A Neutron Diffraction Refinement of the Structure of β-D,L-Arabinopyranose*

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Abstract. $C_5H_{10}O_5$, $M_r = 150.13$, monoclinic, $P2_1/c$, $Z = 4$. A neutron diffraction refinement of the structure has been completed at room temperature. The cell dimensions and heavy-atom coordinates are in excellent agreement with the previous X-ray diffraction study [Kim & Jeffrey (1967), *Acta Cryst.* **22**, 537–549]: $a = 5.916$ (3) [5.925 (4)], $b = 7.813$ (3) [7.820 (3)], $c = 13.339$ (6) [13.354 (6)] Å, $\beta = 99.57$ (1) [99.45 (6)]°, $V = 607.97$ [610.34] Å^3, $D_n = 1.640$ [1.638] Mg m^{-3}, $\lambda_n = 1.0415$ Å [Be(002) reflection plane] (the X-ray cell dimensions are given in square brackets). The hydrogen bonding is the same as that deduced from X-rays, but more precisely determined. Infinite chains link all the hydroxyls except the anomeric hydroxyl with H···O bond lengths of 1.753, 1.858, 1.863 Å and O–H···O angles of 172, 162 and 170°. The anomeric hydroxyls form isolated hydrogen bonds to the ring oxygens, with lengths and angles of 1.811 Å and 169°.

Introduction. The crystal structure of β-D,L-arabino-pyranose was determined by Kim & Jeffrey (1967) by X-ray methods. This neutron refinement was carried out to provide more precise data relating to the geometry of the hydrogen bonding. β-D,L-Arabino-pyranose was obtained from Sigma Chemical Company. Suitable crystals for neutron data collection were obtained by slow evaporation of a 95% ethanol–water solution at room temperature.

The crystal and experimental data, given in Table 1, were measured on the Brookhaven High Flux Beam Reactor diffractometer as described in Takagi & Jeffrey (1977). The initial coordinates were those from the X-ray study and refinement was by full-matrix least-squares calculations (Busing, Martin & Levy, 1962). Refinement parameters and the neutron scattering lengths used are defined in Takagi & Jeffrey (1977). The final refinement data are given in Table 1. The final positional parameters are given in Table 2 for the L

Table 1. *Neutron diffraction experimental data and refinement parameters for* β-D,L-*arabinopyranose*

Crystal weight: 0.0019 g
Crystal volume: 1.1607 mm^3
Crystal faces: (100) (010) (001) ($\bar{1}$00) (00$\bar{1}$) (10$\bar{2}$) ($\bar{1}$04) (03$\bar{4}$) (2$\bar{2}$$\bar{1}$) (166)
Number of reflections measured: 4112 (hkl and $hk\bar{l}$ and partial hkl and $\bar{h}k\bar{l}$)
Number of unique reflections: 2243, 2036 with $F_o^2 > 0.0$
Data-collection mode: θ–2θ step scan with fixed width 3.0° for 2$\theta \le 60°$; variable width calculated by 1.5° + 3.0° tan θ for 60° < 2$\theta \le 105°$.
Absorption correction: *ABSOR* (Templeton & Templeton, 1973)
μ(neutron) = 0.252 mm^{-1}
Maximum, minimum and average corrections to F_o^2: 1.343, 1.151, 1.221
Extinction parameter, g (Coppens & Hamilton, 1970): 0.10 (2) × 10^4
R between symmetry-equivalent F_o^2 's = 0.034
Final refinement cycles
Number of reflections in refinement, m = 2036 ($F_o^2 > 0.0$)
Number of variables, n = 182

	$2036\ F_o^2$	$2243\ F_o^2$
Function refined, $\sum w\lvert F_o^2 - k^2 F_c^2\rvert^2$		
$R = \sum\lvert F_o^2 - k^2 F_c^2\rvert / \sum\lvert F_o^2\rvert$	0.058	0.061
$R_w = (\sum w\lvert F_o^2 - k^2 F_c^2\rvert / \sum w\lvert F_o^2\rvert^2)^{1/2}$	0.055	0.061
$S = [\sum w\lvert F_o^2 - k^2 F_c^2\rvert^2/(m-n)]^{1/2}$	0.994	

$w^{-1} = \sigma_c^2(F_o^2) + (0.02 F_o^2)^2$, where σ_c is from counting statistics

enantiomer.§ The atomic notation and thermal ellipsoids are given in Fig. 1, molecular dimensions in Fig. 2, and the hydrogen bonding in Fig. 3. Calculation of distances and angles, with their estimated standard deviations, was made using the variance–covariance matrix (Busing, Martin & Levy, 1964). 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, for which the $\langle$r.m.s.$\lvert U_{ij} - U_{ij_{RBM}}\rvert\rangle$ was 0.0004 Å^2. The thermal-motion corrections to the bond lengths, made for the model which also included atoms O(1), O(2), O(3) and O(4), are given in Table 3.

Table 2. *Fractional atomic coordinates* (× 10⁵) *for β-L-arabinopyranose in β-D,L-arabinopyranose*

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

	x	y	z
C(1)	−6271 (15)	6863 (12)	62858 (6)
C(2)	−17044 (14)	13572 (11)	71761 (6)
C(3)	−41569 (14)	19402 (11)	67806 (6)
C(4)	−41504 (15)	33049 (11)	59570 (6)
C(5)	−29541 (17)	25834 (13)	51255 (6)
O(1)	−17947 (21)	−7830 (15)	59071 (9)
O(2)	−15935 (18)	1208 (14)	79583 (7)
O(3)	−52296 (19)	26031 (15)	75736 (9)
O(4)	−31418 (20)	48710 (14)	63538 (8)
O(5)	−6692 (19)	19977 (14)	55370 (8)
H(C1)	12162 (35)	4260 (30)	65384 (18)
H(C2)	−6849 (33)	24566 (26)	75100 (14)
H(C3)	−51313 (33)	8309 (26)	64260 (16)
H(C4)	−59309 (34)	36111 (30)	56198 (16)
H(C51)	−39632 (44)	15330 (33)	47336 (17)
H(C52)	−27141 (45)	35692 (33)	45696 (16)
H(O1)	−9483 (40)	−13521 (29)	54389 (17)
H(O2)	−26455 (36)	−8285 (25)	77232 (15)
H(O3)	−56258 (39)	16692 (28)	79947 (16)
H(O4)	−14705 (35)	47805 (28)	64911 (17)

Table 3. *Thermal-motion corrections* (Å) *for β-L-arabinopyranose in β-D,L-arabinopyranose*

	Rigid-body thermal motion*	Riding motion† (lower bound)	Riding motion†
C–C	0·004		
C–O	0·004		
C–H (on ring)	0·003	0·005	0·023
O–H		0·002	0·016

* Using the model consisting of the six atoms of the pyranose ring and atoms O(1), O(2), O(3) and O(4).

† See Busing & Levy (1964) for definition.

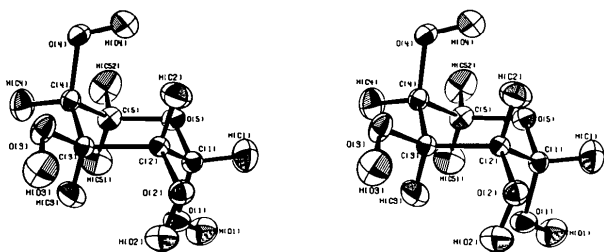Fig. 1. Atomic notation and thermal ellipsoids at 50% probability (Johnson, 1976) for β-L-arabinopyranose in β-D,L-arabino-pyranose.

Discussion. The molecular dimensions involving C and O atoms observed by neutron diffraction are in excellent agreement with those from the X-ray analysis. The mean and largest differences in the C—C bonds are 0·0022 and 0·005 Å, respectively. Greater differences are observed in the C—O bonds, with the neutron
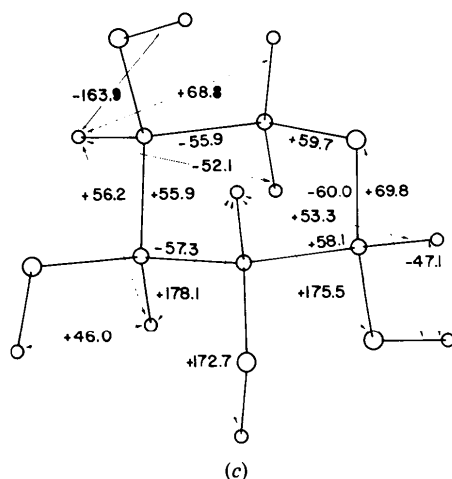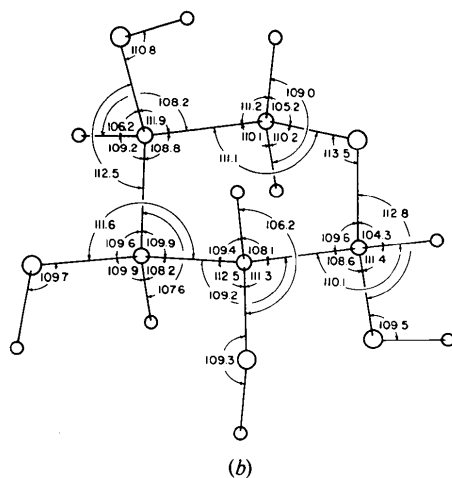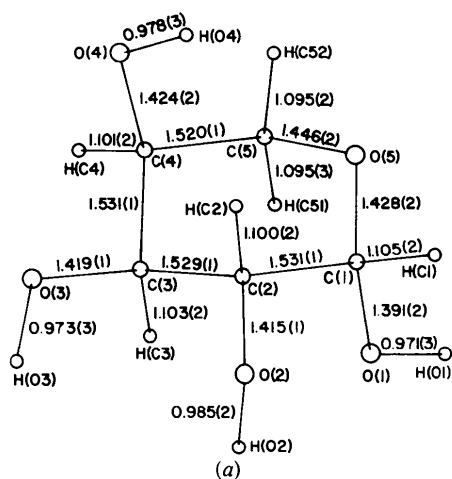

(a)

(b)

(c)

Fig. 2. Molecular dimensions of β-L-arabinopyranose in β-D,L-arabinopyranose. (a) Bond lengths (Å), (b) bond angles (°), (c) torsion angles (°). E.s.d.'s for angles are 0·1°, except for those involving C—C(5)—H, O—C(5)—H, and C—O—H, 0·2°.

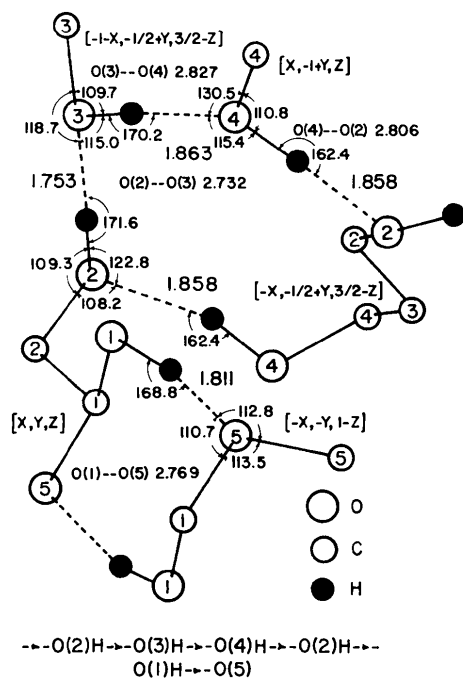$-$-$O(2)H$-$▸$-O(3)H$-$▸$-O(4)H$-$▸$-O(2)H$-$▸$-
$O(1)H$-$▸$-O(5)

Fig. 3. Hydrogen bonding in β-D,L-arabinopyranose.

values always the smaller, as is commonly observed in such comparisons of X-ray and neutron C—O bond lengths. The largest difference is in C(3)—O(3), 0·013 Å, and the mean is 0·0058 Å. It is interesting to note that the sequence of bond lengths C(1)—C(2) = C(3)—C(4) > C(2)—C(3) > C(4)—C(5) is observed in both determinations, indicating that although these bond-length differences are small, they are related to the small distortions in the ring structure from a strain-free conformation. There is a similar parallel in the X-ray and neutron values of the valence angles, with the ring valence angles in the sequence O > C(5) > C(1) ≃ C(2) ≃ C(3) > C(4) in both determinations. The ring torsion angles agree in both determinations to 0·5°. The Cremer & Pople (1975) puckering parameters are $Q = 0·584$ Å, $\theta = 2·07°$, $\varphi = 139·5°$, compared with values of 0·584 Å, 2·11°, 132·7° from the X-ray data.

The hydrogen bonding, shown in Fig. 3, consists of infinite chains and isolated links. The H···O bond lengths in the infinite chains have a mean value of 1·825 Å, slightly longer than the mean of 1·815 Å based on 23 other neutron diffraction measurements of type IA bonds (see Jeffrey & Takagi, 1978). The three O—H···O angles have a mean value of 168°, i.e. slightly more linear than the theoretically predicted and generally observed value of 165° (Newton, Jeffrey & Takagi, 1979).

The isolated bonds are from the anomeric hydroxyls to the ring oxygens. The same type of isolated links (type IIB, Jeffrey & Takagi, 1978) is observed in the crystal structure of β-L-arabinopyranose (H···O,

1·820 Å, O—H···O, 170°; Takagi & Jeffrey, 1977), and in α-D-glucopyranose (H···O, 1·914 Å, O—H···O, 161°; Brown & Levy, 1965), and with less accuracy of X-ray determination in the crystal structures of D,L-mannopyranose (Planinsek & Rosenstein, 1967) and α-L-fucopyranose (Longchambon, Ohannessian, Avenel & Neuman, 1975).

Both the anomeric hydroxyls and the ring oxygens act as 'chain stoppers' in carbohydrate hydrogen-bonding schemes; the former because of the electronic structure of the oxygen associated with the anomeric effect (cf. Jeffrey, Gress & Takagi, 1977; Tse & Newton, 1977), the latter because it has no hydrogen attached to form a hydrogen bond. There will therefore be energetic advantages to linking them together, rather than incorporating them in long chains involving other hydroxyls, where they disrupt the maximum cooperative effect achieved by having 'infinite' chains of hydrogen bonds (Jeffrey & Lewis, 1978).

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