

The Crystal Structure of Methyl α -D-Lyxofuranoside

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The crystal structure of methyl α -D-lyxofuranoside has been determined by three-dimensional X-ray analysis. The phase problem was solved by a computer procedure based on direct methods. The furanose ring conformation is C_3 -endo, atom C_3 being displaced by 0.652 Å from the best four atom least-square plane. The anomeric bond C_1-O_1 is short (1.382 Å). The observed parameters of the equatorial C_2-O_2 bond (C_2 in-plane) indicate deviations from normal values analogous to those of the equatorial C-O bond parameters involving puckered C-atoms in other furanoses. All the oxygen atoms except O_1 are engaged in the hydrogen bond system which forms two-dimensional networks parallel to the *ac*-plane.

During the last few years the crystal structures of several carbohydrate compounds have been accurately determined by X-ray or neutron diffraction methods.¹ In a number of these structures the carbohydrate component is in the furanose form represented by a ribose residue and, in one case, by a fructosyl group. In all cases the furanose ring is found to be puckered as the atom C_2 or C_3 is displaced by more than 0.5 Å from the least-squares plane defined by the remaining ring atoms. Differences and similarities of the resulting conformeric possibilities and their influence on the molecular parameters have been thoroughly discussed by Sundaralingam.² By the puckering the eclipsed conformations are avoided and the conformation angles (projected valency angles), representing the coherent twistings of the ring bonds, range up to about 40°. The projected angles between adjacent C-OH bonds are found to be about 50° for *cis*-related groups and about 75° for equatorially directed *trans*-groups. The expected angular value for axially directed *trans*-hydroxyls is about 160°. Sundaralingam points out that equatorial C-O bonds at puckered atoms are shortened and the exocyclic angles are widened relative to the tetrahedral angle. Shortened anomeric bonds are observed in pyranoses and in pyranosides having equatorial glycosidic groups.³ Hitherto only one furanosidic C-O bond length, namely that in sucrose,⁴ has been

Table 1. $|U|$ -distribution of the $hk0$ -projection.

Range of $ U $	Number of reflections	Range of $ U $	Number of reflections
0.00—0.01	9	0.15—0.20	29
0.01—0.02	14	0.20—0.25	17
0.02—0.03	16	0.25—0.30	6
0.03—0.04	18	0.30—0.35	3
0.04—0.05	16	0.35—0.40	2
0.05—0.10	56	0.40—0.50	2
0.10—0.15	20	0.50—1.00	0

accurately determined. This bond is of normal length. Distinction between the ring C—O bonds is observed in both rings of sucrose, frequently in ribose residues,^{2,5} in α -L-sorbose,⁶ and in pyranosides having normal anomeric bonds.³

We thought it of interest to examine in detail the structure of a compound in which the furanose moiety constitutes the major part of the molecule. A number of methyl pentofuranosides placed at our disposal were submitted to preliminary X-ray investigations which favoured the choice of the methyl α -D-lyxofuranoside as an object for further examination.⁷ The lyxoside has a configuration different from those in the furanose moieties included in earlier structure determinations. The structural details of the methyl α -D-lyxofuranoside may thus furnish valuable supplements to our knowledge of furanose conformations. In view of the earlier observations made on anomeric bonds the C₁—O₁ bond length in the lyxoside should be of considerable interest.

CRYSTAL DATA. EXPERIMENTAL

We recapitulate the crystal data of the methyl α -D-lyxofuranoside presented previously,⁷ m.p. 96.5—97.0°C, $[\alpha]_D^{20} = +128^\circ$; crystals needle shaped, elongated along c , forms {100} and {010} developed; unit cell dimensions $a = 10.34 \text{ \AA}$, $b = 15.56 \text{ \AA}$, $c = 4.63 \text{ \AA}$, all accurate to about 0.5 %; space group $P2_12_12_1$; $Z = 4$; $D_{\text{calc}} = 1.46 \text{ g-cm}^{-3}$. The cell volume is 744.9 \AA^3 , and the asymmetric unit is one molecule C₆H₁₂O₅.

Table 2. (a) χ - and ψ_0 -values for the 14 sign sets satisfying χ -criterion. (b) χ - and ψ_0 -values for the total sets when 20 additional signs have been determined.

No.	(a)		(b)	
	χ	ψ_0	χ	ψ_0
1	0.304	3.28	0.937	7.88
2	0.308	3.25	0.967	7.60
3	0.340	3.45	1.068	7.53
4	0.281	2.92	0.976	6.76
5	0.287	2.86	0.998	6.83
6	0.289	2.60	0.929	8.37
7	0.303	2.68	1.019	6.84
8	0.289	2.79	0.939	7.00
9	0.303	2.82	1.034	7.80
10	0.289	2.65	0.873	6.77
11	0.277	2.67	1.029	7.34
12	0.292	2.61	0.827	5.70
13	0.306	2.75	1.224	6.90
14	0.291	2.70	1.163	6.30

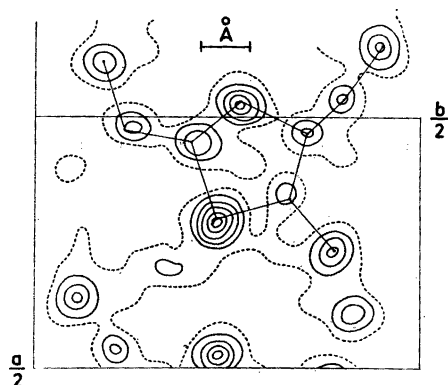


Fig. 1. Fourier map of the $hk0$ -projection based on the 76 signs determined by the computer procedure.

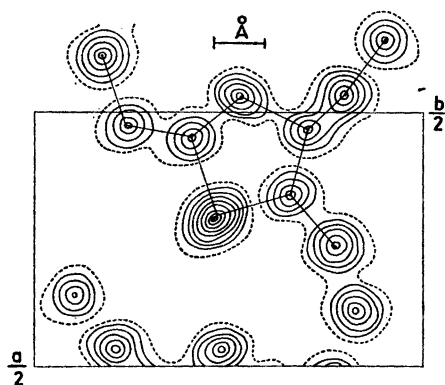


Fig. 2. Final electron density map of the $hk0$ -projection.

The X-rays reflected from the single crystals (cross sections about 0.07×0.1 mm²) exposed to Ni-filtered Cu-radiation ($\lambda = 1.542$ Å), were recorded at room temperature by the multiple film technique. Of the number of independent reflections obtainable from the layer lines $0kl-4kl$ and $hk0-hk2$ a total of 502 had measurable intensities. These were measured on integrated equi-inclination Weissenberg photographs by using a Hilger & Watts photometer. The weak reflections were estimated visually.

DETERMINATION OF THE STRUCTURE

The phase problem was solved for the $hk0$ -reflections by a computer procedure based on direct methods.^{8,9} The programs used (written in FORTRAN IV for UNIVAC 1107) are described in an earlier publication.¹⁰

The $|U|$ -distribution of the $hk0$ -projection (plane group pgg) is listed in Table 1. As one would expect from this distribution, the programmed systematic application of Harker-Kasper inequalities gave no indications about signs.

In order to specify the origin the signs $S(850)$ and $S(780)$ were chosen to be positive. 16 of the largest unitary structure factors were selected for sign permutation. Of the $2^{16} = 65536$ sign combinations tested by the machine, 14 satisfied the χ -criterion. The corresponding values of χ together with the ψ_0 -values obtained by the zero-check are listed in Table 2(a).

Since none of the sets are associated with the desired combination of large χ and small ψ_0 , all 14 sign combinations were used in turn as basis for evaluation of 20 additional signs by Sayre's sign relationship. The χ - and ψ_0 -values for the total set (in this case containing 38 signs) are given in Table 2(b), which shows the set number 14, associated with the next largest χ and the next smallest ψ_0 , should be regarded as the most probable one.

On the basis of this set, 38 additional signs were determined by Sayre's relationship, and the 76 signs thus established were used in evaluating the Fourier map which is reproduced in Fig. 1.

Table 3. Fractional coordinates for oxygen atoms and carbon atoms. (Estimated standard deviations in parentheses.) For numbering of atoms, see Fig. 3.

	<i>x</i>	<i>y</i>	<i>z</i>
O ₁	0.2126 (0.0005)	0.3974 (0.0004)	0.4251 (0.0017)
O ₂	0.5093 (0.0005)	0.3834 (0.0003)	0.2711 (0.0016)
O ₃	0.4668 (0.0004)	0.2262 (0.0003)	-0.0105 (0.0015)
O ₄	0.2179 (0.0004)	0.2659 (0.0003)	0.1959 (0.0015)
O ₅	0.1414 (0.0005)	0.0874 (0.0003)	0.2347 (0.0016)
C ₁	0.2804 (0.0007)	0.3470 (0.0004)	0.2319 (0.0022)
C ₂	0.4128 (0.0007)	0.3266 (0.0005)	0.3684 (0.0022)
C ₃	0.4345 (0.0006)	0.2335 (0.0005)	0.2857 (0.0021)
C ₄	0.2983 (0.0007)	0.1997 (0.0005)	0.3234 (0.0020)
C ₅	0.2718 (0.0007)	0.1143 (0.0006)	0.1841 (0.0022)
C ₆	0.1103 (0.0008)	0.4473 (0.0005)	0.3004 (0.0029)

The trial parameters derived from this map gave $R_{hk0}=40.0\%$. Applying a program based on the "minimum residual method",¹¹ the R -value was reduced to 15%. Two cycles of isotropic least-squares refinement reduced it further to 8.6%. Fig. 2 shows the final Fourier map. An examination of the signs corresponding to $R_{hk0}=8.6\%$ showed that 4 signs had been obtained incorrectly.

Using the x - and y -parameters arrived at by the two-dimensional analysis, and a model of the molecule, approximate *relative* z -parameters were determined. By allowing the molecule to move in small steps parallel to the z -axis and calculating the R_{hk1} -value for each step, a minimum $(R_{hk1})_{\min}=28.0\%$ was obtained. The corresponding z -parameters were used as starting coordinates in the three-dimensional refinement.

REFINEMENT OF THE STRUCTURE

A three-dimensional full-matrix least-squares refinement was carried out using a program written by Gantzel, Sparks and Trueblood¹² (revised for

Table 4. Anisotropic thermal vibration parameters. (Estimated standard deviations in parentheses). For numbering of atoms, see Fig. 3.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O ₁	0.0066 (0.0005)	0.0041 (0.0003)	0.0603 (0.0047)	0.0028 (0.0008)	0.0032 (0.0028)	-0.0058 (0.0018)
O ₂	0.0058 (0.0004)	0.0044 (0.0003)	0.0303 (0.0039)	-0.0020 (0.0006)	0.0040 (0.0027)	0.0018 (0.0018)
O ₃	0.0051 (0.0004)	0.0042 (0.0003)	0.0357 (0.0037)	-0.0006 (0.0007)	0.0044 (0.0026)	-0.0048 (0.0019)
O ₄	0.0042 (0.0004)	0.0030 (0.0002)	0.0684 (0.0047)	0.0012 (0.0005)	-0.0092 (0.0026)	0.0009 (0.0017)
O ₅	0.0062 (0.0004)	0.0037 (0.0002)	0.0363 (0.0036)	-0.0014 (0.0006)	0.0055 (0.0027)	-0.0011 (0.0016)
C ₁	0.0049 (0.0005)	0.0032 (0.0003)	0.0465 (0.0061)	0.0010 (0.0007)	-0.0031 (0.0039)	-0.0034 (0.0025)
C ₂	0.0050 (0.0005)	0.0036 (0.0003)	0.0487 (0.0061)	-0.0015 (0.0008)	-0.0005 (0.0037)	0.0023 (0.0024)
C ₃	0.0047 (0.0005)	0.0040 (0.0003)	0.0274 (0.0053)	-0.0002 (0.0007)	-0.0027 (0.0034)	-0.0029 (0.0025)
C ₄	0.0045 (0.0006)	0.0033 (0.0003)	0.0420 (0.0063)	0.0011 (0.0007)	-0.0068 (0.0036)	0.0009 (0.0022)
C ₅	0.0059 (0.0006)	0.0044 (0.0003)	0.0518 (0.0068)	-0.0020 (0.0008)	0.0045 (0.0039)	-0.0024 (0.0027)
C ₆	0.0085 (0.0008)	0.0025 (0.0003)	0.1048 (0.0099)	0.0013 (0.0009)	-0.0143 (0.0052)	-0.0035 (0.0031)

UNIVAC 1107 by cand. real. Chr. Rømming, University of Oslo). The weighting scheme No. 1:

$$\begin{aligned} &\text{for } F_o = \text{FB}, & W &= A1(F_o)^{B1} \\ &\text{for } F_o \leq \text{FB}, & W &= A2(F_o)^{B2} \end{aligned}$$

was adapted by taking

$$A1=10.0, A2=15.0, B1=0.0, B2=-0.5 \text{ and } \text{FB}=2.0.$$

The atomic form factors used were those of Hanson, Herman, Lea and Skillman.¹³

After three cycles of isotropic refinement, anisotropic thermal vibration parameters were introduced for the oxygen and carbon atoms. The positions of the hydrogen atoms of the furanose ring and the methylene group were calculated by assuming tetrahedral C-H bonds of length 1.05 Å. Those of the methyl group were localized from a total difference Fourier map, from which also the coordinates of one of the hydroxyl hydrogen atoms could be

Table 5. Fractional coordinates for hydrogen atoms. (Estimated standard deviations in parentheses). Atoms numbered from 1 to 6 are attached to carbon atoms of the same numbers (see Fig. 3); atoms numbered 7, 8, and 9 are attached to O₂, O₃ and O₄, respectively.

	<i>x</i>	<i>y</i>	<i>z</i>
H ₁	0.288 (0.007)	0.392 (0.005)	0.011 (0.017)
H ₂	0.407 (0.008)	0.334 (0.005)	0.619 (0.018)
H ₃	0.505 (0.007)	0.198 (0.005)	0.439 (0.018)
H ₄	0.289 (0.007)	0.181 (0.005)	0.575 (0.018)
H ₅	0.340 (0.007)	0.058 (0.005)	0.279 (0.018)
H ₅ '	0.301 (0.007)	0.113 (0.005)	-0.023 (0.017)
H ₆	0.134 (0.007)	0.498 (0.005)	0.138 (0.021)
H ₆ '	0.093 (0.007)	0.498 (0.005)	0.397 (0.021)
H ₆ ''	0.059 (0.007)	0.425 (0.005)	0.174 (0.017)
H ₇	0.553 (0.007)	0.385 (0.005)	0.108 (0.019)
H ₈	0.545 (0.007)	0.222 (0.005)	0.005 (0.018)
H ₉	0.073 (0.007)	0.089 (0.005)	0.435 (0.018)

determined. The two missing hydroxyl hydrogens were placed on the straight lines between hydrogen bonded oxygen atoms at distances 0.9 Å from the two hydroxyl oxygens left. All hydrogen atoms were given the isotropic thermal parameter $B=2.5 \text{ \AA}^2$, and reflections corresponding to $\sin \theta/\lambda < 0.5$ were included in the refinement of their positional parameters. The *R*-value arrived at for 502 observed reflections was 6.8 %.

Fractional coordinates and anisotropic thermal vibration parameters together with the estimated standard deviations (E.S.D., estimated from the inverse matrix of the normal equations) are given in Tables 3, 4, and 5. The expressions for the anisotropic and isotropic thermal vibrations, respectively, are:

$$\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$$

and $\exp (-B \cdot \sin^2 \theta / \lambda^2)$

Table 6. Root mean square amplitudes for the atomic anisotropic thermal vibrations along the principal axes, and the components of these axes along the crystal axes. For numbering of atoms, see Fig. 3.

	Principal axis	$(\bar{U}^2)^{1/2}$ (Å)	P_x	P_y	P_z
O ₁	1	0.165	0.080	-0.033	-0.049
	2	0.230	0.054	0.046	0.092
	3	0.266	0.006	0.031	-0.189
O ₂	1	0.158	0.074	0.018	-0.125
	2	0.192	0.055	0.007	0.175
	3	0.239	0.028	-0.061	-0.016
O ₃	1	0.159	0.088	-0.003	-0.087
	2	0.189	0.036	0.032	0.170
	3	0.238	0.015	-0.056	0.101
O ₄	1	0.137	0.091	-0.019	0.043
	2	0.194	0.028	0.062	0.009
	3	0.277	0.019	-0.001	-0.212
O ₅	1	0.167	0.082	0.014	-0.103
	2	0.200	0.026	0.038	0.164
	3	0.223	0.044	-0.050	0.095
C ₁	1	0.159	0.094	-0.015	0.018
	2	0.191	0.017	0.056	0.096
	3	0.232	0.017	0.027	-0.193
C ₂	1	0.158	0.092	0.020	-0.005
	2	0.209	0.029	-0.055	0.089
	3	0.234	0.011	-0.026	-0.197
C ₃	1	0.152	0.082	0.009	0.112
	2	0.175	0.052	-0.014	-0.176
	3	0.223	0.000	-0.062	0.055
C ₄	1	0.142	0.089	-0.014	0.068
	2	0.205	0.021	0.063	0.011
	3	0.220	0.031	-0.001	-0.205
C ₅	1	0.169	0.092	0.018	-0.031
	2	0.225	0.011	-0.047	-0.146
	3	0.250	0.029	-0.040	0.156
C ₆	1	0.172	0.029	-0.061	-0.002
	2	0.208	0.089	0.018	0.055
	3	0.344	0.023	0.006	-0.209

The principal axes of the thermal vibration ellipsoids for the oxygen and the carbon atoms were derived from the temperature parameters in Table 4. Root mean square amplitudes for the atomic anisotropic thermal vibrations along the principal axes are given in Table 6.

Observed and calculated structure factors may be found in Table 7.

Table 7. Observed and calculated structure factors.

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
67.4	59.3	20.0	21.2	20.0	20.0	21.2	20.0	21.2	20.0	4	0	4	7.1	6.5	6	9	2	8.1	9.7
0	0	0	0	0	0	0	0	0	0	4	1	1	32.4	32.3	6	10	0	10.0	-9.7
0	0	2	21.5	19.7	1	1	1	14.7	17.0	4	1	2	18.0	16.2	6	10	2	10.0	11.0
0	0	1	27.2	24.3	1	1	2	6.7	7.8	4	1	3	7.1	7.1	6	10	2	8.4	8.4
0	0	1	17.0	15.2	1	1	3	21.3	25.0	4	1	4	9.8	9.8	6	11	1	19.9	19.9
0	0	2	55.8	67.5	2	2	0	6.2	6.4	4	1	5	49.8	44.3	6	11	2	4.8	4.4
0	0	1	24.4	28.7	1	1	0	26.9	29.4	4	1	2	34.5	31.7	6	12	2	3.2	3.2
0	0	3	1.5	2.3	3	3	0	17.9	19.4	4	2	2	12.5	14.5	6	12	2	3.4	3.4
0	0	3	7.6	7.7	3	3	0	59.5	64.3	4	2	2	14.1	13.6	6	13	2	7.5	6.7
0	0	3	5.3	4.9	3	3	0	25.8	26.3	4	3	3	15.9	15.9	6	13	2	3.0	3.0
0	0	3	35.3	35.4	3	3	0	11.7	12.1	4	3	4	12.5	12.5	6	14	1	4.3	4.3
0	0	3	3.7	3.0	3	3	0	14.6	14.6	4	3	5	35.6	31.5	6	15	1	3.9	4.6
0	0	3	14.3	14.1	3	3	0	25.8	26.3	4	3	6	21.5	21.1	6	16	1	4.4	4.3
0	0	4	27.9	31.0	4	4	0	11.7	12.1	4	3	7	15.9	15.9	6	16	1	4.3	4.3
0	0	4	7.2	7.1	4	4	0	27.3	27.3	4	3	8	7.6	7.6	6	16	1	2.3	2.3
0	0	4	20.0	19.3	4	4	0	14.9	15.2	4	3	9	15.9	15.9	6	17	0	12.5	12.9
0	0	4	9.3	8.4	4	4	0	22.8	23.7	4	4	0	32.2	29.7	6	17	1	3.7	3.1
0	0	5	20.4	21.7	5	5	0	19.3	19.7	4	4	1	29.9	28.8	6	18	0	8.0	6.7
0	0	5	32.6	30.7	5	5	0	15.2	15.2	4	4	2	12.5	12.1	6	19	0	29.7	29.7
0	0	5	46.7	5.8	5	5	0	11.7	12.1	4	4	3	14.1	14.2	6	20	0	29.7	29.7
0	0	5	58.1	64.7	5	5	0	20.7	22.5	4	4	4	12.2	12.2	6	21	0	12.3	12.5
0	0	5	11.0	11.2	5	5	0	25.2	24.4	4	4	5	12.2	12.2	6	22	0	11.2	10.7
0	0	5	13.2	12.8	5	5	0	13.1	13.1	4	4	6	12.4	11.9	6	23	0	11.2	10.7
0	0	5	12.9	12.1	5	5	0	20.9	21.5	4	4	7	8.6	8.6	6	24	0	19.7	19.9
0	0	5	15.9	15.6	5	5	0	10.4	10.4	4	4	8	12.4	11.9	6	25	0	13.7	13.2
0	0	5	10.0	8.5	5	5	0	13.9	14.4	4	4	9	17.7	16.6	6	26	0	10.7	10.6
0	0	5	23.7	23.6	5	5	0	10.4	8.5	4	4	10	4.9	5.7	6	27	0	13.7	13.2
0	0	5	25.2	24.9	5	5	0	19.9	19.9	4	4	11	4.9	5.7	6	28	0	15.6	15.6
0	0	5	4.8	4.1	5	5	0	8.2	8.5	4	4	12	25.2	24.8	6	29	0	15.6	15.6
0	0	5	14.5	15.0	5	5	0	8.2	8.5	4	4	13	6.7	6.6	6	30	0	9.0	8.7
0	0	5	15.9	14.8	5	5	0	12.4	12.1	4	4	14	6.1	7.7	6	31	0	6.6	6.6
0	0	5	11.6	12.3	5	5	0	12.4	12.1	4	4	15	6.1	7.7	6	32	0	15.9	14.8
0	0	5	8.9	9.4	5	5	0	12.4	12.1	4	4	16	12.4	11.9	6	33	0	15.9	14.8
0	0	5	5.3	6.1	5	5	0	12.4	12.1	4	4	17	12.4	11.9	6	34	0	15.9	14.8
0	0	5	12.3	12.3	5	5	0	12.3	12.3	4	4	18	12.3	12.3	6	35	0	12.3	12.3
0	0	5	9.2	9.4	5	5	0	11.1	11.1	4	4	19	9.2	9.2	6	36	0	9.2	9.2
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	20	11.1	11.1	6	37	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	21	11.1	11.1	6	38	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	22	11.1	11.1	6	39	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	23	11.1	11.1	6	40	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	24	11.1	11.1	6	41	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	25	11.1	11.1	6	42	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	26	11.1	11.1	6	43	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	27	11.1	11.1	6	44	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	28	11.1	11.1	6	45	0	11.1	11.1
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0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	31	11.1	11.1	6	48	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	32	11.1	11.1	6	49	0	11.1	11.1
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0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	35	11.1	11.1	6	52	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	36	11.1	11.1	6	53	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	37	11.1	11.1	6	54	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	38	11.1	11.1	6	55	0	11.1	11.1
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0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	40	11.1	11.1	6	57	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	41	11.1	11.1	6	58	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	42	11.1	11.1	6	59	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	43	11.1	11.1	6	60	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	44	11.1	11.1	6	61	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	45	11.1	11.1	6	62	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	46	11.1	11.1	6	63	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	47	11.1	11.1	6	64	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	48	11.1	11.1	6	65	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	49	11.1	11.1	6	66	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	50	11.1	11.1	6	67	0	11.1	11.1
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0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	56	11.1	11.1	6	73	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	57	11.1	11.1	6	74	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	58	11.1	11.1	6	75	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	59	11.1	11.1	6	76	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	60	11.1	11.1	6	77	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	61	11.1	11.1	6	78	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	62	11.1	11.1	6	79	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1	4	4	63	11.1	11.1	6	80	0	11.1	11.1
0	0	5	12.3	12.3	5	5	0	11.1	11.1										

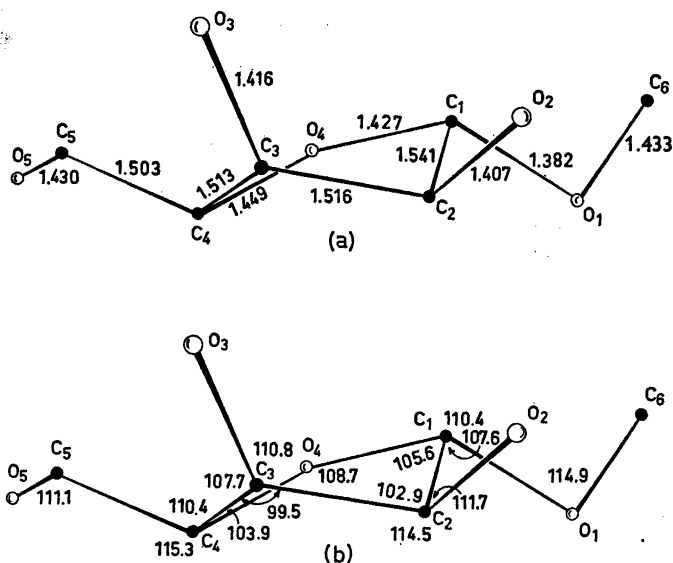


Fig. 3. Schematic drawing of the methyl α -D-lyxofuranoside molecule; (a) and (b) include the bond lengths and angles, respectively.

A final difference Fourier map, calculated with the phases determined by the parameters corresponding to $R=6.8\%$ contained no larger density fluctuations than $0.40 \text{ e}\cdot\text{\AA}^{-3}$, the E.S.D. of the electron density¹⁴ being $\sigma(\rho)=0.16 \text{ e}\cdot\text{\AA}^{-3}$.

DESCRIPTION OF THE STRUCTURE

Fig. 3 shows a schematic drawing of the methyl α -D-lyxofuranoside molecule in the crystalline state. Least-squares planes were calculated for every possible combination of four ring atoms. The best plane clearly is that defined by atoms C₁, C₂, C₄, and O₄, their deviations from the plane being 0.026 \AA , -0.016 \AA , 0.017 \AA , and -0.028 \AA , respectively. The relative displacement of atom C₃ is -0.652 \AA , and the conformation is thus the C₃-endo type.¹⁵ From considering the possible interactions between the exocyclic groups in different methyl pentofuranosides Bishop and Cooper¹⁶ suggested that C₂-exo-C₃-endo (alternatively C₃-exo) would be the preferred conformation of the methyl α -lyxofuranoside. Its present conformation, however, seems to be a stable one; the *cis* distances O₂-O₃ and O₃-C₅ are both 2.81 \AA , the *trans* distance O₁-O₂ is 3.15 \AA .

The angles between the least-squares plane of the furanose ring and the bonds C₁-O₁, C₂-O₂, C₃-O₃, and C₄-C₅ are close to 61° , 29° , 79° , and 26° , respectively.

The bond lengths of the lyxofuranoside (Table 8) are in general agreement with the available data on accurately determined furanose structures.^{2,17}

Table 8. Interatomic distances and angles (see Fig. 3), and their standard deviations.

Bond	Å	σ (Å)	Angle	(°)	σ (°)
O ₄ -C ₁	1.427	0.008	O ₄ -C ₁ -C ₂	105.6	0.5
C ₁ -C ₂	1.541	0.011	C ₁ -C ₂ -C ₃	102.9	0.6
C ₂ -C ₃	1.516	0.011	C ₂ -C ₃ -C ₄	99.5	0.6
C ₃ -C ₄	1.513	0.010	C ₃ -C ₄ -O ₄	103.9	0.6
O ₄ -C ₄	1.449	0.009	C ₄ -O ₄ -C ₁	108.7	0.5
C ₁ -O ₁	1.382	0.011	O ₄ -C ₁ -O ₁	110.4	0.6
O ₁ -C ₁	1.433	0.011	C ₁ -O ₁ -C ₂	114.9	0.8
C ₂ -O ₂	1.407	0.009	O ₁ -C ₁ -C ₂	107.6	0.8
C ₃ -O ₃	1.416	0.012	C ₁ -C ₂ -O ₂	111.7	0.7
C ₄ -C ₅	1.503	0.012	O ₂ -C ₂ -C ₃	114.5	0.6
C ₅ -O ₅	1.430	0.009	C ₂ -C ₃ -O ₃	110.8	0.7
			O ₃ -C ₃ -C ₄	107.7	0.7
			C ₃ -C ₄ -C ₅	115.3	0.7
			C ₄ -C ₅ -O ₅	111.1	0.7
			C ₅ -C ₄ -O ₄	110.4	0.7

However, the difference between the two C—O ring bonds is not significant in the present structure, but the anomeric C—O distance is markedly shortened (1.382 Å). These observations are analogous to those made on pyranoses and on pyranosides having equatorial glycosidic groups.³ Noteworthy is also the resemblance between the equatorial C₂—O₂ bond parameters in the lyxoside (C—O 1.407 Å, C—C—O 113.1°) and the parameters of the equatorial C—O bonds involving puckered atoms in other furanoses (C—O 1.407 Å, C—C—O 115.3°).² This could mean that the indicated shortening of the C₂—O₂ bond is real and that a shortened bond length and a widened exocyclic angle are features characterising an *equatorial* furanose C—O bond, no matter whether the carbon atom is involved in the puckering or not.

The *bond angles* presented in Table 8 resemble those found in the furanose compounds already referred to. Except the angle at O₄ (108.7°) all the internal

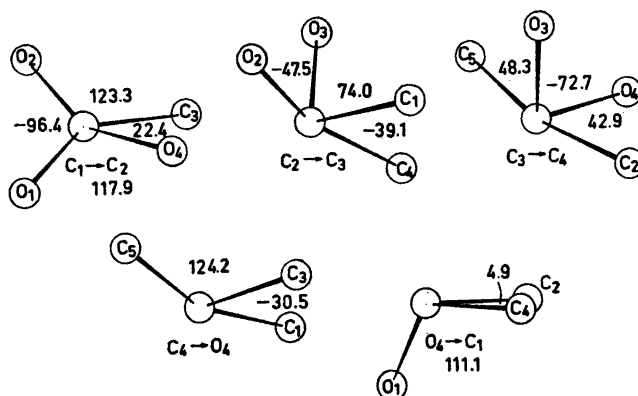


Fig. 4. Projected valency angles of the lyxofuranoside. An angle is called positive when measured counter-clock-wise from the near to the far atom.

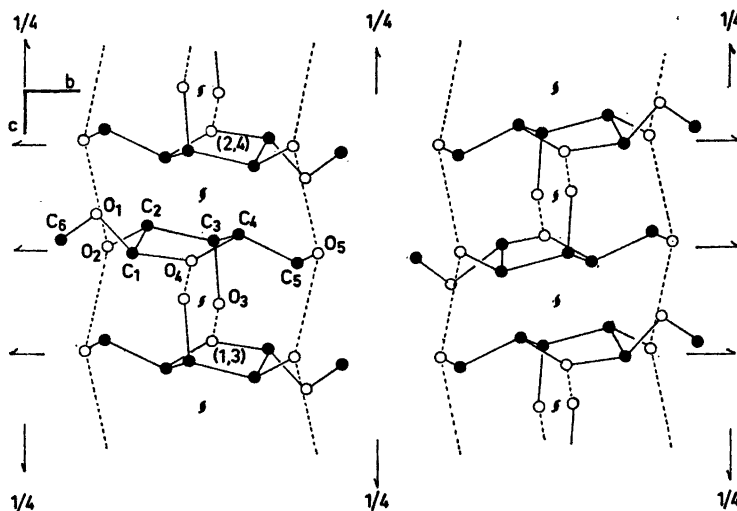


Fig. 5. The structure of methyl α -D-lyxofuranoside projected along a . The numbering of the molecules corresponds to that in Table 9 and indicates that four molecules are linked to a "central" one by hydrogen bonds.

angles are significantly smaller than the tetrahedral angle, the smallest being that at the exoplanar atom C_3 (99.5°). The average exocyclic angles at C_1 and C_3 are approximately tetrahedral, whereas, relative to this, those at C_2 and C_4 , involving typical equatorial bonds, are widened by almost 4° .

Fig. 4 shows the *conformation angles* as projected along each ring bond of the lyxoside. The angle between the *cis*-related O_2 and O_3 is close to the expected value of 50° . Also O_3 and C_5 , which are *cis*, project at about 50° .

Table 9. Interatomic distances and angles of the hydrogen bonding system. The numbers n of the symbols $(O)_n$ represent the four molecules surrounding the "central" molecule (see Fig. 5).

Bond	\AA	σ (\AA)
$O_4 \cdots (O_3)_3$	2.738	0.006
$O_3 \cdots (O_5)_1$	2.749	0.010
$O_2 \cdots (O_5)_2$	2.703	0.010
Angle	$^\circ$	σ ($^\circ$)
$C_1 - O_4 \cdots (O_3)_3$	115.3	0.4
$C_4 - O_4 \cdots (O_3)_3$	134.7	0.4
$C_3 - O_3 \cdots (O_4)_1$	121.6	0.4
$C_2 - O_2 \cdots (O_5)_1$	136.8	0.6
$C_5 - O_3 \cdots (O_5)_2$	101.1	0.6
$(O_5)_1 \cdots O_3 \cdots (O_5)_2$	116.3	0.3
$C_5 - O_5 \cdots (O_2)_3$	106.3	0.5
$C_5 - O_5 \cdots (O_3)_4$	124.5	0.6
$(O_2)_3 \cdots O_5 \cdots (O_2)_4$	116.3	0.3

Concerning the ring bonds, the successive conformation angles are roughly the same as in other C_3 -endo puckered rings. It may, however, be of some value to compare in details the conformations of the lyxoside and the furanose moiety in adenylic acid (AMP; reviewed by Sundaralingam²). The *endo*-displacement of C_3 is about 0.65 Å in both compounds, but the exactly opposite twistings of the bonds O_4-C_1 in the two rings lead to exactly reversed deviations of the atoms C_4 , O_4 , C_1 , and C_2 from their respective least-squares planes. The conformations of the two furanose rings are related in such a way that the conformation angles in the sequence $C_3-C_2-C_1-O_4-C_4-C_3$ of one ring appear one by one, with signs reversed, in the sequence $C_3-C_4-O_4-C_1-C_2-C_3$ of the other.

The crystal structure. The lyxofuranoside molecules are distributed in layers which are parallel to the *ab*-plane and separated by $c/2$ or approximately 2.3 Å. Within each layer the closest molecular approaches correspond to van der Waals' contacts. Hydrogen bonds are thus established only between molecules of different layers. Each molecule is linked to four others two of which belong to the layer above and two to that below. Except O_1 , all the oxygen atoms are engaged in hydrogen bonds. O_2 and O_5 are both associated with one acceptor and one donor bond, O_3 is a bond donor and O_4 necessarily an acceptor. Hydrogen bond distances and angles are listed in Table 9.

The present hydrogen bonding system forms two-dimensional molecular networks parallel to the *ac*-plane (Fig. 5). Stacked side by side in the *b*-direction the networks are held together by van der Waals' forces.

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