

## Structural Chemistry of Carbohydrates. III. Crystal and Molecular Structure of 4-O- $\beta$ -D-Galactopyranosyl- $\alpha$ -D-glucopyranose Monohydrate ( $\alpha$ -Lactose Monohydrate)\*

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$\alpha$ -Lactose, commonly called milk sugar, is a disaccharide of galactose and glucose, linked  $\beta$ -1,4, with glucose as the reducing unit. Suitable crystals for the X-ray analysis were obtained by evaporation of an aqueous solution of the compound to dryness. The crystal data are:  $a = 7.982 \pm 0.002$ ,  $b = 21.652 \pm 0.003$ ,  $c = 4.824 \pm 0.001$  Å and  $\beta = 109.57 \pm 0.03^\circ$  ( $\lambda$ Cu  $K\alpha = 1.5418$ ). Space group  $P2_1$ .  $D_x = 1.540$  g.cm.<sup>-3</sup>,  $D_m = 1.537$  g.cm.<sup>-3</sup>. There are two molecules of  $\alpha$ -lactose monohydrate per unit cell. The structure analysis was performed with a total of 1296 reflections collected on a Picker diffractometer. The structure was solved by initially finding a fragment of the molecule in the Patterson synthesis and then applying the tangent formula. Least-squares refinement reduced  $R$  to 0.027. Difference synthesis showed all hydrogen atoms and also indicated the partial (7%) random substitution of  $\alpha$ -lactose molecules by the  $\beta$ -anomer. The molecule shows a departure from the fully extended conformation. This conformation is stabilized by an intramolecular hydrogen bond. The molecules related by the  $a$  translation are strung together in sheets by three hydrogen bonds; two involving the glucose residues and one involving the galactose residues. A fourth hydrogen bond links the sheets of molecules parallel to the  $a$  axis in such a way that infinite zigzagging chains of hydrogen bonds run parallel to the  $c$  axis.

### Introduction

The crystal structure of  $\alpha$ -lactose monohydrate (4-O- $\beta$ -D-galactopyranosyl- $\alpha$ -D-glucopyranose monohydrate) has been accurately determined as part of a general program of research in these laboratories on the detailed structures of the carbohydrates. Lactose is a constituent of milk. It is a 'mixed' disaccharide containing a galactose and a glucose unit linked through a  $\beta$ -1,4-linkage (Fig. 1). Its structural analysis was specifically initiated to provide more structural information about the galactose moiety which was encountered in a previous investigation (Fries & Sundaralingam, 1971), and also to gain more information on the solid state hydrogen bonding scheme and conformation of the  $\beta$ -1,4 glycosidic bond which is present in a variety of natural polysaccharides, e.g. cellulose and chitin. In addition it was of interest to obtain further information on the effect of the nature and the orientation (axial or equatorial) of the substituents on the conformation of the pyranoside ring in various sugars (Sundaralingam, 1968, 1970).

This investigation represents the second crystallographic study of a disaccharide exhibiting the  $\beta$ -1,4 glycosidic bond, the first being that of  $\beta$ -cellobiose (Jacobson, Wunderlich & Lipscomb, 1961; Brown, 1966; Chu & Jeffrey, 1967) which is composed of two similar  $\beta$ -D-glucopyranose units. Although the chain

conformation in cellulose is fairly well established the precise mode of interchain packing and hydrogen bonding is still a subject of much controversy.

### Experimental

The crystals were grown by slow evaporation from a saturated aqueous solution of commercially available  $\alpha$ -lactose monohydrate, C<sub>12</sub>O<sub>11</sub>H<sub>22</sub>·H<sub>2</sub>O. The crystals were quite hard and exhibited no cleavage planes, which is indicative of a three-dimensional network of hydrogen bonds within the lattice.

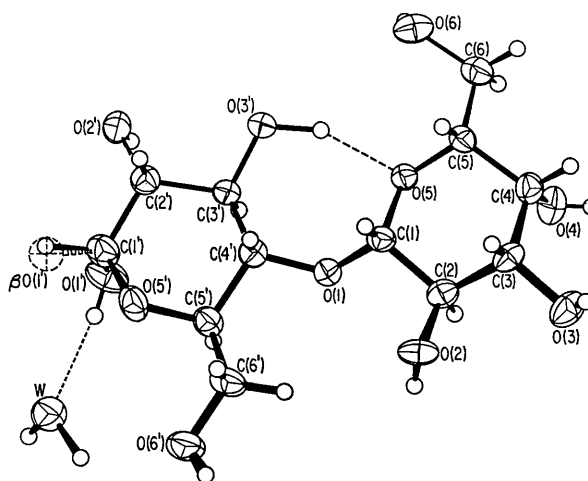


Fig. 1. The thermal ellipsoid plot (Johnson, 1965) showing the anisotropic vibration of the non-hydrogen atoms.

\* The papers in *J. Amer. Chem. Soc.* (1965) 87, 599 and *Biopolymers*, (1968), 6, 189 by M. Sundaralingam are designated as parts I and II respectively of this series.

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A crystal with dimensions of  $0.30 \times 0.20 \times 0.40$  mm was cut out from one of these chunks and was used in the entire analysis. Preliminary photographic data showed that the crystal belongs to the monoclinic system. The systematically absent reflections,  $0k0$  for  $k=2n+1$ , indicated that the space group is  $P2_1$  (and not  $P2_1/m$ ) since the molecule contains asymmetric carbon atoms. Accurate unit-cell dimensions were determined from about 12 reflections with  $2\theta > 40^\circ$  measured on a Picker automatic diffractometer using Ni filtered Cu  $K\alpha$  radi-

ation. The crystal data are summarized in Table 1. The crystal was mounted with the  $a$  axis coincident with the  $\varphi$  axis of the goniostat. A total of 1398 reflections with  $2\theta$  values less than  $134^\circ$  were measured using the  $\theta-2\theta$  scan mode, at a scan speed of  $2^\circ$  per minute, and nickel filtered Cu  $K\alpha$  radiation. Of these 1296 reflections were considered observed based on a cut-off criterion that the observed intensity,  $I$ , should be greater than  $1.2\sigma(I)$ , where  $\sigma(I)$  is the standard deviation in the observed intensity. The intensities were corrected for the variation in the standard reflection which was measured at frequent intervals to monitor any variation in the crystal alignment. The standard reflection showed a random variation of  $2\frac{1}{2}\%$ . The Lorentz and polarization corrections were also applied but absorption corrections were not made since the crystal used was within the optimum size. The reduced data were placed on an approximately absolute scale with a Wilson (1942) plot.

#### Determination of the structure

A sharpened origin removed Patterson synthesis, revealed the position of one of the pyranose rings. The standard structure factor - Fourier techniques - did not yield the structure. Hence, the partial structural information was combined with the tangent formula (Karle & Hauptman, 1956) which consisted of a hypothetical structure (fragment) of 12 atoms - 6 carbon atoms representing the pyranose ring and 6 oxygen atoms attached to the carbon atoms. Subsequently it was shown that the hypothetical structure represented the glucose unit with no substituent at O(5') and an axial oxygen at C(1'). The  $\Sigma_2$  relationships were generated for 339 reflections with  $E > 1.20$ . The origin defining reflections were chosen in accordance with the requirements for space group  $P2_1$ . They were

$h$	$k$	$l$	$E$
1	0	$\bar{1}$	2.09
2	0	$\bar{3}$	1.75
4	13	3	2.12

Starting phases were then calculated for the first 127 reflexions with  $E > 1.50$  using the twelve atomic sites

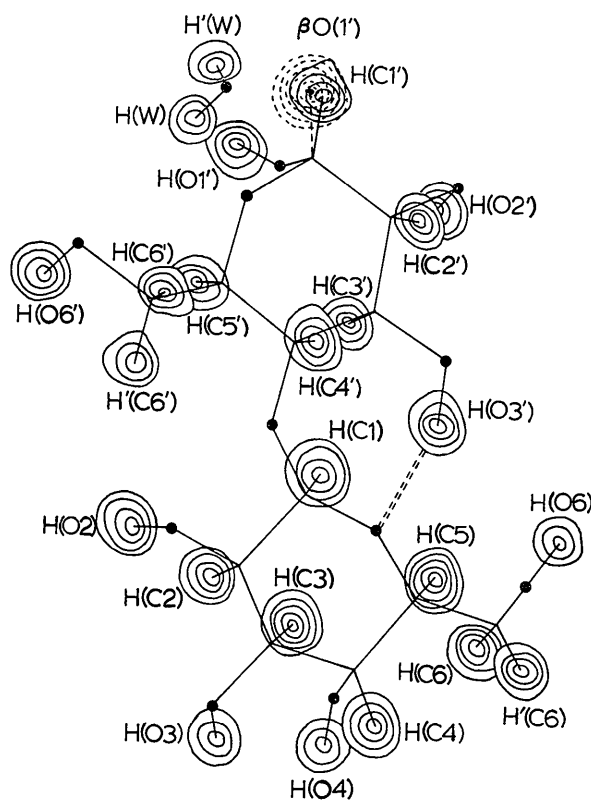


Fig. 2. A difference electron density map showing the locations of the hydrogen atoms (solid contours) and the  $\beta O(1')$  atom (broken contours). The contours are plotted at intervals of  $0.1 \text{ e.}\text{\AA}^{-3}$ , beginning at  $0.1 \text{ e.}\text{\AA}^{-3}$ .

Table 1. Crystal data for  $\alpha$ -D-lactose monohydrate

m.p.	250 - 1 °C
Crystal system	monoclinic
$a$	$7.982 \pm 0.002 \text{ \AA}$
$b$	$21.562 \pm 0.003$
$c$	$4.824 \pm 0.001$
$\beta$	$109.57 \pm 0.03^\circ$
Systematic group absences	$0k0, k=2n+1$
Space group	$P2_1$
$V$	$782.3 \text{ \AA}^3$
$Z$	2
$D_x$	$1.542 \text{ g.cm}^{-3}$
$D_m$	$1.544 \text{ g.cm}^{-3}$ in carbon tetrachloride-benzene mixture
$\mu$ for Cu $K\alpha$	$12.2 \text{ cm}^{-1}$
Crystal dimensions	$0.3 \times 0.2 \times 0.4 \text{ mm}$

derived above. The phases were accepted for input to subsequent tangent formula refinements if their associated calculated and observed structure amplitudes satisfied the criterion  $|F_c|/|F_o| \geq 0.50$ . The phases were then refined by the tangent formula, using a set of programs developed by Hall (1967) and additional phases were propagated until all the 339 reflections chosen initially were refined. An  $E$  map computed with these reflections and the refined phases clearly revealed the positions of all the heavy atoms in the molecule including that of the water molecule.

### Refinement of the structure

Three cycles of isotropic full-matrix least-squares refinement followed by a cycle of anisotropic refinement brought the  $R$  value down to 0.07. A difference electron density map with the non-hydrogen atoms included in the structure factor calculation revealed 19 of the 24 hydrogen atoms (Fig. 2). The hydrogen electron densities ranged from 0.35 to 0.55 e.Å<sup>-3</sup>, with the exception of the hydrogen attached to C(1') where the electron density was about 1.00 e.Å<sup>-3</sup>. A second difference map computed after a second cycle of anisotropic least-squares refinement in which the hydrogen atoms were included with an isotropic temperature factor  $B=4.0$  Å<sup>2</sup> but not refined revealed the remaining five hydrogen atoms ranging in electron densities from 0.30 to 0.45 e.Å<sup>-3</sup>. This map additionally showed a residual electron density of 0.60 e.Å<sup>-3</sup> near the position assigned to H(C1').

Apparently the residual density is due to the presence of a small amount of the  $\beta$ -anomer, and represents the oxygen atom in the equatorial position. The  $\beta$ -oxygen was located about 1.40 Å from C(1'). The torsional angle O(1')-C(1')-O(5)-C(5) was  $-173^\circ$  which is close to the value expected for a  $\beta$ -anomer. Therefore, in the next least-squares cycle the occupancy parameters of  $\alpha$ O(1') and  $\beta$ O(1') were refined independent of constraints. When the refinement converged the occupancy parameter of  $\alpha$ O(1') was  $0.924 \pm 0.01$  and that of  $\beta$ O(1') was  $0.075 \pm 0.01$  hence indicating the presence of about 7% of the  $\beta$ -anomer in the crystal structure.

An analysis of the distribution of the  $\sum(|\Delta F|)^2$  as a function of  $|F|$  showed that the weighting scheme [ $w = 1/\sigma^2(F)$ ] should be as follows:

$$\begin{aligned}\sigma(F) &= 1.3 |F| \text{ for } |F| \leq 16 \\ \sigma(F) &= 1 + 0.019 |F| \text{ for } |F| > 16\end{aligned}$$

Using the new weighting scheme two cycles of anisotropic refinement on the heavy atom parameters, followed by two cycles of isotropic refinement on the hydrogen atoms and  $\beta$ O(1') reduced the  $R$  value to 0.027 and the weighted  $R$  to 0.031. The  $R$  value for all the 1398 reflections (both observed and unobserved) is 0.031. The average shift in the parameters in the final cycle was less than  $\frac{1}{20}$  the estimated standard errors, the maximum being 0.18  $\sigma$ .

As a matter of interest the 24 hydrogen atoms were subjected to two rounds of anisotropic refinement. Although the hydrogen atom parameters converged, the drop in  $R$  (0.025) was not considered significant

Table 2. Positional and anisotropic thermal parameters of the heavy atoms

The anisotropic temperature factor is of the form  $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$ .

	$x \times 10^5$	$y \times 10^5$	$z \times 10^5$	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
C(1)	22747 (36)	34031 (16)	39038 (60)	88 (5)	13 (1)	288 (13)	3 (1)	51 (6)	7 (2)
C(2)	36079 (39)	39241 (16)	42648 (63)	102 (5)	16 (1)	291 (14)	-4 (2)	45 (7)	1 (2)
C(3)	30803 (39)	44897 (16)	56702 (65)	119 (6)	15 (1)	319 (15)	-10 (2)	63 (7)	-6 (3)
C(4)	11435 (43)	46720	40301 (68)	140 (6)	12 (1)	368 (15)	-2 (2)	86 (8)	-10 (2)
C(5)	-462 (37)	41041 (16)	38683 (64)	100 (5)	12 (1)	379 (15)	2 (2)	75 (7)	-10 (3)
C(6)	-19777 (42)	42372 (17)	21408 (77)	107 (6)	17 (1)	523 (19)	5 (2)	71 (8)	-5 (3)
O(1)	26711 (25)	29441 (12)	22056 (42)	106 (3)	11 (1)	357 (10)	-1 (1)	91 (5)	2 (2)
O(2)	53208 (24)	37081 (14)	60255 (45)	72 (4)	25 (1)	399 (11)	1 (1)	22 (5)	-1 (2)
O(3)	42755 (32)	49844 (13)	56556 (50)	180 (5)	18 (1)	452 (12)	-25 (1)	102 (6)	-30 (2)
O(4)	9457 (32)	48604 (13)	11142 (46)	177 (5)	13 (1)	381 (11)	-4 (1)	67 (6)	6 (2)
O(5)	5091 (23)	36080 (12)	23479 (43)	73 (3)	11 (1)	398 (10)	-1 (1)	39 (4)	-11 (2)
O(6)	-30237 (27)	36980 (14)	19878 (49)	107 (4)	23 (1)	454 (12)	-6 (1)	70 (5)	-3 (2)
C(1')	19181 (39)	10398 (18)	9644 (67)	111 (6)	16 (1)	386 (15)	8 (2)	31 (8)	3 (3)
C(2')	3239 (40)	14025 (16)	12064 (65)	108 (5)	13 (1)	360 (15)	2 (2)	44 (7)	4 (2)
C(3')	5416 (39)	20917 (16)	8064 (71)	88 (5)	12 (1)	442 (16)	2 (1)	73 (7)	7 (3)
C(4')	23610 (38)	23129 (16)	28504 (61)	101 (5)	13 (1)	332 (14)	2 (2)	61 (7)	3 (2)
C(5')	38571 (40)	19233 (17)	24441 (66)	110 (5)	14 (1)	361 (15)	7 (2)	69 (7)	7 (3)
C(6')	56833 (42)	20924 (18)	45416 (81)	89 (6)	19 (1)	560 (20)	7 (2)	42 (8)	-7 (3)
O(1')	19004 (31)	10699 (16)	-19173 (49)	136 (4)	27 (1)	328 (11)	14 (2)	63 (6)	-17 (2)
O(2')	-13082 (28)	11634 (12)	-7738 (50)	126 (4)	12 (1)	476 (12)	-3 (1)	59 (5)	5 (2)
O(3')	-8848 (27)	23986 (13)	14357 (57)	89 (4)	13 (1)	802 (16)	2 (1)	121 (6)	-3 (2)
O(5')	35420 (29)	12918 (13)	29925 (48)	135 (4)	14 (1)	404 (11)	10 (1)	44 (5)	9 (2)
O(6')	70387 (29)	17312 (14)	39816 (59)	113 (4)	24 (1)	679 (16)	15 (1)	120 (7)	38 (3)
W	52885 (30)	5777 (14)	91198 (52)	146 (4)	19 (1)	514 (13)	7 (1)	100 (6)	13 (2)
$\beta$ O(1')	2330 (48)	559 (17)	2669 (87)	3.47*					

\* Isotropic thermal parameter. The  $x$ ,  $y$  and  $z$  values for  $\beta$ O(1') have been multiplied by  $10^4$ . Occupancy parameters of O(1') and  $\beta$ O(1') are 0.93 and 0.07 respectively; these are independent values and were not constrained to total unity.

and hence only the isotropic parameters of the hydrogen atoms are presented. The scattering factors for O and C were those given by Cromer & Waber (1965) and for H were those given by Stewart, Davidson & Simpson (1965). The distribution of Σw(ΔF)² as a function of (F) plotted at the conclusion of the refinement was constant to within 10%. The positional and anisotropic thermal parameters of the heavy atoms are listed in Table 2 along with the estimated standard errors from the inverse full matrix. The corresponding parameters for the hydrogen atoms are listed in Table 3. The observed and calculated structure factors are given in Table 4.

Table 3 (cont.)

Table 3 (cont.) showing isotropic thermal parameters for H(C3) through H(W). The table lists parameters for each atom, including B, H'(W), and H(W) values.

Table 4. Observed and calculated structure amplitudes (x 10³)

The columns are the running index k, 10|F\_o| and 10|F\_c| respectively. Unobserved reflexions are marked with an asterisk.

Table 4: Observed and calculated structure amplitudes (x 10³). This is a large table with multiple columns containing data for various reflections, including indices k, observed amplitudes, and calculated amplitudes.

## Discussion of the structure

## Bond distances

The bond distances and bond angles involving non-hydrogen atoms are given in Tables 5 and 6 respectively. The average estimated standard deviations in the bond distances and valence angles involving non-hydrogen atoms are 0.004 Å and 0.2° respectively.

The bond lengths for both the  $\beta$ -galactosyl and  $\alpha$ -glucosyl moieties are all in good agreement with the values encountered in many previous investigations of mono and disaccharides (Berman, Chu & Jeffrey, 1967). In this structure the ring C–C bonds are in the range 1.516–1.536 Å, average 1.529 Å; the smallest and the largest values being associated with the C(3) atom of the galactosyl moiety. The exocyclic C(5)–C(6) bond

distance is 1.514 Å for both the galactosyl and glucosyl units.

The exocyclic C(5)–C(6) bond distances and the ring C–C bond distances have been tabulated for the more accurately ( $\sigma(l) < 0.006$  Å) determined carbohydrate structures in Table 7. Although in individual compounds the variation in the bond distances may be significant, the result of averaging the bond distances shows a remarkable constancy in the value of the four ring C–C bond distances. The average of the sixty ring C–C bond distances is 1.524 Å, somewhat shorter than the normal C–C single bond distance. On the other hand the average value (1.515 Å) of the exocyclic C–C bond is about 0.01 Å shorter than the average ring bond. Apart from the effect due to thermal motion which tends to shorten bonds involving terminal atoms, the

Table 5. Bond lengths involving the non-hydrogen atoms

Estimated standard deviations are given in parentheses.

Galactose moiety			Glucose moiety		
Ring	C(1)–C(2)	1.517 (5) Å	C(1')–C(2')	1.531 (5) Å	
	C(2)–C(3)	1.523 (5)	C(2')–C(3')	1.516 (5)	
	C(3)–C(4)	1.533 (4)	C(3')–C(4')	1.533 (4)	
	C(4)–C(5)	1.536 (4)	C(4')–C(5')	1.525 (5)	
	C(5)–C(6)	1.514 (4)	C(5')–C(6')	1.514 (4)	
Ring	C(1)–O(5)	1.427 (3)	C(1')–O(5')	1.443 (4)	
	C(5)–O(5)	1.448 (4)	C(5')–O(5')	1.425 (5)	
Bridge	C(1)–O(1)	1.389 (4)	C(1')–O(1')	1.387 (4)	
	C(2)–O(2)	1.425 (3)	C(2')–O(2')	1.429 (3)	
	C(3)–O(3)	1.433 (4)	C(3')–O(3')	1.434 (4)	
Axial	C(4)–O(4)	1.421 (4)	Bridge	C(4')–O(1)	1.437 (4)
	C(6)–O(6)	1.419 (5)		C(6')–O(6')	1.430 (5)
			C(1')– $\beta$ O(1')	1.29 (4)	

Table 6. Bond angles involving the non-hydrogen atoms

Estimated standard deviations are given in parentheses.

Galactose moiety		Glucose moiety	
C(1)–C(2)–C(3)	110.9 (0.2)°	C(1')–C(2')–C(3')	110.9 (0.2)°
C(2)–C(3)–C(4)	110.9 (0.2)	C(2')–C(3')–C(4')	110.3 (0.2)
C(3)–C(4)–C(5)	108.9 (0.2)	C(3')–C(4')–C(5')	111.1 (0.2)
C(4)–C(5)–O(5)	109.0 (0.2)	C(4')–C(5')–O(5')	107.9 (0.2)
C(5)–O(5)–C(1)	112.2 (0.2)	C(5')–O(5')–C(1')	114.1 (0.2)
O(5)–C(1)–C(2)	111.2 (0.2)	O(5')–C(1')–C(2')	109.7 (0.2)
O(5)–C(1)–O(1)	107.0 (0.2)	O(5')–C(1')–O(1')	111.5 (0.2)
C(2)–C(1)–O(1)	107.7 (0.2)	C(2')–C(1')–O(1')	108.8 (0.2)
C(1)–C(2)–O(2)	108.8 (0.2)	C(1')–C(2')–O(2')	111.1 (0.2)
C(3)–C(2)–O(2)	110.5 (0.2)	C(3')–C(2')–O(2')	112.7 (0.2)
C(2)–C(3)–O(3)	108.1 (0.2)	C(2')–C(3')–O(3')	107.0 (0.2)
C(4)–C(3)–O(3)	111.4 (0.2)	C(4')–C(3')–O(3')	111.6 (0.2)
C(3)–C(4)–O(4)	110.0 (0.2)	C(3')–C(4')–O(1)	110.6 (0.2)
C(5)–C(4)–O(4)	108.4 (0.2)	C(5')–C(4')–O(1)	107.0 (0.2)
C(4)–C(5)–C(6)	112.0 (0.2)	C(4')–C(5')–C(6')	113.7 (0.2)
O(5)–C(5)–C(6)	106.8 (0.2)	O(5')–C(5')–C(6')	107.2 (0.2)
C(5)–C(6)–O(6)	110.3 (0.2)	C(5')–C(6')–O(6')	111.2 (0.2)
		O(5')–C(1')– $\beta$ O(1')	84 (1.4)
		C(2')–C(1')– $\beta$ O(1')	114 (1.4)
		O(1')–C(1')– $\beta$ O(1')	126 (1.4)
Bridge	C(1)–O(1)–C(4')	117.1 (0.2)	

shortening may also be due to the fact that the C(5)–C(6) bond involves a primary and a secondary carbon atom while the ring C–C bonds are between secondary carbon atoms. A similar shortening of the exocyclic C(4')–C(5') bond has also been observed in ribofuranosides (Sundaralingam, 1965a).

The intraring C–O bonds, C(1)–O(5) and C(5)–O(5), are unequal in the galactose moiety (Sundaralingam, 1965b), the latter bond being about  $5\sigma$  greater than the former. However, a comparison with related  $\beta$ -glucosides indicates that in general the ring C–O bonds are equal within the experimental errors (Berman *et al.*, 1967). The equatorial anomeric C(1)–O(1) bond distance,  $1.389 \pm 0.004$  Å, is shortened, and is in agreement with the observations made previously (Berman *et al.*, 1967).

The ring C–O bond distances in the glucose moiety show the reverse trend, C(1')–O(5') > C(5')–O(5') in contrast to that generally observed in related structures (Berman *et al.*, 1969). This anomaly may be in part

contributed by the disorder in the crystal, *i.e.* presence of about 7% of the  $\beta$ -lactose. However, again the anomeric C(1')–O(1') bond distance,  $1.387 \pm 0.004$  Å, is shortened and is in agreement with previous observations by Berman *et al.* (1967).

The exocyclic C–O bond distances excluding the anomeric and bridge C–O bonds fall in the range 1.419–1.434 Å, the mean being 1.428 Å. These values are in good agreement with the value normally associated with a C–O single bond distance. The bridge C(4')–O(1) bond distance is 1.446 Å and is in good agreement with the corresponding bond in cellobiose. These values appear to be longer than the normal C–O bond distance.

The bond distances involving the C–H bonds are in the range 0.91–1.07 Å, average being 1.01 Å for the galactose moiety and 1.03 Å for the glucose moiety. These values are in excellent agreement with the values found in some precisely determined X-ray structures (Stewart, Davidson & Simpson, 1965). The O–H bond

Table 7. The C–C bond distances in some accurately determined pyranosides

	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)	C(5)–C(6)	e.s.d.
$\alpha$ -D-Glucose (Brown & Levy, 1965)	1.534 Å	1.525 Å	1.518 Å	1.529 Å	1.510 Å	0.003 Å
Methyl $\alpha$ -D-glucopyranoside (Berman & Kim, 1968)	1.529	1.517	1.529	1.525	1.507	0.004
$\alpha$ -L-Sorbose (Kim & Rosenstein, 1967)	1.515	1.527	1.511	1.515	—	0.006
$\alpha$ -D-Galactosamine-L-phosphate (Fries & Sundaralingam, 1971)	1.537	1.507	1.525	1.520	1.522	0.006
$\alpha$ -Lactose monohydrate (nonreducing)	1.517	1.523	1.533	1.536	1.514	0.005
(reducing)	1.531	1.516	1.533	1.525	1.514	0.005
(This investigation)						
Sucrose (Brown & Levy, 1963)	1.534	1.520	1.524	1.523	1.523	0.003
$\beta$ -D-Glucose (Chu & Jeffrey, 1968)	1.525	1.520	1.511	1.529	1.513	0.005
Cellobiose (nonreducing)	1.525	1.520	1.543	1.532	1.519	0.005
(reducing)	1.514	1.519	1.530	1.527	1.501	0.005
(Chu & Jeffrey, 1968)						
Methyl- $\beta$ -D-maltopyranoside (nonreducing)	1.518	1.516	1.531	1.533	1.526	
(reducing)	1.510	1.535	1.513	1.512	1.513	
(Chu & Jeffrey, 1968)						
$\beta$ -DL-Arabinose (Kim & Jeffrey, 1967)	1.532	1.528	1.533	1.515	—	0.005
Methyl- $\beta$ -D-xyloside (Brown, Cox & Llewellyn, 1966)	1.519 (4)	1.517	1.503	1.522	—	0.004
$\beta$ -Lyxose (Hordvik, 1966)	1.538 (5)	1.528	1.509	1.525	—	0.005
Mean	1.525	1.524	1.523	1.525	1.515	
Range	1.510 to 1.538	1.507 to 1.533	1.503 to 1.543	1.512 to 1.536	1.501 to 1.526	

These distances were not corrected for thermal motion.

distances are consistently shorter, average 0.80 Å, as is generally observed in X-ray investigations.

### Bond angles

Among the internal ring angles those involving the ring oxygen atoms are the largest. The ring oxygen angle of 114.1° involving the glucose unit is 1.9° larger than the ring oxygen angle of 112.2° in the galactose unit. In general the valence angle at the ring oxygen of the pyranosides shows considerable variation, range 110 to 116° (Sundaralingam, 1968). However, at present there appears to be no correlation between this angle and the involvement of the ring oxygen in hydrogen bonding, nor is there a trend in the ring oxygen angle for the axial and equatorial glycosides.

The smallest ring angles involve the C(5') atom and the C(4) atom of the glucose and galactose units respectively. The remaining ring angles are greater than the tetrahedral value. The axial hydroxyl at position 4 of the galactose moiety may be responsible for the reduction of the valence angle C(3)-C(4)-C(5) in comparison with the corresponding angle in the glucose moiety.

The exocyclic angles show a wide range, 106.8 to 113.7°. Consideration of the pairs of exocyclic angles

at the ring atoms reveals that in general they are unequal, the greatest difference occurring at C(5). The C(4)-C(5)-C(6) angle is consistently larger than the O(5)-C(5)-C(6) angle. Of particular interest is the bond angle involving the bridge oxygen atom. This angle of 117.1° is significantly larger than the value of 116.1° in cellobiose, similar to the angle of 117.6° in methyl  $\beta$ -D-maltopyranoside (Chu & Jeffrey, 1968), and smaller than the mean value of 119.1° in cyclohexaamylose (Hybl, Rundle & Williams, 1965). Thus it appears that the bridge valency angles in di-, oligo- and polysaccharides possess some amount of flexibility from the mean value, the  $\beta$ -1,4-linked disaccharides have a mean value of 116.6° (lactose and cellobiose) while the  $\alpha$ -1,4-linked derivatives have a mean value of 118.4°. A comparison of the bridge angles in disaccharides and alkyl glycosides has already been published (Sundaralingam, 1968).

### The molecular conformation

The torsional angles  $\varphi_1, \varphi_1', \varphi_2, \varphi_2'$  (Sundaralingam, 1968) about the bridge bonds C(1)-O(1) and O(1)-C(4') are given in Table 8. These angles differ by as much as 12 to 14° between lactose and cellobiose. In a fully extended conformation the angles  $\varphi_1$  and  $\varphi_2$  are close

Table 8. Torsional angles about the bridge bonds\*

	$\varphi_1$	$\varphi_1'$	$\varphi_2$	$\varphi_2'$	$\varphi$	$\varphi'$
$\alpha$ -Lactose monohydrate	-92.6°	146.2	94.6	-143.0	-32	189 (191)†
$\beta$ -Cellobiose	-77.8	167.3	106.0	-127.3	-30	208

\*  $\varphi_1, \varphi_1', \varphi_2,$  and  $\varphi_2'$  are defined according to Sundaralingam (1968) while  $\varphi$  and  $\varphi'$  are defined according to Ramchandran *et al.* (1963).  $\varphi_1$  O(5)-C(1)-O(1)-C(4'),  $\varphi_1'$  C(2)-C(1)-O(1)-C(4'),  $\varphi_2$  C(1)-O(1)-C(4')-C(3'),  $\varphi_2'$  C(1)-O(1)-C(4')-C(5'),  $\varphi$  O(4)-C(1)-O(1)-C(4'),  $\varphi'$  C(1)-O(1)-C(4')-O(1').

† The value in parenthesis is for the  $\beta$ -oxygen atom at C(1').

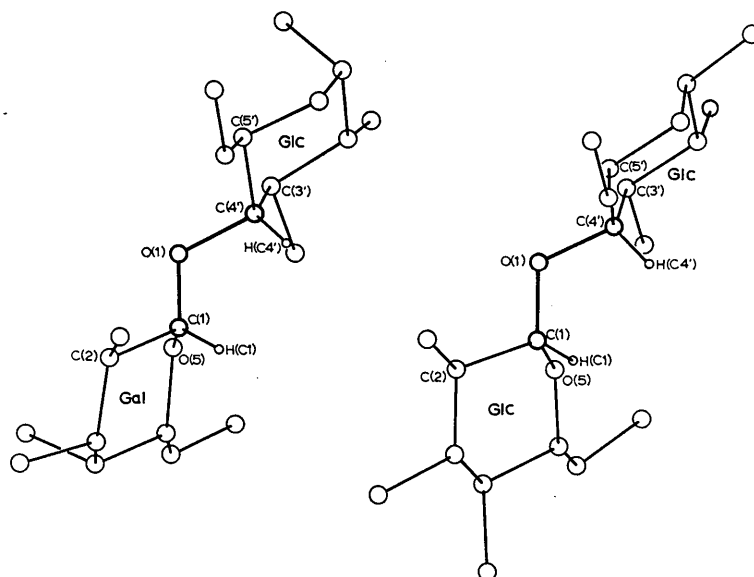


Fig. 3. A view of lactose (left) and cellobiose (right) normal to the plane of atoms C(1), O(1) and C(4').

to  $-110$  and  $+110^\circ$  respectively. In lactose  $\varphi_1 = -92.6$  and  $\varphi_2 = 94.6^\circ$ , thus the molecule exhibits a symmetrical twist about the bridge bonds, while an asymmetrical twist is exhibited by cellobiose,  $-77.8$  and  $106.0^\circ$ . These values are compared with the torsional angles  $\varphi$  and  $\varphi'$  describing the free rotation about the bridge bonds as defined by Ramachandran, Ramakrishnan & Sasisekharan (1963) are also shown in Table 8. For lactose these values fall slightly outside the fully allowed region where a good hydrogen bond [O(3')-H...O(5)] can be formed (Ramachandran *et al.*, 1963). The major difference (about  $19^\circ$ ) between the conformations of lactose and cellobiose is in  $\varphi'$ . A view normal to the plane containing the C(1), O(1), and C(4') atoms is shown in Fig. 3 to illustrate the differences in the conformation of lactose and cellobiose.

The departure from the fully extended conformation for the  $\beta$ -1,4 linkage is undoubtedly promoted by the intramolecular hydrogen bond which is observed both in  $\alpha$ -lactose and  $\beta$ -cellobiose. It is most reasonable to state that there is a strong driving force for the formation of the intramolecular hydrogen bond in the  $\beta$ -1,4 linked di-, oligo- and polysaccharides. The presence of the intramolecular hydrogen bond in lactose and cellobiose lends support to the proposed chain conformations of cellulose (Hermans, 1943) and chitin (Carlström, 1962).

In the crystal structure of  $\alpha$ -lactose monohydrate, the mean torsional angles about the ring bonds of the galactose and glucose moieties are  $56.1$  and  $56.6^\circ$  res-

pectively, Table 9. A comparison of the torsional angles of the ring bonds of the  $\beta$ -galactose moiety and the  $\alpha$ -glucose moiety shows remarkable agreement, whereas it has been pointed out earlier (Sundaralingam, 1970) that in the case of some other pyranosides the conformations of the six-membered rings are correlated with the nature and orientation of the substituents. Within each residue the torsional angles differ by as much as  $13.6^\circ$ , the smallest values being  $-50.2$  and  $-50.5^\circ$ , about the C(2)-C(3) and C(2')-C(3') bonds respectively, and the largest values being  $63.8$  and  $62.3^\circ$ , about the C(5)-O(5) and C(5')-O(5') bonds respectively. The pyranoside rings show a greater puckering about the C(1)-O(5), O(5)-C(5) and C(5)-C(4) bonds and a smaller puckering about the C(1)-C(2), C(2)-C(3) and C(3)-C(4) bonds (Sundaralingam, 1970) in comparison with the torsional angle of  $55^\circ$  in cyclohexane.

The torsional angles involving the extraring atoms are also shown in Table 9. In general these angles are greater than the values observed for the ring bonds. The O(1)-C(1)-C(2)-O(2) and O(2)-C(2)-C(3)-O(3) angles are the largest two angles in the galactose moiety while in the glucose moiety the largest two angles are O(3')-C(3')-C(4')-O(1) and O(1)-C(4')-C(5')-C(6'). It is interesting that the torsion angles involving both equatorial substituents are considerably greater than those involving an equatorial and an axial substituent (Table 9).

The conformation about the exocyclic C(5)-C(6) bond is *gauche-trans* in both the glucose and galactose

Table 9. A comparison of the intracyclic and extracyclic torsional angles in the galactose and glucose moieties

	Galactose moiety		Glucose moiety	
Intracyclic Torsional Angles	C(1)-C(2)	53.7 (3) <sup>o</sup>	C(1')-C(2')	53.8 (3) <sup>o</sup>
	C(2)-C(3)	-51.4 (3)	C(2')-C(3')	-51.2 (3)
	C(3)-C(4)	54.2 (3)	C(3')-C(4')	53.5 (3)
	C(4)-C(5)	-59.1 (3)	C(4')-C(5')	-57.5 (3)
	C(5)-O(5)	61.7 (4)	C(5')-O(5')	62.9 (3)
	O(5)-C(1)	-60.8 (3)	O(5')-C(1')	-61.6 (3)
Extracyclic Torsional Angles	O(5)C(5)C(6)O(6)	59.4 (3)	O(5')C(5')C(6')O(6')	63.2 (4)
	C(4)C(5)C(6)O(6)	178.7 (3)	C(4')C(5')C(6')O(6')	-177.6 (3)
	O(1)--O(2)	-67.5 (3)	O(1')--O(2')	57.8 (3)
	O(2)--O(3)	65.5 (3)	O(2')--O(3')	61.9 (3)
	O(3)--O(4)	56.0 (3)	O(3')--O(1')	-69.0 (3)
	O(4)--C(6)	-57.5 (3)	O(1)--C(6')	62.8 (3)

Table 10. Conformation of the hydroxymethyl group

	Torsional angles		Torsional angles	
	O(5)-C(5)-C(6)-O(6)	C(4)-C(5)-C(6)-O(6)	O(5)-C(5)-C(6)-O(6)	C(4)-C(5)-C(6)-O(6)
Range	49 to 73 <sup>o</sup>	-165 to 168 <sup>o</sup>	-60 to -68 <sup>o</sup>	54 to 60 <sup>o</sup>
Spread	24	27	8	6
Average	62.6	-173.8	-62.2	56.6
Number of structures	14		9	
Conformation	<i>gauche-trans</i>		<i>gauche-gauche</i>	



moieties. This is one of the two preferred conformations (Sundaralingam, 1968). The torsional angles O(5)-C(5)-C(6)-O(6) and C(4)-C(5)-C(6)-O(6) were calculated for about 23 known carbohydrates. The pertinent statistics are given in Table 10. It is noteworthy that the spread in the *ganche* torsion angles is much larger in the case of *ganche-trans* than in the *ganche-ganche*. Moreover, the *ganche* angles differ from the ideal value of  $60^\circ$  as observed in the ribofuranosides. An examination of the available disaccharides indicates that the conformation about the C(5)-C(6) bond of the non-reducing sugar is *ganche-trans*, while the conformation of the reducing sugar is either *ganche-trans* or *ganche-ganche*. It should be pointed out that the *ganche-ganche* conformation is not favored in the galactosides because of unfavorable interaction between oxygen atoms O(6) and O(4) (O(4) is now in the axial orientation) (Sundaralingam, 1970). Although the favored conformations for the galactosides are the *ganche-trans* and *trans-ganche*, only the former conformation has been observed so far in the known galactosides:

$\alpha$ -lactose monohydrate, methyl-6-bromo-6-deoxy- $\alpha$ -D-galactopyranoside (Robertson & Sheldrick, 1965) and  $\alpha$ -D-galactosamine-1-phosphate monohydrate (Fries & Sundaralingam, 1969).

The hydrogen atoms on adjacent carbon atoms of the pyranose system may be in *trans* or *ganche* orientation, Table 11. The deviation of the H-C-C-H torsional angles from the ideal *ganche* or *trans* arrangement is not surprising in view of the distortions of the pyranoside ring from the symmetric chair conformation discussed above.

The orientation of the O-H groups with respect to the C-H bonds are also given in Table 11. As has been observed previously (Sundaralingam, 1968), the H-C-O-H torsional angles show a preference for a *ganche* (*cis*) conformation. The *trans* conformation is observed only for the atom sequence H(C2')-C(2')-O(2')-H(O2'). It is noteworthy that the *ganche* (*cis*) conformation is the preferred conformation when the hydroxyl group is esterified, e.g. acetates, amides, phosphates and sulfates (Sundaralingam, 1969).

Table 11. Torsional angles involving the hydrogen atoms

Estimated standard deviations are given in parentheses.

Galactose		Glucose	
H(C1)--H(C2)*	171 (3) <sup>o</sup>	H(C1')--H(C2')	56 (3) <sup>o</sup>
H(C2)--H(C3)	-174 (3)	H(C2')--H(C3')	175 (3)
H(C3)--H(C4)	61 (3)	H(C3')--H(C4')	174 (3)
H(C4)--H(C5)	-61 (3)	H(C4')--H(C5')	-174 (2)
H(C5)--H(C6)	177 (3)	H(C5')--H(C6')	-172 (3)
H(C5)--H'(C6)	65 (3)	H(C5')--H'(C6')	78 (3)
H(C2)--H(O2)†	-7 (3)	H(C1')--H(O1')	-70 (4)
H(C3)--H(O3)	-28 (4)	H(C2')--H(O2')	167 (4)
H(C4)--H(O4)	22 (3)	H(C3')--H(O3')	-71 (4)
H(C6)--H(O6)	0 (4)	H(C6')--H(O6')	-145 (5)
H'(C6)--H(O6)	120 (4)	H'(C6')--H(O6')	-40 (5)

\* Refers to the torsional angle H(C1)-C(1)-C(2)-H(C2).

† Refers to the torsional angle H(C2)-C(2)-O(2)-H(O2).

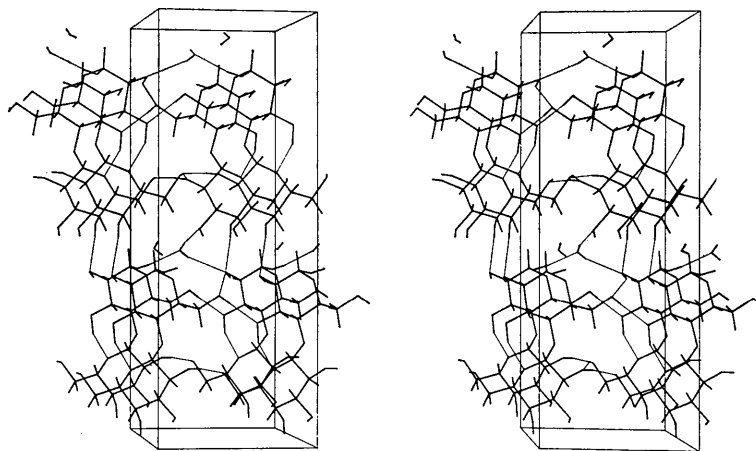


Fig. 4. A stereoscopic diagram showing the packing and the hydrogen bonding scheme including that of the disordered oxygen atom  $\beta$ O(1'). A survey of the carbohydrate crystal structures (Sundaralingam, unpublished results) indicates that the overlap of the sugar rings found here is a characteristic property of the packing of sugars in the crystalline state.

*Molecular packing and hydrogen bonding*

The molecules are oriented in the cell with their long axis parallel to the twofold screw axes (Figs. 4 and 5). The water molecules are embedded between the chains of the disaccharide molecules related by the screw axis, so that the water is hydrogen bonded to four different lactose molecules. Besides the water hydrogen bonds there are 10 hydrogen bonds involving the lactose molecule, Table 12. The most notable of these is the intramolecular hydrogen bond,  $O(3')-H\cdots O(5)=2.811$  Å. A similar hydrogen bond was observed in cellobiose. The glucose ring oxygen is not involved in hydrogen bonding, although in cellobiose both the ring oxygen atoms were involved in hydrogen bonding.  $O(3')$  serves as donor in the intramolecular hydrogen bond, it also accepts a hydrogen bond from  $O(6')H$  of a translation related molecule. It appears that  $O(3')$  in cellobiose is probably also involved in a very weak acceptor hydrogen bond, the donor atom being  $O(4)H$ . The environment of this hydrogen bond is shown in Fig. 6.

The lactose molecules in the *a* axial direction are held together in hydrogen bonded sheets by at least three hydrogen bonds:  $O(6)-H\cdots O(3)$ ,  $O(2)-H\cdots O(6)$  and  $O(6)-H\cdots O(2)$ . These sheets parallel to the *ab* plane and separated by translation along the *c* axis are connected by the hydrogen bond  $O(2)\cdots H-O(6)$ . Thus, there are infinite ribbons of hydrogen bonds  $\cdots O(2)-H \rightarrow O(6)-H \rightarrow O(2)\cdots$  running parallel to the *c* axis.

There is an additional intersheet hydrogen bond,  $O(2)-H\cdots O(6)$ . Apart from the hydrogen bonds the only short intermolecular contact is  $2.16$  Å involving  $H(C2)$  (*x, y, z*) and  $H(C3)$  (*x, y, -1+z*), Fig. 5. The intrasheet bonds are mainly hydrogen bonds while the intersheet interactions involve both hydrogen bonds and van der Waals interactions. The latter interaction is due to the characteristic staggered arrangement of the sugar rings on top of each other (Sundaralingam, unpublished results).

The only hydrogen bond between the twofold screw related molecules is  $O(4)-H\cdots O(2')$  which is also the only hydrogen bond involving a galactose and a glucose residue in the crystal structure. However, in the  $\beta$ -lactose isomer there appears to be an additional hydrogen bond  $\beta O(1')-H\cdots O(3)$  between glucose and galactose units (Table 12).

It is intriguing to note that the  $\beta$ -anomer can be accommodated in the lattice with no apparent sacrifice in the number of hydrogen bonds. Although the hydrogen bond  $O(1')-H\cdots O(W)$  is absent for the  $\beta$ -anomer, there appears to be a compensating hydrogen bond which can potentially form between the  $\beta$ -hydroxyl group and  $O(3)$  of a symmetry related molecule, Table 12 and Fig. 4. Consequently, the stability of the lattice should not be diminished. Therefore, crystalline  $\beta$ -D-lactose monohydrate, if this form exists, might very well be isomorphous with the  $\alpha$ -anomer.

Table 12. *Hydrogen bond lengths and angles*

$O(3')\cdots O(5)$	I	2.811 (4) Å	$C(3')-O(3')\cdots O(5)$	99.2 (2)°
$H(O3')\cdots O(5)$	I	1.79 (5)	$O(3')-H(O3')\cdots O(5)$	155 (3)
			$C(5)-O(5)\cdots O(3')$	126.3 (2)
			$C(1)-O(5)\cdots O(3')$	93.7 (2)
$O(6')\cdots O(3')$	II	2.773 (4)	$C(6')-O(6')\cdots O(3')$	113.8
$H(O6')\cdots O(3')$	II	1.99 (7)	$O(6')-H(O6')\cdots O(3')$	160
$O(2)\cdots O(6)$	II	2.695 (4)	$C(2)-O(2)\cdots O(6)$	100.2
$H(O2)\cdots O(6)$	II	1.92 (4)	$O(2)-H(O2)\cdots O(6)$	169
$W\cdots O(2')$	III	2.981 (4)	$W-H(W)\cdots O(2')$	149
$H(W)\cdots O(2')$	III	2.39 (4)		
$O(1')\cdots W$	I	2.790 (4)	$C(1')-O(1')\cdots W$	96.8
$H(O1')\cdots W$		2.04 (4)	$O(1')-H(O1')\cdots W$	163
$O(6)\cdots O(2)$	IV	2.734 (3)	$C(6)-O(6)\cdots O(2)$	96.7
$H(O6)\cdots O(2)$	IV	2.03 (3)	$O(6)-H(O6)\cdots O(2)$	162
$O(2')\cdots O(6')$	IV	2.721 (3)	$C(2')-O(2')\cdots O(6')$	120.6
$H(O2')\cdots O(6')$	IV	2.08 (4)	$O(2')-H(O2')\cdots O(6')$	139
$O(4)\cdots O(2')$	V	2.835 (4)	$C(4)-O(4)\cdots O(2')$	111.2
$H(O4)\cdots O(2')$	V	2.11 (4)	$O(4)-H(O4)\cdots O(2')$	171
$O(3)\cdots W$	VI	2.748 (4)	$C(3)-O(3)\cdots W$	103.6
$H(O3)\cdots W$	VI	1.94 (4)	$O(3)-H(O3)\cdots W$	171.9
$W\cdots O(3)$	VII	2.747 (4)	$W-H(W)\cdots O(3)$	169
$H'(W)\cdots O(3)$	VII	1.88 (5)		
$O(3)\cdots \beta O(1')$	VI	2.84 (4)	$C(3)-O(3)\cdots \beta O(1')$	154

Symmetry code I *x, y, z*; II  $1+x, y, z$ ; III  $1+x, y, 1+z$ ; IV  $-1+x, y, -1+z$ ; V  $-x, \frac{1}{2}+y, -z$ ; VI  $1+x, \frac{1}{2}+y, 1+z$ ; VII  $-1+x, \frac{1}{2}+y, -1+z$ .

The distribution of the donor and acceptor hydrogen bonds involving the oxygen atoms in lactose is given in Table 13. The most common hydrogen-bonding pattern of an O-H group is its involvement in one donor and one acceptor hydrogen bond. This is definitely the preferred mode of hydrogen bonding of the O-H groups of the sugars (Jeffrey & Rosenstein, 1964). A rather unusual hydrogen bonding is displayed by the O(2')-H group which is involved in a donor and two acceptor hydrogen bonds. Similar hydrogen bonding

was not observed in cellobiose, Table 13. The donor hydrogen bonding scheme is similar in both lactose and cellobiose while there are some differences in the acceptor hydrogen bonding scheme. For the  $\beta$ -anomers O(3)-H donate a hydrogen bond and accept two hydrogen bonds. The bridge oxygen atom has not so far been observed in hydrogen bonding (Sundaralingam, 1968), although it has been involved in hydrogen bonding in some currently proposed models for cellulose. The interchain hydrogen bonding in cellulose microfibrils is

Table 13. *The distribution of the donor and acceptor hydrogen bonds in lactose monohydrate*

	Number of donor <sup>a</sup> hydrogen bonds	Number of acceptor hydrogen bonds	Total number of hydrogen bonds
O(1)	0 (0)	0 (0)	0 (0)
O(2)	1 (1)	1 (1)	2 (2)
O(3)	1 (1)	1 (1)	2 (2)
O(4)	1 (1)	0 (1)	1 (2)
O(6)	1 (1)	1 (1)	2 (2)
O(5)	0 (0)	1 (1) <sup>b</sup>	1 (1)
O(1')	1 (1)	0 (0)	1 (1)
O(2')	1 (1)	2 (1)	3 (2)
O(3') <sup>c</sup>	1 (1) <sup>b</sup>	1 (0)	2 (1)
O(5')	0 (0)	0 (1)	0 (1)
O(6')	1 (1)	1 (1)	2 (2)
O <sub>w</sub>	2	2	4
$\beta$ O(1') <sup>d</sup>	1	0	1
$\beta$ O <sub>w</sub>	2	1	3

<sup>a</sup> For comparison the corresponding numbers for cellobiose are given in parentheses.

<sup>b</sup> Involved in intramolecular hydrogen bond.

<sup>c</sup> O(3') probably is involved in a very weak hydrogen bond (see text).

<sup>d</sup> The designation  $\beta$  is for the  $\beta$ -lactose anomer in the lattice.

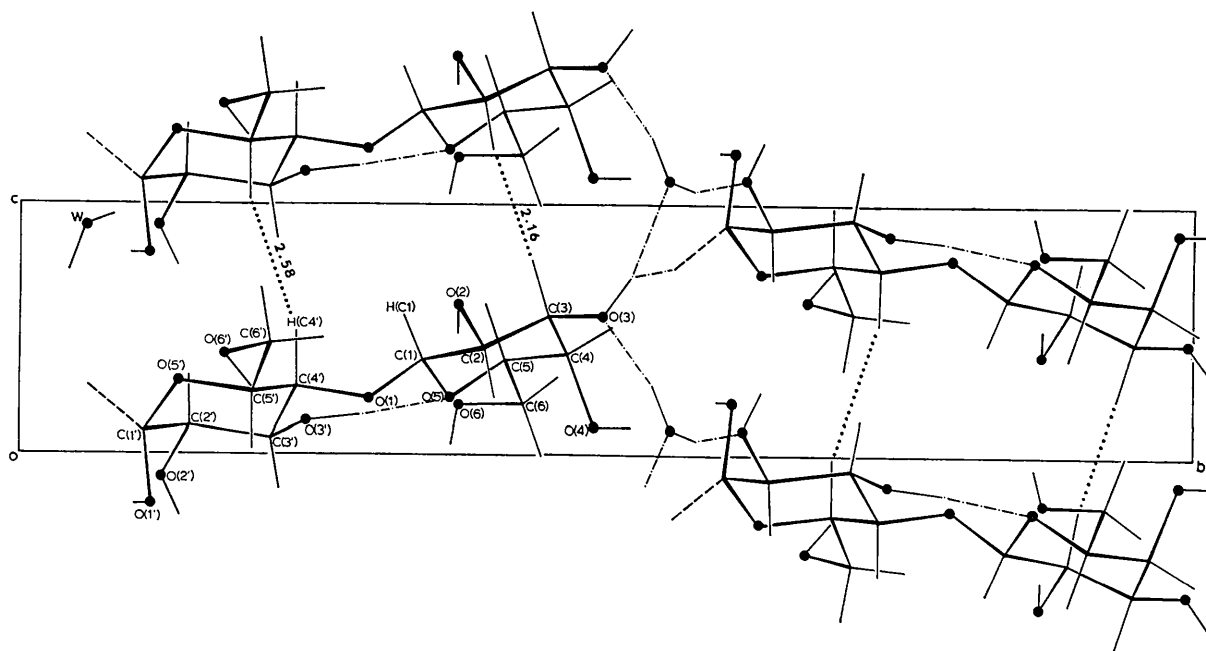


Fig. 5. A view of the molecular packing down the  $a$  axis. The water molecule is hydrogen bonded to four lactose molecules, two related by the  $c$ -axis translation and two related by  $a$ -axis translation (only one is shown). There is a short (2.16 Å) intermolecular contact between H(C2) and H(C3). A van der Waals contact (2.58 Å) occurs between H(C4') and H(C5'). These contacts involve the axial hydrogen atoms. Similar contacts may contribute to interchain interaction in cellulose microfibrils.

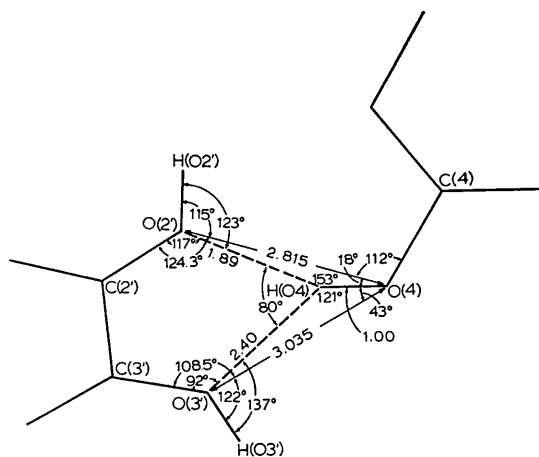


Fig. 6. Illustration showing a possible weak hydrogen bond between O(3') and O(4) in cellulose. Note O(3')---H(O4) is 2.40 Å.

currently being investigated in these laboratories in the light of the intermolecular hydrogen bonding in  $\alpha$ -lactose monohydrates.

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## Structure Cristalline du Bronze de Vanadium $\text{Cu}_x\text{V}_4\text{O}_{11}$

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The single-crystal structure determination of a new vanadium bronze gives its composition as  $\text{Cu}_x\text{V}_4\text{O}_{11}$  ( $x=1.82$ ).  $\text{Cu}_x\text{V}_4\text{O}_{11}$  is monoclinic with space group  $Cm$  and the parameters  $a=15.38$ ,  $b=3.61$ ,  $c=7.37$  Å,  $\beta=102^\circ$ . Double strings of  $\text{VO}_6$  octahedra forming  $(\text{V}_4\text{O}_{11})_n$  sheets by edge and corner sharing are held together by copper ions. The  $\text{Cu}_x\text{V}_4\text{O}_{11}$  vanadium bronze can be considered as the second member of a new group of  $M_xB_2nO_{4n+3}$  compounds ( $x \leq n$ ).

Une étude approfondie du système  $\text{Cu}_2\text{O}-\text{V}_2\text{O}_5-\text{VO}_2$  a été effectuée par Casalot (1968). Plusieurs phases de type 'bronzes oxygénés' ont été préparées et étudiées.

Récemment Galy, Lavaud, Casalot & Hagenmüller (1970) ont déterminé la structure fine des phases  $\text{Cu}_x\text{V}_2\text{O}_5\beta$  et  $\epsilon$ . Une fusion prolongée de  $\text{Cu}_x\text{V}_2\text{O}_5$   $\epsilon$  en-