

## The Crystal Structures of Methyl $\alpha$ -L-Arabinopyranoside and Methyl $\beta$ -L-Arabinopyranoside\*

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Methyl  $\alpha$ -L-arabinopyranoside,  $C_6H_{12}O_5$ , crystallizes in space group  $P2_12_12_1$ , with  $a = 9.343(1)$ ,  $b = 17.031(1)$ ,  $c = 4.724(1)$  Å,  $Z = 4$ . Methyl  $\beta$ -L-arabinopyranoside,  $C_6H_{12}O_5$ , crystallizes in space group  $P2_12_12_1$ , with  $a = 7.763(2)$ ,  $b = 16.577(2)$ ,  $c = 5.906(1)$  Å,  $Z = 4$ . The structures were solved with *MULTAN* and refined to  $R(F)$  values of 0.025 for 953 independent reflections, and 0.037 for 964 unique reflections respectively. The  ${}^4C_1$  (*L*) chair conformations are very similar in both structures, as are the C–C bond lengths. The acetal C–O bond lengths differ significantly and the differences are in agreement with those predicted by *ab initio* quantum-mechanical calculations. Both structures have the infinite-chain type of hydrogen bonding with an additional isolated bond to the ring oxygens in the case of the  $\alpha$ -pyranoside.

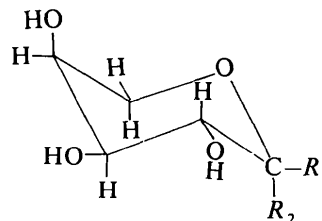
### Introduction

Comparisons between  $\alpha$  and  $\beta$  configurations of the same methyl pyranoside are interesting because of the difference in the electronic structure of the acetal group with the configuration at the anomeric C atom. This difference has been discussed by Jeffrey, Pople, Binkley & Vishveshwara (1978) using *ab initio* 431-G Hartree Fock calculations on a model compound, dimethoxymethane. It results in differences in bond lengths and valence angles, which in turn should cause differences in ring conformation, since the Sacchse chair is a *rigid* conformation (*cf.* Dunitz & Waser, 1972). These two structure analyses form part of a program aimed at distinguishing between effects of the intra- and intermolecular interactions on the detail of pyranose ring conformations in the crystalline state.

### Experimental

Transparent crystals of methyl  $\alpha$ -L-arabinopyranoside (I) and methyl  $\beta$ -L-arabinopyranoside (II) ( $C_6H_{12}O_5$ ,  $M_r = 164.16$ ) were obtained from the private collection of Professor R. Reeves of Louisiana State University, to whom we are grateful both for his foresight in collecting carbohydrate crystals and for making them available to us. It should be noted that it is a peculiarity of carbohydrate nomenclature that methyl  $\alpha$ -L-arabinoside (I) has the  $\beta$  configuration at the anomeric carbon atom C(1) when compared with that of a methyl  $\alpha$ -D-hexopyranoside, and similarly methyl  $\beta$ -L-

arabinoside has the  $\alpha$  configuration at C(1) relative to a hexopyranoside. The crystal data are given in Table 1.



(I)  $R_1 = OCH_3$ ,  $R_2 = H$

(II)  $R_1 = H$ ,  $R_2 = OCH_3$

The cell constants and intensities for both crystals were determined with graphite-monochromated  $Cu K\alpha$  radiation on a CAD-4 diffractometer. The cell constants given in Table 1 were obtained by least-squares refinement of the setting angles of 25 reflections with  $119^\circ < 2\theta < 136^\circ$  for (I) and of 24 reflections with  $108^\circ < 2\theta < 145^\circ$  for (II). A summary of the experimental conditions used in the data collection and the final values of the refinement parameters for the two structures are given in Table 1. The three reflections used as standards for both crystals did not show any intensity decrease after 35.3 and 61.6 h of X-ray exposure for (I) and (II) respectively. Absorption and  $L_p$  corrections were made for both structures using *ABSOR* (Templeton & Templeton, 1973). The crystal structures were solved with *MULTAN* (Germain, Main & Woolfson, 1971), using for phase generation 150 reflections with  $E \geq 1.32$  and 1.36 for (I) and (II) respectively. The refinements were by full-matrix least squares using *FLINUS*, a local version of *ORFLS*

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Table 1. *Crystal data and experimental and refinement parameters for the crystal structures of methyl  $\alpha$ -L-arabinopyranoside (I) and methyl  $\beta$ -L-arabinopyranoside (II)*

	(I) C <sub>6</sub> H <sub>12</sub> O <sub>5</sub>	(II) C <sub>6</sub> H <sub>12</sub> O <sub>5</sub>
Crystal data		
<i>a</i>	9.343 (1) Å	7.763 (2) Å
<i>b</i>	17.031 (1)	16.577 (2)
<i>c</i>	4.724 (1)	5.906 (1)
<i>V</i>	751.69 Å <sup>3</sup>	760.03 Å <sup>3</sup>
<i>M<sub>r</sub></i>	164.16	164.16
<i>D<sub>c</sub></i>	1.450 g cm <sup>-3</sup>	1.435 g cm <sup>-3</sup>
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Experimental and refinement data		
Crystal dimensions	0.15 × 0.15 × 0.26 mm	0.08 × 0.12 × 0.25 mm
Crystal faces	6 {110} {011} {021}	6 {100} {010} {001}
Number of reflections		
Total measured	3036 ( $2\theta_{\max} = 156^\circ$ )	4131 ( $2\theta_{\max} = 156^\circ$ )
Averaged	953 (18 with $F_o^2 \leq \sigma_{F_o^2}$ )	964 (32 with $F_o^2 \leq \sigma_{F_o^2}$ )
Data collection mode	$\theta$ - $2\theta$ scan	$\theta$ - $2\theta$ scan
$2\theta$ scan width	$3.15^\circ + 0.426^\circ \tan \theta$	$3.45^\circ + 0.426^\circ \tan \theta$
Absorption correction	ABSOR (Templeton & Templeton, 1973)	
$\mu$ (Cu <i>K</i> $\alpha$ )	10.52 cm <sup>-1</sup>	10.41 cm <sup>-1</sup>
Maximum correction to $F_o^2$	1.30	1.21
Minimum correction to $F_o^2$	1.11	1.09
Average correction to $F_o^2$	1.17	1.11
Final refinement cycles		
Number of reflections, <i>m</i>	953	964
Number of variables, <i>n</i>	149	149
$R = \sum  F_o - kF_c  / \sum F_o$ (all reflections)	0.025	0.037
$R_w = (\sum w F_o - kF_c ^2 / \sum wF_o^2)^{1/2}$ (all reflections)	0.022	0.048
$S = [\sum w F_o - kF_c ^2 / (m - n)]^{1/2}$	0.95	1.98
$w^{-1}$	$[\sigma_c^2(F_o^2) + (0.012F_o^2)^2] / 4F_o^2$	$[\sigma_c^2(F_o^2) + (0.035F_o^2)^2] / 4F_o^2$
	(where $\sigma_c$ is from counting statistics)	
Extinction parameter, <i>g</i>	$0.13 (1) \times 10^4$	$0.16 (6) \times 10^4$

Table 2. *Fractional coordinates ( $\times 10^4$ ) for non-hydrogen atoms in methyl  $\alpha$ -L-arabinopyranoside (I) and methyl  $\beta$ -L-arabinopyranoside (II)*

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

	(I)			(II)		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	10443 (2)	6113 (1)	2153 (4)	-280 (3)	8465 (1)	4889 (4)
C(2)	8992 (2)	5731 (1)	2700 (4)	-882 (3)	7753 (1)	3434 (3)
C(3)	7822 (2)	6188 (1)	1198 (4)	-1437 (3)	8050 (1)	1113 (3)
C(4)	7861 (2)	7045 (1)	2085 (4)	-2794 (3)	8711 (1)	1353 (4)
C(5)	9344 (2)	7364 (1)	1498 (5)	-2067 (4)	9372 (1)	2842 (5)
C(6)	12902 (2)	5869 (1)	2893 (8)	2106 (4)	9315 (2)	5437 (7)
O(1)	11454 (1)	5744 (1)	3796 (4)	1255 (2)	8758 (1)	3985 (3)
O(2)	9024 (2)	4940 (1)	1713 (3)	404 (2)	7143 (1)	3305 (3)
O(3)	6433 (1)	5858 (1)	1588 (3)	-2110 (2)	7411 (1)	-235 (3)
O(4)	7539 (2)	7092 (1)	5021 (3)	-4372 (2)	8415 (1)	2237 (3)
O(5)	10403 (1)	6921 (1)	3000 (3)	-1587 (2)	9061 (1)	5018 (3)

(Busing, Martin & Levy, 1962), to minimize  $\sum w|F_o - kF_c|^2$ . All the H atoms were located from difference syntheses. The non-hydrogen and H atom parameters were refined anisotropically and isotropically respec-

tively, together with the Zachariasen isotropic extinction parameter, *g* (Coppens & Hamilton, 1970).

The atomic scattering factors for O and C were those tabulated by Doyle & Turner (1968) and those for H

Table 3. Fractional coordinates ( $\times 10^3$ ), isotropic thermal parameters ( $\text{\AA}^2$ ) and bond distances ( $\text{\AA}$ ) for the hydrogen atoms in methyl  $\alpha$ -L-arabinopyranoside (I) and methyl  $\beta$ -L-arabinopyranoside (II)

Methyl $\alpha$ -L-arabinopyranoside (I)					
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (iso)	C, O—H
H(C1)	1072 (2)	610 (1)	18 (5)	3.1 (4)	0.97 (2)
H(C2)	882 (2)	575 (1)	478 (4)	2.1 (4)	1.00 (2)
H(C3)	803 (2)	615 (1)	-82 (4)	2.4 (4)	0.98 (2)
H(C4)	716 (2)	734 (1)	101 (4)	2.3 (4)	0.97 (2)
H(C51)	958 (2)	736 (1)	-64 (5)	3.7 (5)	1.03 (2)
H(C52)	945 (2)	793 (1)	219 (4)	3.4 (4)	1.02 (2)
H(C61)	1318 (2)	642 (1)	305 (5)	4.7 (5)	0.98 (2)
H(C62)	1351 (3)	554 (2)	420 (6)	7.2 (8)	1.01 (3)
H(C63)	1306 (4)	568 (2)	89 (7)	8.9 (1.0)	1.01 (3)
H(O2)	906 (3)	469 (1)	298 (6)	4.9 (7)	0.74 (3)
H(O3)	637 (3)	564 (1)	297 (6)	5.0 (7)	0.75 (3)
H(O4)	684 (3)	742 (1)	531 (7)	6.1 (7)	0.87 (3)
Methyl $\beta$ -L-arabinopyranoside (II)					
H(C1)	-7 (3)	831 (1)	657 (5)	2.1 (5)	1.04 (3)
H(C2)	-186 (3)	752 (1)	418 (4)	1.9 (5)	0.96 (2)
H(C3)	-42 (3)	827 (1)	40 (5)	1.9 (5)	0.97 (3)
H(C4)	-326 (4)	893 (2)	-8 (6)	4.3 (7)	0.99 (3)
H(C51)	-302 (4)	980 (2)	296 (6)	4.3 (7)	1.03 (3)
H(C52)	-115 (4)	960 (2)	208 (5)	3.0 (6)	0.92 (3)
H(C61)	148 (4)	983 (2)	556 (6)	4.3 (7)	0.99 (3)
H(C62)	184 (6)	912 (3)	698 (8)	7.4 (1.1)	0.99 (5)
H(C63)	341 (5)	945 (2)	485 (7)	5.6 (9)	1.09 (4)
H(O2)	133 (5)	733 (2)	246 (7)	5.1 (8)	0.93 (4)
H(O3)	-116 (4)	708 (2)	-72 (5)	3.2 (6)	0.96 (3)
H(O4)	-420 (5)	830 (2)	371 (7)	4.7 (8)	0.90 (4)

were given by Stewart, Davidson & Simpson (1965). The final positional and isotropic thermal parameters are given in Tables 2 and 3. The conformation and atomic numbering of (I) and (II) are shown in Figs. 1 and 2 respectively. The molecular dimensions for non-hydrogen atoms are reported in Figs. 3 and 4. Calculations of distances and angles with their estimated standard deviations were made using *FREDFUN*, a local version of *ORFFE* (Busing, Martin & Levy, 1964). The C—H and O—H bond distances and their estimated standard deviations are included in Table 3. Rigid-body approximations (Schomaker &

Trueblood, 1968) are good.\* Thermal-motion corrections would lengthen the C—C bonds by 0.007 and 0.005  $\text{\AA}$  for (I) and (II) respectively and the C—O bonds by 0.006 and 0.005  $\text{\AA}$  for (I) and (II) respectively over the uncorrected values shown in Figs. 3 and 4.

## Discussion

### The molecular structures

The molecules of methyl  $\alpha$ -L-arabinopyranoside (I) and methyl  $\beta$ -L-arabinopyranoside (II) have the normal  ${}^4C_1$  (*L*) chair conformation with very small differences between the ring torsion angles. The largest difference is only  $0.7^\circ$  in the value for C(1)—C(2)—C(3)—C(4). The puckering parameters, as defined by Cremer & Pople (1975), are  $q_2 = 0.015$ ,  $q_3 = 0.581$ ,  $Q = 0.582 \text{ \AA}$ ,  $\theta = 1.47$ ,  $\varphi_2 = 79.16^\circ$  for (I), as compared with  $q_2 = 0.018$ ,  $q_3 = 0.576$ ,  $Q = 0.577 \text{ \AA}$ ,  $\theta = 1.78$ ,  $\varphi_2 = 90.80^\circ$  for (II). In both compounds the direction of distortion is more towards the boat conformation ( $\varphi_2 = 120^\circ$ ) than the twist-boat ( $\varphi_2 = 30^\circ$ ). In both structures, the conformation about the glycosidic bond C(1)—O(1) is greater than  $60^\circ$ , *i.e.*  $-79.5^\circ$  for (I) and  $68.9^\circ$  for (II).

The C—C bond lengths range from 1.514  $\text{\AA}$  [C(4)—C(5) in (II)] to 1.533  $\text{\AA}$  [C(1)—C(2) in (II)] with a mean of 1.5212  $\text{\AA}$ . There is a systematic sequence in that C(1)—C(2) > C(3)—C(4) > C(2)—C(3) > C(4)—C(5) in both structures, which suggests that these small differences are related to the almost identical ring conformations. The C—OH distances range from 1.419 to 1.426  $\text{\AA}$ , with a mean of 1.4232  $\text{\AA}$ . As predicted from the theoretical *ab initio* quantum-mechanical calculations (Jeffrey, Pople, Binkley & Vishveshwara, 1978) on a model compound,  $\text{H}_3\text{C—O—CH}_2\text{—O—CH}_3$ , the acetal geometry is significantly different in the two

\* Lists of structure factors, anisotropic thermal parameters, bond angles involving H and results of rigid-body-motion analyses have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33278 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

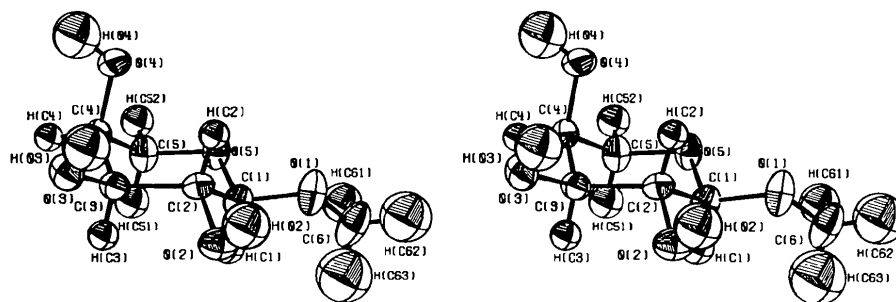


Fig. 1. Methyl  $\alpha$ -L-arabinopyranoside (I). The thermal ellipsoids are at 50% probability (Johnson, 1976).

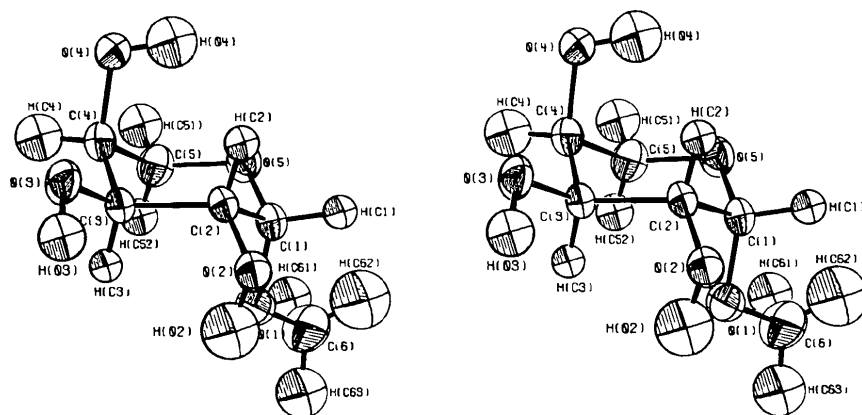


Fig. 2. Methyl  $\beta$ -L-arabinopyranoside (II). The thermal ellipsoids are at 50% probability (Johnson, 1976).

structures. As shown in Table 4, experiment and theory agree that the glycosidic bond is shortest in both anomers and the O—C(1)—O valence angle is smallest when the anomeric carbon C(1) has the  $\beta$  configuration, *i.e.* in (I). The two external bonds of the C—O—C—O—C sequence tend to be longer than the two internal bonds in both structures, and the O valence angles are greater than tetrahedral in both structures.

### The hydrogen bonding

The hydrogen-bond structures in (I) and (II) are shown in Figs. 5 and 6. The H...O distances and O—H...O angles obtained by normalizing the covalent O—H to a standard neutron diffraction value of 0.97 Å are given in Table 5. The procedure has been shown to

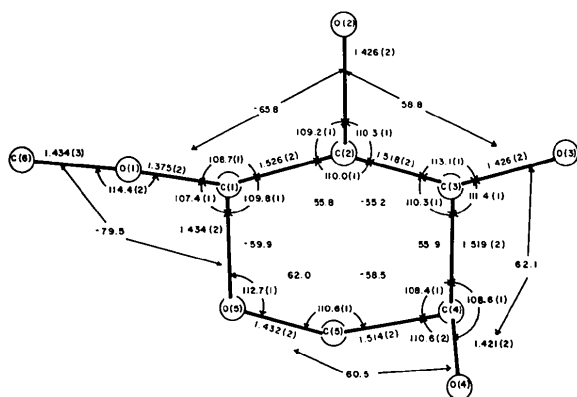


Fig. 3. Bond lengths (Å), bond angles ( $^{\circ}$ ) and torsion angles ( $^{\circ}$ ) in methyl  $\alpha$ -L-arabinopyranoside (I). A table of bond angles involving the H atoms has been deposited (see deposition footnote).

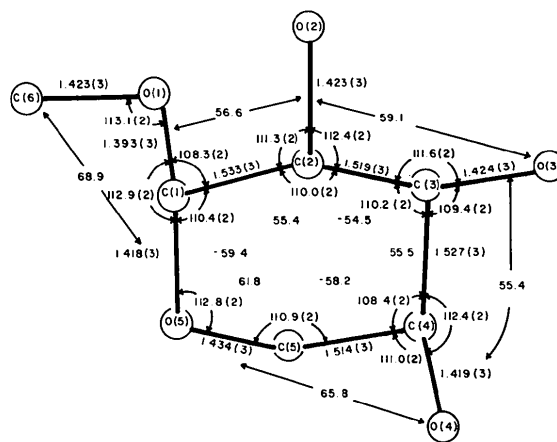


Fig. 4. Bond lengths (Å), bond angles ( $^{\circ}$ ) and torsion angles ( $^{\circ}$ ) in methyl  $\beta$ -L-arabinopyranoside (II). A table of bond angles involving the H atoms has been deposited (see deposition footnote).

Table 4. *Experimental versus theoretical bond geometry for the acetal moiety in methyl  $\alpha$ -L-arabinopyranoside (I) and methyl  $\beta$ -L-arabinopyranoside (II)*

	C(5) — O(5)	O(5) — C(1)	C(1) — O(1)	O(1) — C(6)	$\alpha$	$\beta$	$\gamma$
(I)	1.432 Å	$\alpha$ 1.434 Å	$\beta$ 1.375 Å	$\gamma$ 1.434 Å	112.7 $^{\circ}$	107.4 $^{\circ}$	114.4 $^{\circ}$
Theory	1.434	1.425	1.399	1.433	115.8	110.9	116.1
(II)	1.434	1.418	1.393	1.423	112.8	112.9	113.1
Theory	1.444	1.423	[1.423]*	[1.444]*	115.9	114.0	[115.9]*

\* The model compound, H<sub>3</sub>C—O—CH<sub>2</sub>—O—CH<sub>3</sub>, has a center of a symmetry at C(1) in this conformation.

Table 5. Normalized hydrogen-bond distances and angles in methyl  $\alpha$ -L-arabinopyranoside (I) and methyl  $\beta$ -L-arabinopyranoside (II)

	H...O <sub>corr</sub> *	$\angle$ O-H...O <sub>corr</sub> *	O...O
Methyl $\alpha$ -L-arabinopyranoside (I)			
O(2)H(O2)...O(3)[ $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$ ]	1.78 Å	161°	2.708 (2) Å
O(3)H(O3)...O(2)[ $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$ ]	1.84	174	2.809 (2)
O(4)H(O4)...O(5)[ $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$ ]	1.83	163	2.772 (2)
Methyl $\beta$ -L-arabinopyranoside (II)			
O(2)H(O2)...O(3)[ $\frac{1}{2}+x, \frac{3}{2}-y, -z$ ]	1.80	166	2.749 (2)
O(3)H(O3)...O(4)[ $\frac{1}{2}+x, \frac{3}{2}-y, -z$ ]	1.84	167	2.791 (2)
O(4)H(O4)...O(2)[ $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$ ]	1.87	159	2.796 (3)

\* Corrected by expanding the covalent O-H bond distances to the neutron diffraction value of 0.97 Å in the direction of the bonds.

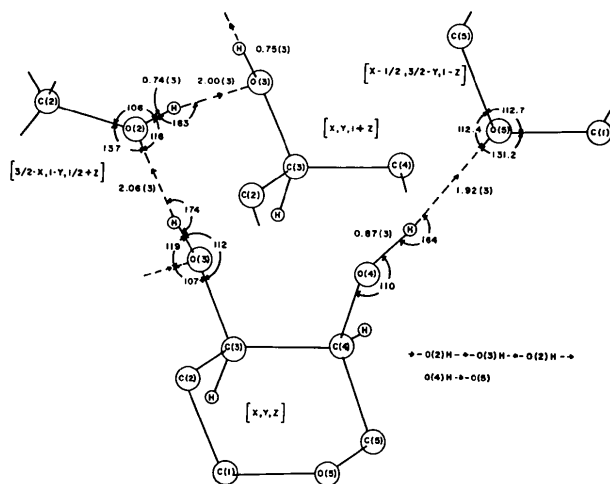


Fig. 5. Hydrogen-bonding structure in the crystal structure of methyl  $\alpha$ -L-arabinopyranoside (I).

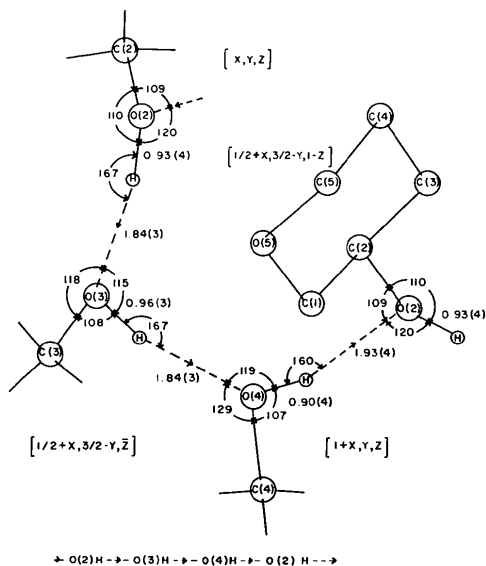


Fig. 6. Hydrogen-bonding structure in the crystal structure of methyl  $\beta$ -L-arabinopyranoside (II).

result in significantly more accurate H...O distances (Jeffrey & Takagi, 1978).

In (I), the hydrogen-bond structure consists of infinite chains and isolated bonds to the ring O atoms. In (II), the hydrogen bonding involves only infinite chains, and the ring O atoms are excluded. In neither structure is the glycosidic O included in the hydrogen bonding.

The range of corrected H...O distances in the infinite chains is 1.78 to 1.87 Å. This lies within the range of bond lengths associated with these type IA bonds in other carbohydrate structures as observed in other methyl pyranosides by Jeffrey, McMullan & Takagi (1977) and classified by Jeffrey & Takagi (1978). The H(4)-O(5) bond of 1.83 Å, type IIB, is shorter than the expected value of ~1.90 Å.

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## The Crystal and Molecular Structure of 1-Acetyl-3-benzamido-4-(2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyloxy)- $\Delta^3$ -2-pyrrolinone

BY ANTHONY MERCER AND JAMES TROTTER

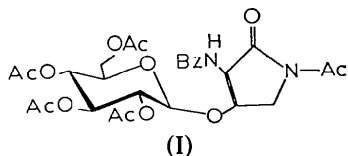
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Crystals of the title compound are monoclinic,  $a = 19.629(5)$ ,  $b = 7.504(2)$ ,  $c = 9.830(2)$  Å,  $\beta = 90.53(2)^\circ$ ,  $Z = 2$ , space group  $P2_1$ . The structure was solved by direct methods and was refined by full-matrix least-squares procedures to a final  $R$  of 0.079 for 1838 reflections with  $I \geq 3\sigma(I)$ . The structure consists of a pyranose ring in the chair conformation with the four *O*-acetyl substituents in equatorial positions; the pyranose ring is connected to a planar pyrrolone ring via a  $\beta$ -oxygen bridge. All bond lengths and angles in the molecule are close to the predicted values.

### Introduction

From reactions of glycosyl bromide with 2-phenyl-oxazol-5-one (Rosenthal & Brink, 1975) a  $\beta$ -glycoside considered to be 3-benzamido-1-benzoyl-4-(2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyloxy)- $\Delta^3$ -2-pyrrolinone was produced. On refluxing with acetic anhydride and sodium acetate in pyridine, one benzoate group was exchanged for an acetate group giving the title compound (I). The crystal structure analysis was undertaken to verify the initial assignment of structure based upon mass spectrum, NMR and chemical data.



### Experimental

Recrystallization of 1-acetyl-3-benzamido-4-(2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyloxy)- $\Delta^3$ -2-pyrrolinone from hexane-acetone gave colourless rectangular crystals. The crystal chosen for study was mounted with **b** parallel to the goniostat axis and had dimensions of  $ca$   $0.20 \times 0.20 \times 0.07$  mm. Unit-cell and space-group data were obtained from film and diffractometer

measurements. The unit-cell parameters were refined by a least-squares treatment of  $\sin^2\theta$  values for 19 reflections measured on a diffractometer with Cu  $K\alpha$  radiation.

### Crystal data

$C_{27}H_{30}N_2O_{13}$ ,  $M_r = 590.54$ , monoclinic,  $a = 19.629(5)$ ,  $b = 7.504(2)$ ,  $c = 9.830(2)$  Å,  $\beta = 90.53(2)^\circ$ ,  $U = 1447.8(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.35(1)$  g cm<sup>-3</sup>,  $F(000) = 620$  (20°C, Cu  $K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 9.4$  cm<sup>-1</sup>). Absent reflections  $0k0$ ,  $k \neq 2n$  define the space group  $P2_1$  ( $C_2^2$ , No. 4).

Intensities were measured on a Datex-automated General Electric XRD 6 diffractometer, with a scintillation counter, Cu  $K\alpha$  radiation (Ni filter and pulse-height analyser), and a  $\theta$ - $2\theta$  scan at  $2^\circ$  min<sup>-1</sup> over a range of  $(1.80 + 0.86 \tan \theta)^\circ$  in  $2\theta$ , with 10 s background counts being measured at each end of the scan. Data were measured to  $2\theta = 120^\circ$  (minimum interplanar spacing 0.89 Å). Lorentz and polarization corrections were applied, and the structure amplitudes were derived. No absorption correction was applied because of the low value of  $\mu$ . Of the 2336 independent reflections measured, 498 had intensities less than  $3\sigma(I)$  above background where  $\sigma^2(I) = S + B + (0.05S)^2$  with  $S$  = scan count and  $B$  = time-averaged background count. These reflections were classified as unobserved and given zero weight in the refinement.