SHORT STRUCTURAL PAPERS

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A Lactose–Calcium Chloride Heptahydrate Complex

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Abstract. Orthorhombic, $P2_12_12_1$, $a=21{\cdot}562$ (1), $b=13{\cdot}455$ (1), $c=8{\cdot}792$ (2) Å; $C_{12}H_{22}O_{11}.CaCl_2.7H_2O$, $Z=4$, $\varrho_o=1{\cdot}51$ g cm^{-3}, $\varrho_c=1{\cdot}509$ g cm^{-3}. The complex was crystallized from an aqueous solution of lactose and calcium chloride. The crystals are nearly isostructural with those of lactose–$CaBr_2.7H_2O$.

Introduction. Crystals of the complex were obtained by Herrington's (1934) method. Systematic absences were observed for the reflections $h00$ with h odd, $0k0$ with k odd and $00l$ with l odd. Three-dimensional X-ray diffraction data were collected with an automated diffractometer, by use of a scintillation counter, nickel-filtered copper radiation, and a θ–2θ scanning technique. Measurements were made for each of the 2386 reflections with $2\theta \leq 128°$. Three strong, medium-angle reflections were chosen as standards and were monitored periodically. During data collection, the intensities of the standard reflections decreased by about 5%.

The intensity values were scaled by a least-squares procedure in which the intensities of the standard reflections were used to calculate scale factors as a function of crystal exposure time (Ibers, 1969). The intensities were assigned variances, $\sigma^2(I)$, according to the statistics of the scan and background counts plus a correctional term $(0{\cdot}03S)^2$, S being the scan counts. The intensities and variances were corrected for Lorentz and polarization factors, and absorption corrections were applied by using the computer program *ORABS* (Wehe, Busing & Levy, 1962). Finally, the data were scaled by means of a Wilson (1942) plot.

Assuming that the complex was isostructural with the hydrated calcium bromide complex of lactose (Bugg, 1972), we began refinement using those parameters. The structure was refined by using a modified version of the least-squares program *ORFLS* (Busing, Martin & Levy, 1962). The quantity minimized was $\sum w(F_o^2-F_c^2/k^2)^2$, where k is a scale factor and weight w is equal to $1/\sigma^2(F_o^2)$. Scattering factors for the non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1962), and hydrogen-atom scattering factors were from Stewart, Davidson & Simpson (1965). Non-hydrogen atom positional and anisotropic temperature factors, as well as Zachariasen's (1963) isotropic extinction parameter g [as formulated by Coppens & Hamilton (1970)] were included in the refinement. All hydrogen atoms were located in difference Fourier maps calculated during the latter stages of refinement. The two hydrogen atoms of O(*W*5) (a water molecule that exhibits large apparent thermal motion) were included in structure factor calculations, but not in the least-squares refinement; positional parameters and isotropic temperature factors for the remaining hydrogen atoms were included in the refinement. A difference Fourier map also indicated that, like the crystal structures of lactose monohydrate (Fries, Rao & Sundaralingam, 1971) and lactose–$CaBr_2.7H_2O$ (Bugg, 1972), this complex contains a mixture of α and β anomers of lactose. Two positions were assigned to O(1′), and their popu-

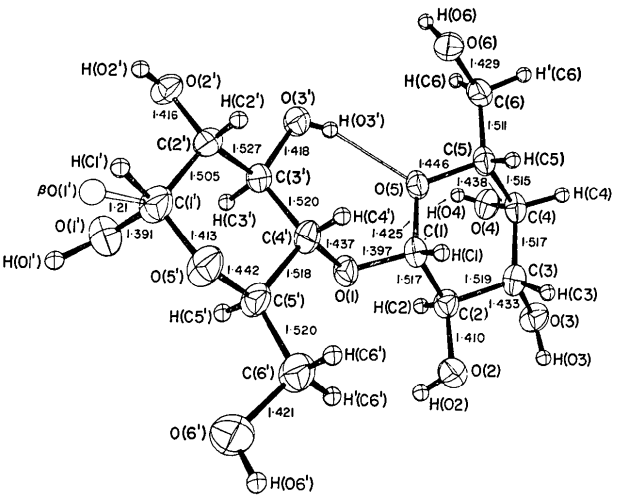

Fig. 1. Molecular conformation and atomic numbering of the lactose molecule. The nonhydrogen atoms are represented by thermal ellipsoids scaled to include 50% probability. The hydrogen atoms are represented by spheres of 0·1 Å radius. The β oxygen atom is shown attached by an open bond to atom C(1′). Bond lengths involving nonhydrogen atoms are given; the estimated standard deviations in bond lengths are 0·004–0·007 Å, except for the C(1′)–βO(1′) bond length, which has a standard deviation of about 0·06 Å. [This drawing was prepared by using the program *ORTEP* (Johnson, 1965.]

lations were included as parameters in the refinement. The population parameters, which were not constrained to a total value of 1·0, converged to values of 0·951 (12) for the αO(1′) position and 0·050 (11) for the βO(1′) position, thereby indicating that about 95% of the lactose molecules are in the α form. The final R index ($\sum||F_o|-|F_c||/\sum|F_o|$) is 0·046. The final goodness-of-fit, $[\sum w(F_o^2-F_c^2/k^2)^2/(m-s)]^{1/2}$, where m is the number of reflections used and s is the number of parameters refined, is 1·64. A final three-dimensional difference Fourier map showed several peaks and troughs with magnitudes ranging from 0·3 to 0·5 eÅ^{-3} in the immediate vicinity of the calcium ion. There were no other peaks or troughs in excess of 0·3 eÅ^{-3} in the map.

Table 1 lists the final heavy-atom parameters and their estimated standard deviations. Table 2 gives the hydrogen-atom parameters and their estimated standard deviations. The estimated errors in positional coordinates are about 0·001 Å for chloride and calcium ions, 0·002–0·006 Å for carbon and oxygen atoms, and 0·03–0·08 Å for hydrogen atoms. A table of observed and calculated structure factors is available.* Fig. 1 shows the lactose conformation, atomic thermal ellipsoids, and those bond lengths that involve only nonhydrogen atoms. Table 3 lists the bond angles involving only the heavy atoms of lactose.

Discussion. We determined this crystal structure to compare the α:β anomer ratio with those found in the crystal structures of lactose monohydrate (Fries, Rao & Sundaralingam, 1972) and lactose–calcium bromide heptahydrate (Bugg, 1972), and to verify the hydrogen atom positions that were found in the calcium bromide complex of lactose. Our results show

* This table has been deposited with the National Lending Library, England as Supplementary Publication No. SUP. 30051 (12pp). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final heavy-atom parameters and their standard deviations*

The values for calcium and chloride ions have been multiplied by 10^5; all other values have been multiplied by 10^4. Temperature factors are in the form $T=\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-2\beta_{12}hk-2\beta_{13}hl-2\beta_{23}kl)$. The final value of the isotropic extinction parameter is $g=0{\cdot}003$ (2). The isotropic thermal parameter for βO(1′) is shown. The refined occupancy parameters for atom O(1′) and βO(1′) are 0·95(1) and 0·05(1), respectively.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	92165 (4)	54159 (6)	95720 (10)	154 (2)	308 (4)	828 (10)	−1 (2)	−11 (4)	−60 (7)
Cl(1)	93557 (5)	90687 (9)	93973 (18)	181 (3)	520 (8)	1917 (25)	−13 (4)	84 (7)	193 (12)
Cl(2)	69343 (5)	57345 (8)	101864 (13)	200 (2)	387 (6)	1035 (16)	10 (3)	18 (5)	−59 (9)
Lactose									
C(1)	3620 (2)	6967 (3)	5997 (5)	14 (1)	24 (2)	72 (6)	0 (1)	−2 (2)	5 (3)
C(2)	3361 (2)	7538 (3)	7344 (6)	14 (1)	28 (3)	76 (6)	1 (1)	1 (2)	−5 (4)
C(3)	3502 (2)	8637 (3)	7163 (5)	16 (1)	26 (2)	63 (6)	2 (1)	−7 (2)	−9 (3)
C(4)	4177 (2)	8841 (3)	6788 (5)	18 (1)	23 (2)	67 (6)	1 (1)	−3 (2)	1 (3)
C(5)	4388 (2)	8188 (3)	5483 (5)	18 (1)	22 (2)	70 (6)	0 (1)	2 (2)	1 (3)
C(6)	5070 (2)	8290 (3)	5126 (6)	19 (1)	30 (2)	105 (7)	−3 (1)	9 (2)	3 (4)
O(1)	3546 (1)	5950 (2)	6265 (3)	17 (1)	22 (2)	77 (4)	−2 (1)	4 (1)	−7 (2)
O(2)	2711 (2)	7438 (2)	7418 (4)	17 (1)	34 (2)	130 (6)	−2 (1)	12 (2)	0 (3)
O(3)	3364 (2)	9158 (2)	8544 (4)	17 (1)	37 (2)	94 (4)	2 (1)	3 (2)	−20 (3)
O(4)	4549 (2)	8721 (3)	8133 (4)	17 (1)	34 (2)	86 (5)	3 (1)	−7 (2)	−10 (3)
O(5)	4267 (1)	7159 (2)	5860 (3)	16 (1)	23 (1)	79 (4)	−1 (1)	2 (1)	1 (2)
O(6)	5234 (2)	7666 (2)	3873 (4)	24 (1)	46 (2)	82 (4)	7 (1)	16 (2)	6 (3)
C(1′)	3722 (2)	3323 (3)	3766 (6)	15 (1)	34 (3)	131 (8)	−2 (1)	0 (2)	−25 (4)
C(2′)	4265 (2)	4025 (3)	3744 (5)	12 (1)	32 (2)	88 (6)	2 (1)	4 (2)	−6 (3)
C(3′)	4229 (2)	4763 (3)	5059 (5)	13 (1)	25 (2)	91 (6)	−2 (1)	4 (2)	−8 (3)
C(4′)	3615 (2)	5314 (3)	4964 (5)	16 (1)	25 (2)	84 (6)	0 (1)	1 (2)	−15 (4)
C(5′)	3100 (2)	4546 (3)	5024 (5)	13 (1)	30 (2)	106 (7)	1 (1)	1 (2)	−17 (4)
C(6′)	2444 (2)	4954 (4)	4936 (7)	16 (1)	38 (3)	146 (9)	−1 (1)	0 (2)	−21 (4)
O(1′)	3763 (2)	2707 (3)	5032 (5)	21 (1)	34 (2)	162 (7)	−3 (1)	4 (2)	9 (3)
O(2′)	4849 (1)	3547 (2)	3858 (4)	13 (1)	38 (2)	90 (5)	2 (1)	2 (2)	−21 (3)
O(3′)	4760 (1)	5379 (2)	4915 (4)	13 (1)	27 (2)	145 (6)	−4 (1)	6 (2)	−12 (3)
O(5′)	3161 (1)	3868 (2)	3762 (4)	14 (1)	38 (2)	133 (5)	−1 (1)	−7 (2)	−33 (3)
O(6′)	2054 (2)	4115 (3)	5163 (6)	13 (1)	53 (2)	342 (11)	−7 (1)	5 (2)	−21 (4)
βO(1′)	3680 (25)	2571 (46)	3027 (68)	1·4 (1·5)					
Water									
O(W1)	615 (2)	9598 (3)	7826 (4)	15 (1)	90 (3)	119 (6)	−1 (1)	1 (2)	45 (4)
O(W2)	1103 (2)	1921 (3)	6637 (5)	20 (1)	43 (2)	150 (6)	−1 (1)	−1 (2)	−17 (4)
O(W3)	1797 (2)	9948 (4)	6414 (7)	17 (1)	96 (4)	136 (7)	0 (1)	2 (2)	48 (4)
O(W4)	4097 (2)	1219 (4)	9285 (7)	23 (1)	39 (2)	142 (8)	3 (1)	−4 (2)	3 (4)
O(W5)	3050 (2)	2306 (4)	9655 (6)	39 (1)	179 (6)	216 (9)	51 (2)	0 (3)	−3 (6)
O(W6)	2348 (2)	2421 (5)	6909(7)	26 (1)	74 (4)	202 (9)	−6 (2)	1 (2)	−4 (6)
O(W7)	4744 (2)	1942 (3)	6661 (4)	29 (1)	66 (3)	113 (6)	3 (2)	3 (2)	0 (4)

Table 2. *Hydrogen-atom parameters*

The positional parameters have been multiplied by 10^3. H(*W*5) and H′(*W*5) were not included in the least-squares refinement; both were assigned the isotropic temperature factor of O(*W*5).

	x	*y*	*z*	*B* (Å²)
Lactose				
H(C1)	341 (2)	716 (3)	511 (5)	1·9 (0·9)
H(C2)	353 (2)	731 (3)	822 (4)	1·2 (0·8)
H(C3)	321 (2)	892 (3)	645 (5)	2·9 (1·0)
H(C4)	423 (2)	960 (4)	654 (6)	4·4 (1·1)
H(C5)	416 (1)	840 (2)	459 (4)	0·9 (0·7)
H(C6)	546 (3)	815 (5)	593 (8)	7·8 (1·8)
H′(C6)	516 (2)	899 (4)	478 (5)	3·7 (1·0)
H(O2)	262 (2)	698 (4)	778 (7)	4·6 (1·6)
H(O3)	296 (2)	918 (3)	866 (6)	4·1 (1·3)
H(O4)	468 (2)	826 (3)	818 (6)	2·4 (1·3)
H(O6)	564 (3)	747 (5)	422 (10)	10·3 (2·5)
H(C1′)	377 (2)	289 (4)	260 (7)	3·8 (1·7)
H(C2′)	420 (2)	437 (3)	274 (5)	3·2 (1·0)
H(C3′)	425 (2)	436 (3)	607 (5)	2·0 (0·8)
H(C4′)	357 (2)	569 (3)	403 (5)	2·2 (0·9)
H(C5′)	318 (2)	417 (3)	589 (5)	2·4 (0·9)
H(C6′)	236 (2)	529 (4)	384 (6)	4·4 (1·2)
H′(C6′)	235 (2)	545 (4)	573 (6)	4·4 (1·2)
H(O1′)	357 (3)	209 (6)	501 (9)	9·4 (2·4)
H(O2′)	489 (2)	320 (4)	329 (5)	2·9 (1·3)
H(O3′)	470 (3)	586 (4)	509 (7)	5·4 (1·8)
H(O6′)	168 (3)	435 (4)	512 (7)	7·0 (1·7)
Water				
H(*W*1)	25 (2)	946 (3)	815 (5)	1·9 (0·9)
H′(*W*1)	90 (2)	944 (4)	833 (6)	4·0 (1·4)
H(*W*2)	95 (3)	232 (4)	639 (8)	5·2 (1·9)
H′(*W*2)	158 (3)	199 (4)	675 (6)	5·3 (1·4)
H(*W*3)	179 (6)	1000 (11)	679 (15)	15·7 (6·1)
H′(*W*3)	212 (4)	1009 (6)	625 (10)	8·4 (2·8)
H(*W*4)	378 (6)	176 (9)	932 (17)	11·6 (3·2)
H′(*W*4)	407 (3)	102 (5)	879 (7)	1·6 (1·9)
H(*W*5)	270	230	1020	7·67
H′(*W*5)	280	260	920	7·67
H(*W*6)	231 (3)	294 (4)	654 (8)	5·5 (2·0)
H′(*W*6)	250 (4)	203 (7)	676 (13)	10·7 (4·1)
H(*W*7)	498 (2)	160 (4)	611 (6)	3·8 (1·4)
H′(*W*7)	432 (2)	178 (4)	648 (6)	4·0 (1·2)

that approximately 3–7% of the lactose molecules are in the β form, as compared with about 6–9% in lactose monohydrate and 10–14% in the calcium bromide complex. The hydrogen atom coordinates are in agreement with those proposed for the calcium bromide complex, and the hydrogen-bonding scheme described by Bugg (1972) is unchanged.

Table 3. *Bond angles involving heavy atoms of lactose*

Except for angles involving the β oxygen atom, the estimated standard deviations are about 0·3°.

Glucose moiety		Galactose moiety	
C(1′)–C(2′)–C(3′)	111·0°	C(1)–C(2)–C(3)	109·7°
C(2′)–C(3′)–C(4′)	108·6	C(2)–C(3)–C(4)	113·0
C(3′)–C(4′)–C(5′)	107·7	C(3)–C(4)–C(5)	110·3
C(4′)–C(5′)–O(5′)	109·7	C(4)–C(5)–O(5)	109·2
C(5′)–O(5′)–C(1′)	113·9	C(5)–O(5)–C(1)	111·6
O(5′)–C(1′)–C(2′)	109·9	O(5)–C(1)–C(2)	109·5
O(5′)–C(1′)–O(1′)	111·4	O(5)–C(1)–O(1)	107·7
C(2′)–C(1′)–O(1′)	109·6	C(2)–C(1)–O(1)	108·8
C(1′)–C(2′)–O(2′)	114·0	C(1)–C(2)–O(2)	110·7
C(3′)–C(2′)–O(2′)	106·7	C(3)–C(2)–O(2)	107·2
C(2′)–C(3′)–O(3′)	105·8	C(2)–C(3)–O(3)	110·3
C(4′)–C(3′)–O(3′)	114·5	C(4)–C(3)–O(3)	107·2
C(3′)–C(4′)–O(1)	109·7	C(3)–C(4)–O(4)	109·6
C(5′)–C(4′)–O(1)	107·6	C(5)–C(4)–O(4)	113·0
C(4′)–C(5′)–C(6′)	115·7	C(4)–C(5)–C(6)	113·3
O(5′)–C(5′)–C(6′)	106·0	O(5)–C(5)–C(6)	108·0
C(5′)–C(6′)–O(6′)	104·8	C(5)–C(6)–O(6)	110·4
O(5′)–C(1′)–βO(1′)	111·8		
C(2′)–C(1′)–βO(1′)	125·2	Bridge	
O(1′)–C(1′)–βO(1′)	86·3	C(1)–O(1)–C(4′)	116·0

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