β-L-Lyxopyranose: A Neutron Diffraction Refinement*

By S. Nordenson† and Shozo Takagi‡

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, *USA*

and G. A. Jeffrey

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, *USA*

Abstract. $C_5H_{10}O_5$, $M_r = 150 \cdot 13$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 9 \cdot 599$ (3), $b = 10 \cdot 365$ (3), $c = 6 \cdot 524$ (2) Å, $(\lambda_n = 1 \cdot 0516$ Å$)$, $V = 649 \cdot 10$ Å^3. The structure was refined from previous X-ray data [Hordvik (1966). *Acta Chem. Scand.* **20**, 1943–1954], to $R(F^2) = 0 \cdot 048$ for 1463 unique reflections. The C and O parameters agree closely with those from the previous work. The hydrogen bonding consists of a finite chain with two bifurcated interactions. One of these, from O(2)H, is very weak, involving two H⋯O distances of 2·113 and 2·634 Å, at an angle of 91°. The other bifurcated bond, from the anomeric hydroxyl O(1)H, is stronger and consists of interactions at 1·957 and 2·300 Å, at an angle of 106°. There are two normal strong hydrogen bonds with H⋯O distances of 1·718 and 1·793 Å, and O—H⋯O angles of 177 and 171°.

Introduction. Previous X-ray studies of β-L-lyxo-pyranose (I) were by Hordvik (1966) and by Morild (1976) using 1511 Cu *K*α diffractometer data. This study was undertaken primarily to obtain a more accurate description of the hydrogen bonding.

(I)
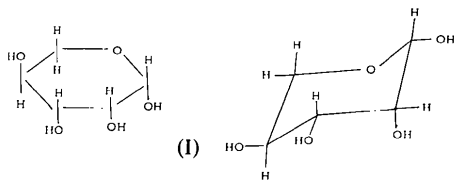
A specimen with volume 4·85 mm³, suitable for neutron diffraction data collection, was obtained by cutting a larger crystal, grown by slow evaporation of an ethanol–water solution. The cell dimensions were obtained by least-squares fit to 29 2θ values with 40 < 2θ < 60° with $\lambda_n = 1 \cdot 0516$ Å. These values are about 0·2% larger than those reported by Hordvik (1966). Absorption and extinction corrections were applied (Templeton & Templeton, 1973; Coppens & Hamilton, 1970). The maximum and minimum absorption corrections were 1·535 and 1·332 respectively. The refined isotropic extinction parameter was $g = 0 \cdot 09(1) \times 10^4$.

The non-hydrogen atom coordinates of Hordvik (1966) with isotropic thermal parameters ($B_c = 2 \cdot 5$, $B_o = 3 \cdot 0$ Å^2) were used to calculate the phases and a difference Fourier synthesis, which showed all the H atoms. Subsequent refinement was by a full-matrix least-squares procedure using isotropic, then anisotropic thermal parameters and, finally, including an isotropic extinction parameter (Coppens & Hamilton, 1970). Several trials with an anisotropic extinction parameter (Becker & Coppens, 1975) failed because two of the components became negative. An inspection of the data showed that $F_{hkl} > F_{\bar{h}kl}$ when $h \leq 2$ and $F_{hkl} < F_{\bar{h}kl}$ when $h > 4$. This may have been caused by some splitting of the strongest reflections in the high-angle region. However, the overall agreement between the 1463 pairs of symmetry-equivalent structure amplitudes was satisfactory, $R(F^2) = 0 \cdot 053$. The parameter refinement was from averaged F^2 values which gave a lower R value than that from the data of either of the separate octants. Refinement on $\sum \omega(F_c^2 - k^2 F_o^2)^2$ with $\omega^{-1} = \sigma_c^2(F_o^2) + (0 \cdot 02 F_o^2)^2$, for 1352 values with $F_o^2 > \sigma(F_o^2)$ gave $R(F^2) = 0 \cdot 048$, $R(\omega F^2) = 0 \cdot 061$. $R(F^2) = 0 \cdot 050$, $R(\omega F^2) = 0 \cdot 064$ for all 1463 reflections. The final parameters are given in Table 1.§ They differ by less than 1 σ from the refinement of the two separate sets of unaveraged data. The scattering lengths used are those described by Takagi & Jeffrey (1977a).

A view of the molecule with the atomic notation is shown in Fig. 1. The H atoms are designated according to the atoms to which they are attached. The bond lengths and valence angles are given in Fig. 2. Table 2 gives the more important torsion angles including those between vicinal C—H bonds which can be useful for calculating NMR J_{ij} values. Results of a rigid-body thermal analysis (Schomaker & Trueblood, 1968) are given in Table 3.* The r.m.s. ΔU_{ij} were 0·0005 for a model with the ring atoms only and 0·0014 for all C and O atoms. The corrected bond lengths are shown in Table 4.* The C—C distances are increased by 0·004 to 0·009 Å, the C—O by 0·003 to 0·008 Å, the C—H by a mean value of 0·006 Å, and the O—H by 0·005 Å.

---

* Tables 3 and 4 have been deposited. See previous footnote.

Table 1. *Fractional atomic coordinates* (×10⁴) *for β-L-lyxopyranose*

The standard deviations are in parentheses, and the differences (*N–X*) between the neutron and X-ray parameters of Morild (1976) are given in square brackets.

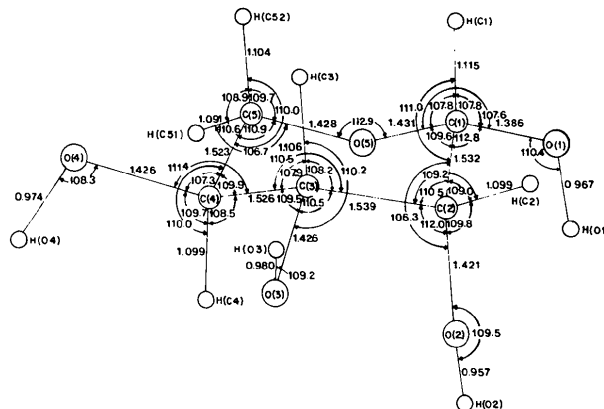|	x	y	z
C(1)	3468 (1) [−2]	1190 (1) [+2]	−713 (2) [−1]
C(2)	3689 (1) [−1]	2556 (1) [−1]	−1550 (2) [+1]
C(3)	3400 (1) [0]	3565 (1) [−3]	127 (2) [−3]
C(4)	4238 (1) [−10]	3259 (1) [0]	2054 (2) [−9]
C(5)	3993 (1) [−3]	1864 (1) [0]	2692 (2) [+2]
O(1)	3808 (2) [0]	239 (1) [−2]	−2121 (2) [+1]
O(2)	5090 (2) [+3]	2608 (1) [−9]	−2254 (2) [0]
O(3)	3748 (2) [+4]	4826 (1) [+1]	−580 (2) [+5]
O(4)	3824 (2) [−7]	4055 (1) [0]	3730 (2) [+4]
O(5)	4324 (2) [0]	1000 (1) [+5]	1058 (2) [+1]
H(C1)	2363 (3) [+100]	1039 (3) [+20]	−245 (5) [−80]
H(C2)	2972 (4) [+90]	2716 (3) [−20]	−2839 (4) [+120]
H(C3)	2281 (3) [+120]	3517 (3) [0]	528 (4) [+40]
H(C4)	5348 (3) [−150]	3414 (3) [−40]	1720 (4) [0]
H(C51)	4666 (4) [0]	1605 (3) [+40]	3976 (4) [−70]
H(C52)	2896 (4) [+70]	1730 (3) [0]	3153 (5) [+10]
H(O1)	4666 (4) [−110]	453 (3) [+40]	−2819 (5) [+90]
H(O2)	5240 (5) [−40]	3401 (3) [−170]	−2972 (6) [+70]
H(O3)	2890 (3) [+200]	5299 (2) [−130]	−892 (4) [+20]
H(O4)	4469 (3) [−150]	4778 (2) [−90]	3821 (4) [−90]
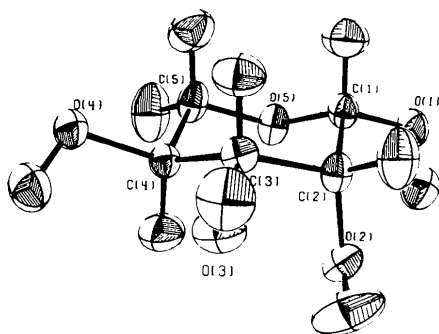
Fig. 1. *β-L-Lyxopyranose.* The thermal ellipsoids are at 50% probability (Johnson, 1976).

Discussion. The molecule has the $^1C_4$ (L) conformation, shown in (I), with a very small deformation in the direction of the $B_{3,0}$ conformation, as shown by the puckering parameters (Cremer & Pople, 1975); $\theta = 177·1$, $\varphi = 187·0°$, $Q = 0·570$, $q_2 = 0·029$, $q_3 = −0·569$ Å. The C—C bond lengths vary by 0·016 Å (2·3 σ) with a mean value of 1·5300 Å. The C—O bond lengths, excluding those of the hemi-acetal group, differ by 0·005 Å (1·7 σ), with a mean of 1·4243 Å. The C—H bond lengths vary by 0·024 Å (3σ) with a mean of 1·1041 Å. That attached to the anomeric C atom C(1) is longer than the mean by 0·011 Å, but this single observation is not significant. The O—H bond lengths vary by 0·022 Å (2·4σ) with a mean of 0·9700 Å. The length of the anomeric O(1)—H bond is very close to the mean value and does not differ significantly from those of the other O—H bonds. The orientations of the O—H bonds vary considerably from the ideal staggered arrangements which would require O—C—O—H torsion angles of ±60 or 180°, as shown by the actual values given in Table 2. That of the glycosidic C(1)—O(1)H

Fig. 2. Molecular dimensions of β-L-lyxopyranose. The bond lengths are in Å with $\sigma_{C-C} = 0·007$, $\sigma_{C-O} = 0·003$, $\sigma_{C-H} = 0·008$, $\sigma_{O-H} = 0·009$. Angles are in degrees with σ_{C-C-O} and $\sigma_{C-O-C} = 0·1$, σ_{C-C-H}, σ_{C-O-H}, and $\sigma_{O-C-H} = 0·3$, $\sigma_{H-C-H} = 0·4$.

Table 2. *Principal torsion angles* (°) *in β-L-lyxopyranose*

C(1)—C(2)—C(3)—C(4)	+52·5
C(2)—C(3)—C(4)—C(5)	−52·0
C(3)—C(4)—C(5)—O(5)	+56·1
C(4)—C(5)—O(5)—C(1)	−62·2
C(5)—O(5)—C(1)—C(2)	+61·6
O(5)—C(1)—C(2)—C(3)	−56·0
O(5)—C(1)—O(1)—H(O1)	−78·2
C(1)—C(2)—O(2)—H(O2)	+171·7
C(2)—C(3)—O(3)—H(O3)	+105·0
C(3)—C(4)—O(4)—H(O4)	−97·2
H(C1)—C(1)—C(2)—H(C2)	−56·9
H(C2)—C(2)—C(3)—H(C3)	+54·4
H(C3)—C(3)—C(4)—H(C4)	−173·5
H(C4)—C(4)—C(5)—H(C51)	+54·9
H(C4)—C(4)—C(5)—H(C52)	+175·2

bond is closest to the ideal value of −60°, in agreement with the quantitative prediction of the *exo*-anomeric effect (see Jeffrey, Pople & Radom, 1974; Jeffrey, 1978).

The anomeric C(1)—O(1) bond length of 1·386 Å agrees well with the theoretical value for the β configuration calculated by *ab initio* quantum mechanics on the model compound, methoxymethanol (Jeffrey, Pople & Radom, 1974). The two ring C—O bonds are equal (within 1σ), whereas the theory predicts a difference of 0·010 Å.
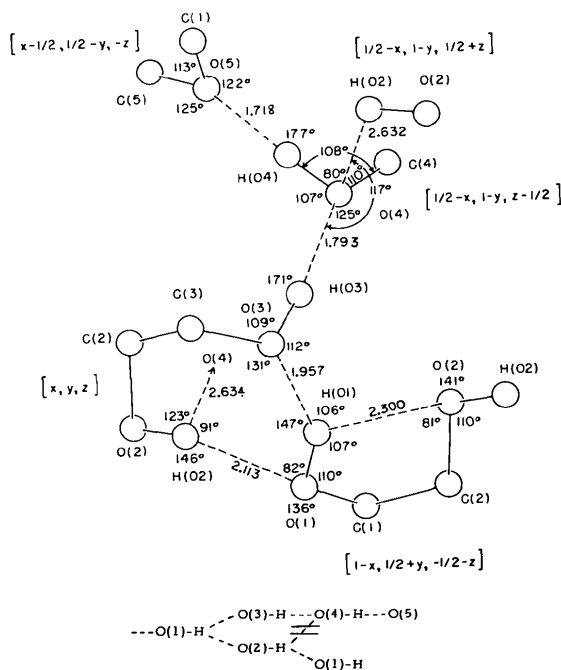

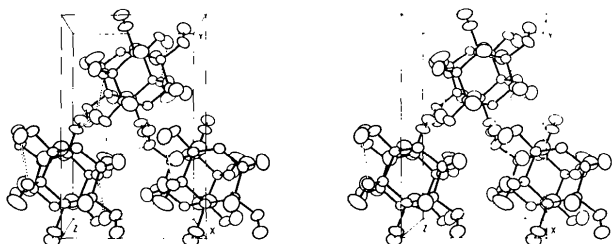Fig. 3. The hydrogen-bonding geometry in the crystal structure of β-L-lyxopyranose.

Fig. 4. The unit-cell contents and molecular packing in the crystal structure of β-L-lyxopyranose.

The hydrogen bonding is shown in Fig. 3. It is more complex than that observed in most pentoses or hexoses (*cf.* Jeffrey & Takagi, 1978) and includes two bifurcated interactions and two normal bonds. It can be described as a finite chain, which originates at O(2)—H and terminates at the ring O atom O(5), with some bifurcated cross-links.

The bifurcated interaction from O(2)—H is very weak and resembles that observed in the neutron diffraction study of methyl α-D-glucopyranoside (Jeffrey, McMullan & Takagi, 1977), where there are two H···O distances of 2·328 and 2·633 Å at an angle of 107°. The bifurcated interaction from O(1)—H is stronger. It is similar to the unsymmetrical bifurcated hydrogen bonds observed in β-D-fructopyranose (Takagi & Jeffrey, 1977b), where the H···O distances are 1·965 and 2·349 Å at an angle of 92°. In both structures, the longer interaction is intramolecular.

The bond from O(3)—H to O(4) is a normal strong bond of the donor—acceptor type with a length shorter than the 'average' value of 1·815 Å (Jeffrey & Takagi, 1978). The hydrogen bond from O(4)H to O(5) is the shortest that has been observed from a hydroxyl to a ring O atom in a carbohydrate structure studied by neutron diffraction.

The molecular packing and the contents of the unit cell are shown in Fig. 4.

References

BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* A31, 417–425.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* 97, 1354–1358.

HORDVIK, A. (1966). *Acta Chem. Scand.* 20, 1943–1954.

JEFFREY, G. A. (1978). *Am. Chem. Soc. Symp. Ser.* In the press.

JEFFREY, G. A., MCMULLAN, R. K. & TAKAGI, S. (1977). *Acta Cryst.* B33, 728–737.

JEFFREY, G. A., POPLE, J. A. & RADOM, L. (1974). *Carbohydr. Res.* 38, 81–95.

JEFFREY, G. A. & TAKAGI, S. (1978). *Acc. Chem. Res.* 11, 264–270.

JOHNSON, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

MORILD, E. (1976). Private communication.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B24, 63–76.

TAKAGI, S. & JEFFREY, G. A. (1977a). *Acta Cryst.* B33, 3033–3040.

TAKAGI, S. & JEFFREY, G. A. (1977b). *Acta Cryst.* B33, 3510–3515.

TEMPLETON, L. K. & TEMPLETON, D. H. (1973). *Amer. Cryst. Assoc. Meet.*, Storrs, CT, Abstr. E-10.