—O_5 and C_5—O_5 is fixed in relation to the molecule, but the dipole resulting from C_1—O_1 and O_1—H will change its direction as O_1—H is rotated about the C_1—O_1 bond. It seems therefore that this dipole-dipole interaction may be quite as considerable for an axial as for an equatorial hydroxyl group on C_1. Hydrogen bonding in a solution or a crystal may fix the direction of the dipole C_1—O_1—H and thus also the magnitude of the repulsive force. It therefore seems likely that the explanation of the fact that α-glucose and not β-glucose crystallizes from an aqueous solution might be found in the crystal energy of α-glucose *versus* that of β-glucose rather than in the dipole effect. A survey of the usual crystalline form of the aldohexoses and aldopentoses [34,35] and their suggested configurations [29] seem-

Table 8. Observed and calculated *hk*0 and 0*kl* structure factors for *β*-arabinose.

k	F_o	F_c	*k*	F_o	F_c	*k*	F_o	F_c
	*hk*0 zone		13	3.8	− 3.6	19	4.3	− 3.0
			14	18.8	+18.0	20	6.5	− 5.4
	0*k*0		15	6.7	− 7.4	21	8.2	+ 8.0
2	9.7	− 9.6	16	8.3	− 7.3			
4	34.6	−37.2	17	11.5	+12.1		5*k*0	
6	27.0	−29.5	18	2.9	− 3.1	1	< 3.0	+ 0.6
8	9.1	− 9.6	19	< 3.1	− 0.8	2	< 3.0	− 0.4
10	13.0	−14.7	20	< 2.9	− 1.1	3	14.4	+15.5
12	< 2.6	+ 0.1	21	3.9	+ 3.1	4	20.1	+21.4
14	12.2	−12.0	22	< 2.4	+ 0.4	5	3.3	− 3.4
16	4.1	+ 5.0	23	3.0	+ 2.1	6	9.0	+ 8.9
18	15.0	−15.0				7	< 3.2	− 1.1
20	4.1	+ 3.1		3*k*0		8	6.8	− 5.7
22	< 2.6	+ 2.3	1	9.8	− 9.0	9	4.2	− 5.3
24	6.2	+ 4.9	2	12.2	+13.4	10	3.0	+ 2.6
			3	6.6	+ 5.8	11	< 3.2	− 1.0
	1*k*0		4	5.6	− 5.5	12	< 3.2	− 1.1
1	25.2	+26.0	5	15.0	−14.8	13	< 3.1	+ 1.0
2	36.8	−36.1	6	25.8	+25.0	14	3.0	+ 1.8
3	< 1.4	− 0.7	7	21.0	−21.0	15	< 2.8	+ 0.4
4	14.2	−14.3	8	19.2	+18.1	16	2.9	− 2.6
5	17.7	+18.2	9	5.8	− 6.2	17	< 2.5	− 0.7
6	18.7	−20.4	10	13.7	−13.7	18	3.3	− 2.7
7	42.0	−43.3	11	11.7	+11.8	19	4.1	− 3.0
8	37.0	−36.2	12	18.0	+19.0			
9	14.8	−14.7	13	23.8	+23.2		6*k*0	
10	5.0	− 6.1	14	< 3.2	+ 0.8	0	< 3.2	+ 1.8
11	29.2	+30.4	15	< 3.2	0.0	1	< 3.2	− 1.5
12	7.8	+ 7.5	16	< 3.2	0.0	2	10.8	+11.5
13	10.7	+10.9	17	< 3.2	+ 1.8	3	< 3.2	− 0.8
14	< 2.9	0.0	18	< 3.0	− 0.6	4	5.8	+ 5.9
15	8.9	− 9.7	19	< 2.9	− 0.4	5	< 3.2	+ 0.6
16	12.5	+12.1	20	6.2	− 5.2	6	9.4	−10.2
17	21.9	−22.6	21	< 2.4	+ 2.0	7	8.9	− 9.0
18	4.0	− 4.6	22	< 2.0	− 0.3	8	< 3.1	+ 1.8
19	< 3.2	+ 1.5				9	3.1	+ 1.7
20	3.6	+ 3.4		4*k*0		10	5.2	− 5.0
21	5.5	+ 4.2	0	< 2.5	+ 4.3	11	< 2.9	− 0.9
22	< 2.6	+ 0.6	1	< 2.6	+ 1.1	12	2.8	− 3.3
23	< 2.3	+ 0.2	2	< 2.6	− 0.8	13	4.0	+ 3.8
24	< 1.9	− 0.2	3	19.8	+20.5	14	< 2.4	− 1.2
			4	15.8	−15.6	15	< 2.2	− 0.6
	2*k*0		5	3.9	+ 2.3	16	< 2.0	− 0.3
0	33.7	+31.9	6	3.9	− 4.8			
1	45.6	+42.8	7	5.5	+ 5.9		7*k*0	
2	19.4	+19.4	8	9.4	+ 9.5	1	3.4	− 3.3
3	6.6	− 7.0	9	8.4	− 7.9	2	< 2.9	− 1.0
4	71.2	−69.6	01	4.8	+ 4.5	3	2.8	+ 2.7
5	25.3	+25.2	11	18.8	+18.8	4	2.5	− 2.7
6	13.0	−12.9	12	8.2	+ 9.8	5	< 2.8	+ 0.5
7	24.0	−24.1	13	< 3.2	− 0.9	6	5.4	− 5.5
8	17.2	+15.6	14	3.8	− 3.5	7	< 2.6	− 0.3
9	22.7	−23.3	15	< 3.2	+ 1.0	8	< 2.5	− 0.2
10	20.6	+20.6	16	< 3.0	+ 1.1	9	< 2.4	+ 1.7
11	< 2.6	+ 0.6	17	< 3.0	− 0.4	10	3.1	− 3.7
12	2.6	− 2.4	18	< 2.7	< 2.0	11	< 2.1	+ 1.0

Table. 8 (cont)

k	F_o	F_c	k	F_o	F_c	k	F_o	F_c
12	< 1.9	+ 1.6	21	5.9	− 5.4	18	11.1	+10.0
			22	2.0	− 1.3	19	< 2.0	− 0.2
	8k0		23	2.6	− 2.2	20	7.4	− 7.0
0	< 2.0	− 0.6	24	5.4	+ 6.7	21	8.4	+ 8.6
1	< 2.0	− 1.5						
2	< 2.0	− 1.2		0k2			0k4	
3	< 1.9	+ 0.4	0	40.7	−41.2	0	5.6	+ 5.4
4	< 1.8	− 0.2	1	< 1.6	+ 2.1	1	13.1	−11.7
5	< 1.8	− 0.3	2	25.8	−25.1	2	7.4	+ 6.6
6	< 1.6	− 0.1	3	13.2	−13.1	3	< 2.5	+ 2.4
			4	32.3	+31.9	4	14.4	+14.9
			5	16.1	+15.5	5	11.6	+12.9
	0kl zone		6	2.2	+ 3.1	6	2.6	+ 3.5
			7	1.8	+ 1.0	7	2.2	− 2.6
	0k0		8	3.1	+ 3.4	8	< 2.5	− 0.5
2	11.4	+10.2	9	13.9	−15.1	9	8.1	− 8.3
4	32.5	−34.8	10	9.2	− 9.5	10	6.9	+ 6.3
6	28.7	+28.3	11	4.7	+ 4.8	11	2.6	+ 2.2
8	10.0	− 8.7	12	< 2.4	+ 0.3	12	< 2.4	− 1.7
10	15.4	+13.5	13	4.9	+ 4.8	13	1.6	+ 1.6
12	< 2.1	− 0.7	14	7.9	− 8.6	14	< 2.3	+ 0.5
14	15.4	+15.2	15	< 2.5	− 1.0	15	4.4	− 4.4
16	4.3	+ 5.0	16	2.2	+ 1.4	16	< 1.9	− 0.1
18	18.2	+18.6	17	6.4	+ 5.5	17	3.3	+ 3.0
20	3.8	+ 3.6	18	12.2	−12.3	18	3.3	+ 3.4
22	2.2	− 1.7	19	7.6	+ 6.7			
24	5.4	+ 6.5	20	6.0	− 5.8		0k5	
			21	1.7	− 1.9	1	4.2	− 3.4
	0k1		22	3.4	− 3.7	2	< 2.4	− 1.6
1	22.0	+25.0	23	3.0	− 3.4	3	1.9	− 2.2
2	91.2	+89.0				4	< 2.4	+ 0.7
3	35.2	−33.7		0k3		5	7.5	+ 7.9
4	21.1	+19.8	1	9.3	− 7.8	6	5.1	+ 5.7
5	38.0	+38.4	2	8.5	− 8.7	7	3.6	+ 3.6
6	28.5	+27.1	3	9.1	+ 9.2	8	< 2.2	− 0.6
7	10.2	−11.0	4	1.9	+ 2.0	9	4.4	+ 5.0
8	19.6	−18.6	5	4.7	− 5.5	10	3.2	+ 3.4
9	22.5	−21.4	6	17.9	−17.3	11	1.6	− 1.4
10	12.2	+12.1	7	2.8	− 3.2	12	3.2	+ 2.2
11	10.1	+ 9.9	8	8.2	− 8.2	13	< 1.6	− 0.1
12	< 2.2	− 2.4	9	4.9	− 5.2	14	2.4	− 3.8
13	11.2	+10.0	10	4.6	+ 4.2			
14	8.7	− 9.6	11	3.3	+ 2.7		0k6	
15	< 2.4	− 1.7	12	3.1	+ 3.8	0	2.9	− 4.1
16	< 2.5	− 2.4	13	4.0	− 4.5	1	< 1.4	+ 0.3
17	< 2.5	+ 0.6	14	9.5	− 9.9	2	1.4	− 2.1
18	< 2.5	0.0	15	3.1	− 2.7	3	6.5	+ 7.6
19	3.1	+ 3.9	16	5.4	+ 5.4	4	1.6	− 2.2
20	7.6	+ 8.2	17	4.0	− 4.0	5	2.6	− 2.9

ingly gives support to this idea. Thus allose crystallizes from dilute methano with equatorial hydroxyl 1*e*, and mannose crystallizes from ethanol with equatorial hydroxyl 1*e*. With respect to mannose it is interesting to note that the "*Δ* 2" form seems to crystallize rather than the 1*a*2*a* form. Further gulose (sirup) seems to appear in β-form with 1*e*. Galactose crystallizes from water or a boiling saturated alcoholic solution in the α-form with 1*a*, but when a large excess of ice-NaCl cooled absolute alcohol is added to a solution of galactose of 0°C, the β-form with 1*e* crystallizes. Lyxose and altrose are known in α- and β-form respectively, but the configuration in which they crystallize can hardly be decided because both conversion forms, as mentioned above, seem to exist in aqueous solution. Proton magnetic resonance spectra of acetylated pyranoses [36] in chloroform show that both acetylated α-D-lyxose and α-D-altrose appear in the C1 configuration, but this does not tell which conversion form would be found in crystals of the pure sugars. Crystalline talose is known in α-form (from ethanol) and β-form (from methanol), but infrared measurements [37] seem to indicate that both conversion forms exist in solution. It has been found that the usual crystalline form of glucose [2], xylose [28] and arabinose [1] have 1*a* configuration, and the same is assumed to be the case with ribose.

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