Table 7. *Intermolecular distances* <4·0 Å *between non-hydrogen atoms*

	Molecule *A*– molecules *A* and *B*			Molecule *B*– molecule *B*	
O(1)–C(16)	21001*	3·80			
O(1)–C(15)	21001	3·99			
O(1)–C(20)	21001	3·72			
N(1)–C(4)	$21\bar{1}01$	3·95	N(2)–C(14)	21000	3·74
C(4)–O(2)	$211\bar{1}1$	3·69			
C(5)–O(2)	$211\bar{1}1$	3·79			
C(8)–C(9)	$211\bar{1}0$	3·73	C(18)–C(19)	$210\bar{1}1$	>4·0
C(10)–O(2)	$211\bar{1}0$	3·52			
C(10)–C(13)	$211\bar{1}0$	3·87			
C(8)–C(5)	$211\bar{1}0$	>4·0	C(18)–C(15)	$210\bar{1}1$	3·76
C(8)–C(6)	$211\bar{1}0$	>4·0	C(18)–C(16)	$210\bar{1}1$	3·93

* Equivalent-position nomenclature: O(1)–C(16) 21001 is taken to mean O(1) at equivalent position 1 to C(16) at equivalent position 2, translated 0, 0, 1 unit cells in the *a*, *b c* directions respectively. (1) x,y,z; (2) $-x, \frac{1}{2}+y, -z$.

radii of the atoms involved. The two independent molecules are situated on sites *A* and *B* respectively. They are held together by two strong hydrogen bonds between N(1)···H(O2) = 2·17 and N(2)···H(O1) = 2·06 Å. Fig. 4 shows some contacts between one molecule (on site *A*) and its nearest neighbors.

Table 7 shows that sites *A* and *B* are almost identical from the point of view of intermolecular distances, and this is in agreement with considerations of energy in an ideal solid solution. These results cannot explain, however, the differences between the thermal motions of molecules on sites *A* and *B*. Perhaps only a small disorder at site *B* is necessary for an understanding of these anomalies.

We thank Professor J. Jacques and Dr J. Gabard for providing the compounds and placing the solubility diagram at our disposal.

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A Neutron Diffraction Refinement of the Crystal Structure of α-L-Rhamnose Monohydrate*

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A three-dimensional neutron diffraction refinement at room temperature of α-L-rhamnose monohydrate has been completed. The heavy-atom coordinates are in good agreement with those from previous X-ray studies. The hydrogen bonding consists of two infinite chains which intersect at a four-coordinated water molecule. The H···O distances in the chains range from 1·740 to 1·981 Å. The anomeric hydroxyl is involved as a donor in the shortest bond and as an acceptor in the longest bond. There is also an isolated asymmetric bifurcated interaction with H···O distances of 1·949 and 2·715 Å, the weak component of which is an intramolecular interaction.

Introduction

Previous X-ray studies of the crystal structure of α-L-rhamnose monohydrate had been carried out by McGeachin & Beevers (1957), by Killean, Lawrence & Sharma (1971), and by Shiono (1971).

This refinement forms part of a neutron diffraction study of carbohydrates aimed at providing the accurate data relating to the hydrogen-atom positions which are necessary to understand the rules which govern the stereochemistry of the hydrogen-bonding in the crystal

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structures of these polyhydric molecules (*cf.* Jeffrey & Takagi, 1978).

Experimental

A large transparent crystal of α-L-rhamnose monohydrate, $C_6H_{12}O_5.H_2O$, was cut to a size suitable for neutron diffraction. The crystal data, experimental data and structure refinement parameters are given in Table 1. The cell constants and the three-dimensional neutron diffraction data ($\sin\theta_{\max}/\lambda = 0{\cdot}779$ Å^{-1}) were collected at room temperature on the Brookhaven High Flux Beam Reactor single-crystal diffractometer as described by Takagi & Jeffrey (1977*a*).

The atomic coordinates for non-hydrogen atoms from one of the two X-ray refinements (Shiono, 1971) were used as the initial values for a full-matrix least-squares refinement using *FLINUS*, a local version of *ORFLS* (Busing, Martin & Levy, 1962). A difference Fourier map revealed the positions of all hydrogen atoms. The refinement parameters and scattering cross-sections used are defined in Takagi & Jeffrey (1977*a*). The final agreement values are reported in Table 1. The final positional parameters for all atoms are listed in Table 2.* The results of a rigid-body motion analysis* (Schomaker & Trueblood, 1968) show a very good fit, especially for the rigid-body model consisting of the six atoms of the pyranose ring. The thermal-motion corrections to the bond lengths, made for the model which also included atoms O(1), O(2), O(3), O(4) and C(6), are given in Table 3. The atomic notation and thermal ellipsoids are shown in Fig. 1 and the molecular dimensions are given in Fig. 2. The calculation of distances and angles with their estimated standard

Table 1. *Crystal data, neutron diffraction experimental and refinement parameters for α-L-rhamnose monohydrate*

Crystal data

$C_6H_{12}O_5.H_2O$, M_r = 182·17, space group $P2_1$, $Z = 2$.

	Neutron	X-ray
a	7·901 (3) Å	7·907 (1) Å
b	7·922 (3)	7·924 (1)
c	6·670 (2)	6·668 (1)
β	95·52 (3)°	95·48 (1)°
V	415·55 Å^3	415·38 Å^3
λ	1·0514 Å	1·5405 Å
D_c	1·456 g cm^{-3}	1·455 g cm^{-3}
D_m		1·457 g cm^{-3} (Killean, Lawrence & Sharma, 1971)

Experimental and refinement data

Crystal weight	0·1164 g
Crystal volume	8·042 mm^3
Crystal faces	$(2\bar{1}0)\,(100)\,(36\bar{1})\,(11,10)\,(1\bar{1}\bar{5})\,(\bar{1}10)\,(\bar{1}01)\,(\bar{6}\bar{6}1)$
Number of reflections	
Total measured	1992 (hkl and $hk\bar{l}$ octants, $2\theta < 110°$)
Unique	1727 (85 with $F_o^2 \le \sigma F_o^2$)
Data collection mode, scan width	θ–2θ step scan with fixed width of 2·80° for $2\theta < 60°$, variable width calculated by 2·2° + 1·254° tan θ for 2θ = 60–110°
Absorption correction	*ABSOR* (Templeton & Templeton, 1973)
μ(neutron)	2·694 cm^{-1}
corr. to F_o^2	max., 1·636; min., 1·472; mean, 1·550
Number of reflections in refinement, m	1727
Number of variables, n	235
Function refined	$\sum w\lvert F_o^2 - k^2F_c^2\rvert^2$, where $w^{-1} = \sigma_c^2(F_o^2) + (0{\cdot}04F_o^2)^2$, where σ_c is from counting statistics
R	0·042
R_w	0·056
S	0·975
Extinction parameter, g	2·4 (1) × 10^4 (eleven reflections with $0{\cdot}5 > E > 0{\cdot}37$ were severely affected)

Table 2. *Fractional atomic coordinates* (×10^4) *for α-L-rhamnose monohydrate*

Estimated standard deviations given in parentheses refer to the least significant digit.

	x	y	z
C(1)	883 (1)	−1322 (2)	791 (1)
C(2)	82 (1)	−910 (2)	2721 (1)
C(3)	1426 (1)	−283 (2)	4337 (1)
C(4)	2332 (1)	1225 (2)	3514 (1)
C(5)	3135 (1)	678 (2)	1610 (1)
C(6)	4022 (2)	2106 (3)	614 (2)
O(1)	1902 (2)	−2766 (2)	1118 (2)
O(2)	−1186 (1)	339 (2)	2248 (2)
O(3)	582 (1)	108 (2)	6055 (1)
O(4)	3595 (2)	1820 (2)	5016 (2)
O(5)	1820 (1)	72*	146 (1)
*W*O	3269 (2)	5302 (3)	4615 (2)
H(C1)	−115 (3)	−1533 (4)	−451 (3)
H(C2)	−504 (3)	−2063 (3)	3249 (3)
H(C3)	2363 (3)	−1300 (4)	4680 (3)
H(C4)	1398 (3)	2232 (3)	3137 (3)
H(C5)	4034 (3)	−356 (4)	2006 (4)
H(C61)	4551 (6)	1653 (7)	−725 (6)
H(C62)	5066 (5)	2598 (7)	1609 (6)
H(C63)	3167 (6)	3118 (6)	206 (7)
H(O1)	1725 (4)	−3467 (4)	−92 (4)
H(O2)	−1897 (3)	419 (4)	3359 (3)
H(O3)	1366 (3)	227 (4)	7227 (3)
H(O4)	3587 (3)	3040 (3)	4940 (4)
H(*W*O1)	2584 (4)	5787 (4)	3480 (4)
H(*W*O2)	4359 (3)	5886 (4)	4693 (4)

* Fixed parameter.

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* Lists of observed and calculated structure factors, anisotropic thermal parameters, the results of a rigid-body-motion analysis, and a comparison of neutron and X-ray analyses for hydrogen bonds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33505 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

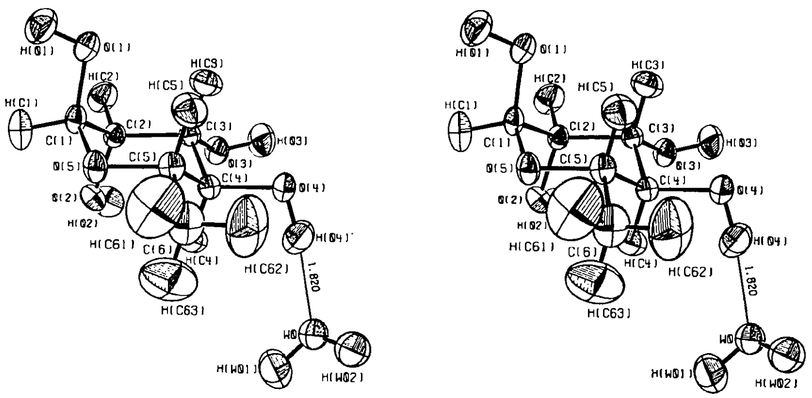

Fig. 1. α-L-Rhamnose monohydrate. The thermal ellipsoids are at 50% probability (Johnson, 1976).

Table 3. *Thermal-motion corrections* (Å) *in α-L-rhamnose monohydrate*

	Rigid-body thermal motion*	Riding motion† (lower bound)	Riding motion†
C–C	0·005 (0·006)		
C–O	0·004 (0·006)		
C–H (on ring)	0·003 (0·005)	0·004	0·021
C–H (methyl)		0·011	0·050
O–H (excluding H_2O)		0·003	0·017

* Using the model which included atoms O(1), O(2), O(3), O(4) and C(6). The values in parentheses also include the hydrogen atoms attached to the pyranose ring.

† See Busing & Levy (1964) for definition.

Table 4. H···O *hydrogen-bond distances involving anomeric hydroxyls from neutron diffraction data*

	O(1) as donor	O(1) as acceptor
α-D-Glucose (Brown & Levy, 1965)	1·914 Å*	no bond
β-L-Arabinose (Takagi & Jeffrey, 1977*a*)	1·820	no bond
β-D-Fructose (Takagi & Jeffrey, 1977*b*)	1·750	1·869, 2·065 Å
α-L-Rhamnose.H_2O (this work)	1·740	1·981
α-L-Xylose (Takagi & Jeffrey, 1978)	1·806	no bond
β-L-Lyxose (Nordenson, Takagi & Jeffrey, 1978)	1·957†	2·113

* Bonded to ring oxygen.

† Involved in bifurcated interaction with O–H···O angle 147°.

deviations was made using *FREDFUN*, a local version of *ORFFE* (Busing, Martin & Levy, 1964). The more accurate X-ray values of the cell dimensions were used.

Discussion

The hydrogen-bonding is illustrated in Fig. 3 and the corresponding numerical data have been deposited.* The hydrogen-bonding consists of two infinite chains involving all the hydroxyls except O(3)H, which intersect at a four-coordinated water molecule, and an isolated *asymmetric bifurcated* interaction from O(3)H to the ring oxygen O(5) and the hydroxyl oxygen O(4).

One of the consequences of the electronic distribution in the hemi-acetal moieties in carbohydrate molecules (Jeffrey, Pople & Radom, 1972, 1974), known as the anomeric effect (Lemieux, 1971), is that the anomeric hydroxyl O(1)–H is expected to be a strong hydrogen-bond donor and a weak hydrogen-bond acceptor. This effect has been predicted theoretically (Tse & Newton, 1977), and observed experimentally in a large number of X-ray structure determinations of carbohydrates (Jeffrey & Lewis, 1978). The data from this structure, together with those from the five other neutron studies of aldo- or keto-pyranoses, strongly support the prediction, as shown in Table 4.

The other three hydrogen bonds in the infinite chain have H···O distances of 1·773, 1·814 and 1·820 Å, which are in good agreement with the corresponding category of donor/acceptor bonds in the three methyl pyranosides that have been studied by neutron diffraction; in those structures the range for this type of bond is 1·736 to 1·810 Å (Jeffrey, McMullan & Takagi, 1977). The mean H···O neutron value for this type of hydrogen bond is 1·815 Å (Jeffrey & Takagi, 1978).

It has been noted that good agreement between X-ray and neutron diffraction positions can be obtained

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* See previous footnote.

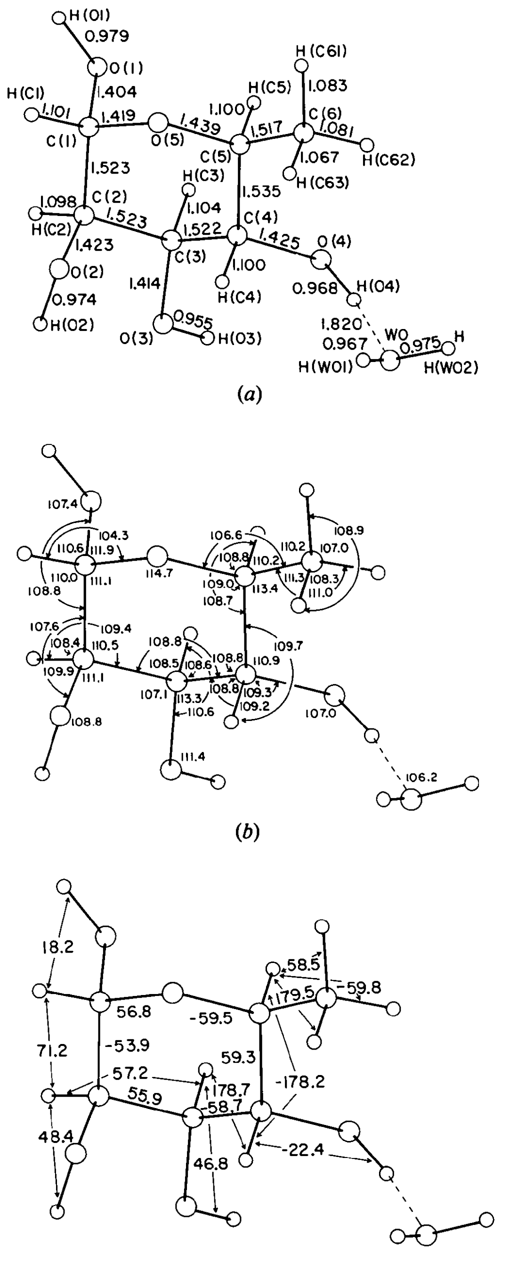

Fig. 2. Molecular dimensions in α-L-rhamnose monohydrate. (*a*) Bond lengths. E.s.d.'s: C–C, 0·001 Å except for C(5)–C(6), 0·002 Å; C–O, 0·001 Å except for C(1)–O(1), C(1)–O(5), 0·002 Å; C–H, 0·002 Å for H(C1) to H(C4), 0·003 Å for H(C5), 0·005 Å for H(C6); O–H, 0·003 Å. (*b*) Bond angles. E.s.d.'s: 0·1° except for C(5)–C(6)–H, H–*W*O–H, H–C(6)–H, 0·4°. (*c*) Torsion angles. E.s.d.'s: same as for bond angles.

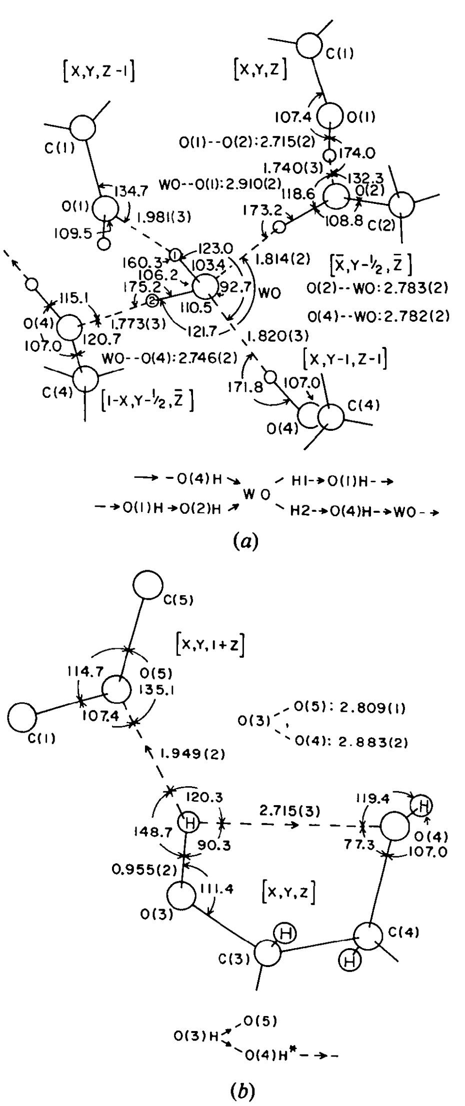

Fig. 3. Hydrogen bonds in α-L-rhamnose monohydrate.

for the hydroxyl hydrogens if the X-ray covalent O–H bond lengths are normalized to 0·97 Å by moving the hydrogen atom in the direction of the O–H bond (Jeffrey, McMullan & Takagi, 1977). This structure is no exception to that observation. The corrected H···O distances from the X-ray analysis of Shiono (1971) agree with the neutron values to better than 0·02 Å [except for the intramolecular interaction O(3)H···O(4), where it is 0·05 Å]. In contrast, the uncorrected X-ray H···O distances were longer than the neutron values by up to 0·31 Å.

As shown in Fig. 2, the C–C bond lengths in this structure range from 1·517 to 1·535 Å, with a mean value of 1·524 Å. The C–OH distances range from 1·404 to 1·425 Å, with a mean of 1·416 Å. These values are in excellent agreement with the corresponding figures for the X-ray structure refinements which are 1·509 to 1·533 Å with a mean of 1·519 Å (Shiono, 1971), 1·509 to 1·543 Å with a mean of 1·524 Å (Killean, Lawrence & Sharma, 1971) for the C–C bonds; 1·420 to 1·433 Å with a mean of 1·428 Å (Shiono, 1971), 1·419 to 1·429 Å with a mean of 1·424 Å (Killean, Lawrence & Sharma, 1971) for the C–OH

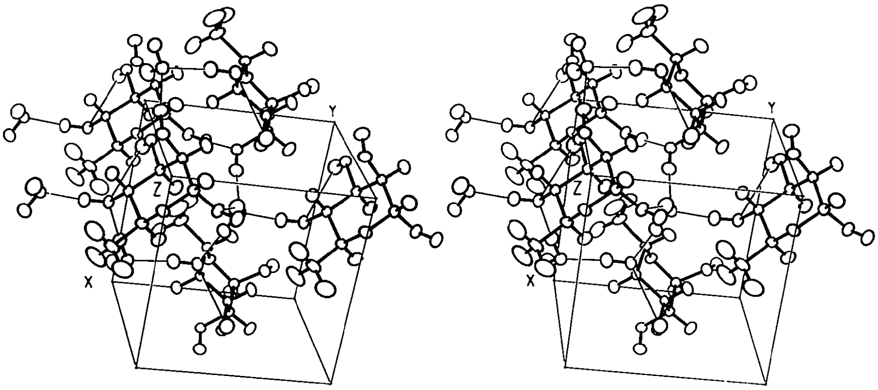

Fig. 4. Stereoview of the unit-cell contents. The thermal ellipsoids are at 30% probability (Johnson, 1976).

bonds [excluding C(1)—OH]. As has been noted in other comparisons of X-ray and neutron diffraction structure analyses, the C—O neutron diffraction values tend to be ~0·005 Å shorter than the X-ray values (Jeffrey, McMullan & Takagi, 1977).

The anomeric effect also influences the C—O bond lengths and angles in the C(5)—O(5)—C(1)—O(1) region of the molecule. The bond lengths of 1·439, 1·419, 1·404 Å are actually in closer agreement with the mean values of these bonds in eight methyl α-D-aldopyranosides (*i.e.*, 1·435, 1·416, 1·404 Å) than with those in nine α-aldopyranoses (*i.e.*, 1·445, 1·428, 1·385 Å) which have been studied. The significance, if any, of this observation is uncertain, at present. The valence bond angles of 114·7 and 111·9° for C(5)—O(5)—C(1) and O(5)—C(1)—O(1), respectively, are in good agreement with the mean values of these angles in nine α-aldopyranoses (*i.e.*, 113·7 and 111·9°), and are larger than the mean values of those in nine β-aldopyranoses (*i.e.*, 112·0 and 106·8°) (Jeffrey, Pople, Binkley & Vishveshwara, 1978).

The C—H bond lengths attached to the ring have a mean value of 1·101 and the methyl C—H bonds 1·077 Å. The O—H bond lengths range from 0·955 to 0·979 Å. The differences between methylene and methyl C—H bond lengths could be the result of differences in thermal motion. As shown in Table 3, corrections between C—H bonds for the minimum and the normal riding motion (Busing & Levy, 1964) would remove these differences (*i.e.*, 1·122 Å for the C—H bond on the ring and 1·127 Å for the methyl C—H bond).

The pyranose ring of the α-L-rhamnose molecule is a slightly distorted $^1C_4$ (L) chair, as shown by the ring torsion angles given in Fig. 2, and by the Cremer & Pople (1975) puckering parameters, which are $\theta = 174 \cdot 6$, $\varphi = 50 \cdot 0°$, $Q = 0 \cdot 580$, $q_2 = 0 \cdot 054$, $q_3 = -0 \cdot 578$ Å.

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