The Crystal and Molecular Structure of Methyl Tetraacetyl-β-D-glucoside

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The crystal structure of methyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside has been determined from 2260 intensity data collected on a four-circle diffractometer with Mo $K\alpha$ radiation. The unit cell is orthorhombic, space group $P2_12_12_1$, $a = 8\cdot089$, $b = 13\cdot251$, $c = 17\cdot359$ Å, and contains four molecules. The structure was solved with direct methods (*MULTAN*). Full-matrix, weighted, least-squares refinement gave a final agreement index of $R = 0\cdot043$ for 1577 observed reflections.

Introduction

The progress in solving complex polymer structures in recent years is mostly due to the introduction of advanced methods, such as conformation and packing analysis, into this field (Zugenmaier & Sarko, 1972, 1973, 1976; Arnott & Scott, 1972; Guss *et al.*, 1975). Precise molecular data of various model compounds are necessary for the application of these methods. A survey for polysaccharides of such data as valence bond lengths, angles, and torsion angles is given by Arnott & Scott (1972). However, very few data are available for models of polysaccharide derivatives. Some acetyl derivatives have been solved in recent years. In continuing the investigation of the acetyl compounds, we have studied the crystal and molecular structure of methyl tetraacetyl-β-D-glucoside and compared the results with those of β-D-acetylcellobiose (Leung, Chanzy, Pérez & Marchessault, 1976).

Crystal data

$C_{15}O_{10}H_{22}$, $M_r = 362\cdot3$, orthorhombic, $P2_12_12_1$, $a = 8\cdot089 \pm 0\cdot003$, $b = 13\cdot251 \pm 0\cdot005$, $c = 17\cdot359 \pm$

Table 1. *Fractional atomic coordinates* ($\times 10^4$; *for* H $\times 10^3$) *for methyl tetraacetyl-β-D-glucoside*

The estimated standard deviations are given in parentheses and refer to the last decimal positions of respective values.

|	x	y	z		x	y	z
O(1)	4092 (3)	3420 (2)	5230 (2)	H(1)	210 (6)	262 (4)	494 (3)
O(2)	2916 (3)	3551 (2)	3651 (2)	H(2)	490 (6)	271 (3)	394 (3)
O(3)	3563 (3)	1785 (2)	2800 (2)	H(3)	180 (6)	186 (4)	359 (3)
O(4)	2528 (4)	4 (2)	3643 (2)	H(4)	471 (6)	63 (3)	386 (3)
O(5)	4074 (3)	1713 (2)	5127 (2)	H(5)	202 (6)	85 (3)	493 (3)
O(6)	5749 (4)	−144 (2)	5056 (2)	H(6A)	346 (6)	−70 (4)	508 (3)
O(2A)	5340 (5)	4386 (3)	3556 (3)	H(6B)	390 (7)	−1 (4)	584 (3)
O(3A)	940 (5)	1745 (5)	2366 (3)	H(11)	364 (7)	283 (4)	633 (4)
O(4A)	4807 (5)	−909 (3)	3362 (3)	H(12)	422 (7)	409 (4)	627 (4)
O(6A)	5690 (6)	−1788 (3)	5296 (3)	H(13)	234 (7)	378 (4)	605 (4)
C(1)	3347 (4)	2626 (3)	4845 (2)	H(21)	171 (8)	514 (5)	321 (4)
C(2)	3721 (4)	2690 (3)	3992 (2)	H(22)	329 (9)	579 (5)	312 (4)
C(3)	3001 (4)	1777 (3)	3586 (2)	H(23)	278 (8)	495 (5)	256 (4)
C(4)	3545 (4)	799 (3)	3966 (2)	H(31)	386 (8)	127 (4)	133 (3)
C(5)	3287 (5)	832 (3)	4831 (3)	H(32)	229 (8)	198 (4)	111 (3)
C(6)	4004 (5)	−70 (3)	5245 (3)	H(33)	400 (8)	239 (4)	147 (3)
C(1M)	3482 (5)	3539 (4)	6006 (3)	H(41)	149 (11)	122 (6)	261 (5)
C(2A)	3872 (6)	4338 (3)	3433 (3)	H(42)	261 (11)	−202 (6)	270 (5)
C(3A)	2383 (6)	1788 (4)	2238 (3)	H(43)	144 (11)	−178 (6)	331 (5)
C(4A)	3317 (8)	−816 (3)	3343 (3)	H(61)	875 (8)	−50 (5)	511 (4)
C(6A)	6444 (6)	−1059 (3)	5095 (3)	H(62)	869 (8)	−163 (5)	503 (4)
C(2M)	2851 (8)	5111 (4)	3021 (3)	H(63)	830 (8)	−105 (5)	426 (4)
C(3M)	3180 (7)	1856 (4)	1465 (3)				
C(4M)	2096 (10)	−1547 (4)	3016 (4)				
C(6M)	8211 (7)	−1034 (3)	4845 (4)				
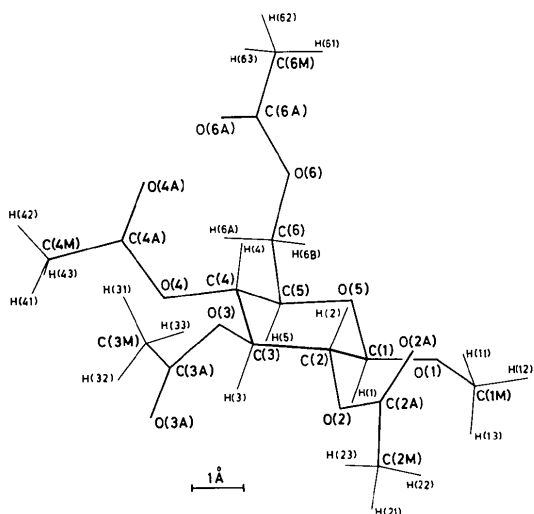
Fig. 1. Projection of one molecule of methyl tetraacetyl-β-D-glucoside on the *xy* plane after application of the rotation R to the coordinates of Table 1.

$0 \cdot 006$ Å, $V = 1860 \cdot 4$ Å^3, $D_c = 1 \cdot 293$, $D_x = 1 \cdot 297 \pm 0 \cdot 007$ g cm^{-3}, $Z = 4$, $F(000) = 768$, Mo $K\alpha$ ($\lambda = 0 \cdot 7107$ Å).

Suitable crystals were obtained by recrystallizing methyl tetraacetyl-β-D-glucoside from saturated acetone solution allowed to evaporate slowly. Precession and Weissenberg photographs exhibited *mmm* Laue symmetry with alternating extinction along the axes indicating the orthorhombic space group $P2_12_12_1$.

A crystal of dimensions $0 \cdot 6 \times 0 \cdot 8 \times 1 \cdot 2$ mm was mounted on a glass fiber with **a** along the spindle axis for data collection. Intensity data were collected at room temperature with a fully automated Nonius four-circle diffractometer. The intensities of two standard reflections were measured periodically during data collection. 2260 independent reflections were recorded of which 1577 had intensities greater than $2\sigma_I$; σ_I being the standard deviation in intensities which was estimated from the total count and the background values. The intensity data were corrected for Lorentz, polarization and absorption effects. In the least-squares
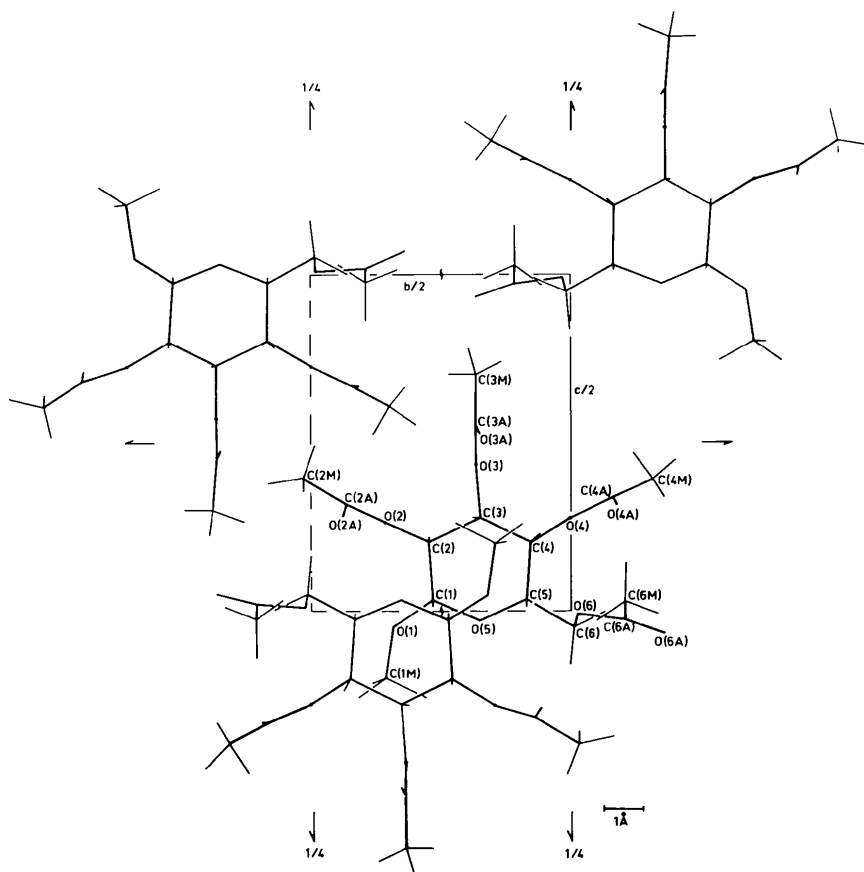

Fig. 2. Projection of methyl tetraacetyl-β-D-glucoside molecules of the crystal on the *bc* plane. Only molecules contributing to close contacts are shown for the illustration of packing.

refinement, extinction corrections were applied to the weighted structure factors.

The phasing model was obtained with *MULTAN* (Main, Woolfson & Germain, 1971). In the refinement cycles the C and O atoms were refined anisotropically. The H atoms were assigned the isotropic U values of the atoms to which they were bonded covalently and only the coordinates were refined. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final R factor obtained with 1577 reflections with $\sigma_I > 2$ is 4·3%, the R value of F^2 is 4·6%. The XRAY 70 and 76 systems (Stewart, 1970/76) were used throughout the calculations.

Results and discussion

The final coordinates of methyl tetraacetyl-β-D-glucoside are listed in Table 1.* Fig. 1 shows the numbering of the atoms and gives a projection of one molecule on the *xy* plane after application of the rotation R to the coordinates of Table 1.

$$R = \begin{pmatrix} 0·419 & 0·680 & 0·603 \\ 0·851 & -0·524 & 0·000 \\ 0·316 & 0·513 & -0·798 \end{pmatrix}.$$

Valence bond lengths, bond angles and torsion angles are listed in Table 2. In Fig. 2 the packing of the molecules in the crystal is illustrated and Table 3 shows the shortest packing contacts.

The pyranose ring of methyl tetraacetyl-β-D-glucoside (TMG) is in the $C1$ chair conformation and O(6) is placed in the vicinity of the ggt position. The ring conformation of TMG compares best with the unprimed ring of β-D-acetylcellobiose (AC) (Leung *et al.*, 1976) while the chair conformation of the primed ring of AC is more pronounced and O(6) is placed near the *gt* position. Only the C(5)—O(5)—C(1)—C(2) ring torsion angle of −67·7° of TMG exceeds considerably the average value of −62·2° (Arnott & Scott, 1972) as do the angles for both AC rings, −70·1 and −69·8°. The O(5)—C(1)—O(1)—C(1M) torsion angle of −76·7° for the O—C(methyl) bond for TMG agrees well with the O(5)—C(1)—O(1)—C(4') angle of −77·1° in AC, connecting two residues. The torsion angles for bonds to pendant ring atoms of TMG lie within 6° of those for AC.

The valence bond lengths of the ring are in agreement with the average values (Arnott & Scott, 1972). Only the C—O lengths to pendant O atoms of

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32942 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† *gg* means: the bond C(6)—O(6) is *gauche* to O(5)- C(5) and *gauche* to C(4)—C(5).

Table 2. *Bond lengths (Å), bond angles and torsion angles (°) for methyl tetraacetyl-β-D-glucoside*

The estimated standard deviations are given in parentheses and refer to the last decimal positions of respective values.

Ring

C(1) C(2)	1·514 (6)	O(5) -C(1)—C(2)	107·5 (3)
C(2)··C(3)	1·516 (5)	C(1)-C(2)—C(3)	109·5 (3)
C(3) C(4)	1·520 (5)	C(2)—C(3) ·C(4)	111·6 (3)
C(4) -C(5)	1·516 (6)	C(3)—C(4)—C(5)	111·4 (3)
C(5) O(5)	1·427 (5)	C(4)—C(5)—O(5)	108·6 (3)
O(5) ··C(1)	1·431 (5)	C(5)—O(5)—C(1)	112·6 (3)

Pendant atoms

C(1)—O(1)	1·385 (5)	O(5)—C(1)—O(1)	107·3 (3)
		C(2)—C(1)—O(1)	110·1 (3)
C(2) -O(2)	1·441 (4)	C(1)—C(2) O(2)	110·8 (3)
		C(3)—C(2)—O(2)	105·5 (3)
C(3) -O(3)	1·439 (5)	C(2)—C(3)—O(3)	108·3 (3)
		C(4)—C(3)—O(3)	109·1 (3)
C(4) -O(4)	1·449 (5)	C(3) -C(4)—O(4)	106·7 (3)
		C(5)—C(4)—O(4)	109·0 (3)
C(5)··C(6)	1·510 (6)	C(4)—C(5)—C(6)	113·4 (3)
		O(5)—C(5)—C(6)	107·7 (3)
C(6)—O(6)	1·453 (5)	C(5)—C(6)—O(6)	108·6 (3)

Methyl groups

O(1)—C(1M)	1·443 (5)	C(1)—O(1)—C(1M)	112·6 (3)

Acetyl groups

O(2)—C(2A)	1·352 (5)	C(2)—O(2)—C(2A)	117·9 (3)
C(2A)—O(2A)	1·209 (6)	O(2)—C(2A)—O(2A)	123·6 (4)
C(2A)—C(2M)	1·497 (7)	O(2)—C(2A)—C(2M)	110·2 (4)
		O(2A)—C(2A)—C(2M)	126·2 (4)
O(3) -C(3A)	1·365 (6)	C(3)- O(3) -C(3A)	117·3 (3)
C(3A) O(3A)	1·190 (7)	O(3)—C(3A)—O(3A)	123·5 (4)
C(3A) -C(3M)	1·491 (7)	O(3)—C(3A)—C(3M)	110·0 (4)
		O(3A)—C(3A)—C(3M)	126·5 (5)
O(4)··C(4A)	1·364 (6)	C(4)—O(4)—C(4A)	117·5 (4)
C(4A)—O(4A)	1·212 (8)	O(4)—C(4A)—O(4A)	122·4 (5)
C(4A)—C(4M)	1·495 (9)	O(4)—C(4A)—C(4M)	110·7 (5)
		O(4A)—C(4A)—C(4M)	127·0 (5)
O(6)—C(6A)	1·339 (5)	C(6)—O(6)—C(6A)	117·2 (3)
C(6A)—O(6A)	1·194 (6)	O(6) -C(6A)—O(6A)	122·2 (5)
C(6A)—C(6M)	1·494 (8)	O(6)—C(6A)—C(6M)	111·6 (4)
		O(6A)—C(6A)—C(6M)	126·3 (4)

Torsion angles
Ring

O(5)—C(1)—C(2)—C(3)	59·5 (3)
C(1)—C(2)—C(3)—C(4)	−52·3 (4)
C(2)—C(3)—C(4)—C(5)	49·3 (4)
C(3)—C(4)—C(5)—O(5)	−53·1 (4)
C(4) -C(5)—O(5)—C(1)	64·1 (3)
C(5)—O(5)—C(1)—C(2)	−67·7 (3)

Pendant atoms

C(5)—O(5)—C(1)—O(1)	173·9 (3)
O(5)—C(1)—C(2)—O(2)	175·4 (2)
C(1)—C(2)—C(3)—O(3)	−172·3 (3)
C(2) -C(3) -C(4)—O(4)	168·2 (3)
C(3)—C(4)—C(5)—C(6)	−172·8 (3)
O(5) ·C(5)—C(6)—O(6)	−64·1 (4)

Table 2 (cont.)

C(3)–C(2)–C(1)–O(1)	176·0 (3)
C(4)–C(3)–C(2)–O(2)	−171·5 (3)
C(5)–C(4)–C(3)–O(3)	168·9 (3)
O(5)–C(5)–C(4)–O(4)	−170·6 (3)
C(1)–O(5)–C(5)–C(6)	−172·7 (3)
C(4)–C(5)–C(6)–O(6)	56·1 (4)

Methyl group

O(5)–C(1)–O(1)–C(1M)	−76·7 (3)

Acetyl groups

C(1)–C(2)–O(2)–C(2A)	108·7 (4)
C(2)–O(2)–C(2A)–O(2A)	−5·2 (6)
C(2)–O(2)–C(2A)–C(2M)	174·2 (3)
C(2)–C(3)–O(3)–C(3A)	−122·6 (3)
C(3)–O(3)–C(3A)–O(3A)	−3·0 (7)
C(3)–O(3)–C(3A)–C(3M)	176·7 (3)
C(3)–C(4)–O(4)–C(4A)	127·5 (4)
C(4)–O(4)–C(4A)–O(4A)	2·4 (6)
C(4)–O(4)–C(4A)–C(4M)	−178·4 (4)
C(5)–C(6)–O(6)–C(6A)	−153·8 (3)
C(6)–O(6)–C(6A)–O(6A)	−2·0 (6)
C(6)–O(6)–C(6A)–C(6M)	176·9 (4)

the ring are slightly longer for TMG, with the exception of C(1)–O(1).

Remarkable are the very small C(3)–C(2)–O(2) and C(5)–C(6)–O(6) bond angles of 105·5 and 108·6°, respectively, which deviate from the established average values by 5·3 and 3·2°, but have corresponding values in either the primed or unprimed residue of AC.

The bond lengths, angles, and torsion angles of the four acetyl groups of TMG vary little. The acetyl groups lie in a plane with the adjacent O and C atoms. The cis positions of O(2A), O(3A) and O(4A) relative to the corresponding ring H atoms are clearly revealed in Fig. 1.

Table 3. Short packing contacts (Å)

H(4)···H(13^i)	2·27		O(3A)···C(4M^{iii})	3·405
H(12)···H(3^i)	2·46		C(1M)···O(3A^i)	3·476
O(4A)···H(33^{ii})	2·47		C(4A)···O(2A^{ii})	3·482
O(1)···H(5^i)	2·57		C(3M)···O(2A^{ii})	3·485
O(5)···H(1^i)	2·60		O(4A)···O(2A^{ii})	3·355
C(1M)···H(3^i)	2·83		O(6)···O(2^i)	3·545
C(1)···H(1^i)	3·07		O(6)···O(1^i)	3·574
O(4A)···C(2A^{ii})	3·311		C(6M)···C(1M^i)	3·629
O(4A)···C(2M^{ii})	3·344		C(6)···C(3M^{iv})	3·634
O(4A)···C(3M^{iii})	3·393		C(6A)···C(2M^i)	3·683

Symmetry code

(i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$

(iii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$ (iv) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$

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