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The Molecular and Crystal Structure of Tetra-O-Acetyl-α-D-Glucopyranosyl Bromide

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Abstrct

The crystal structure of tetra-0-acetyl-α-D-glucopyranosyl bromide as a model compound of cellulose triacetate was determined from three-dimensional intensities obtained with Cuk$_\alpha$ X-ray radiation. The plate-shaped crystals are orthorhombic, space group $P2_12_12_1$, with four molecules in a unit cell of dimensions a = 14.245(2), b = 23.239(1), c = 5.632(2)Å. The final R index is 0.088 and the e. s. d. 's of the cordinates of C and O atoms are 0.017 Å. Bond lengths and angles is the glucopyranosyl ring are very close to those of similar compounds already reported. The ring has the normal Sachse trans configuration with la2e3e4e5e($^4C_1$). The orientations of the coplanar acetyl groups are in good agreement with those predicted by the dichroism of the infrared spectra of C=O stretching.

1. Introduction

Tetra-O-acetyl-α-D-glucopyranosyl bromide, a compound widely known as "acetobromoglucose", is reactive and usually used as a intermediate in the conversion reaction of α-D to β-D anomers.

The information from a model compound are generally of great importance in the study of the molecular crystal structure of crystalline polymers. Cellobiose octaacetate and glucose pentaacetate are applicable to model compounds for cellulose triacetate. Tetra-O-acetyl-α-D-glucopyranosyl bromide can be regarded as a isomorphous replacing compound of penta-O-acetyl α-D-glucose, because both cell parameters are similar within the limits of experimental error; the former is a = 14.245, b = 23.239, c = 5.632 A and the latter is a = 14.713, b = 23.690, c = 5.591 A. From the model compounds the internal rotation angle between the pyranose rings bridged with oxygen atom, bond angle of bridge oxygen and the orientation of the acetyl groups with respect to the pyranose ring are highly informative to explain the molecular structure of cellulose triacetatee. The purpose of this work is to compare the structural details of tetra-O-acetyl-α-D-glucopyranosyl bromide with some known carbohydrate structures, and with the structure of cellulose triacetate deduced from x-ray study.

2. Experimental

Tetra-O-acetyl-α-D-glucopyranosyl bromide was prepared by Lemieux's method[1].

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The single crystals were recrystallized from iso-propyl ether solution. They are colourless plates but were hygroscopic; m. p. 88–89°C. Crystals with dimensions of $0.40 \times 0.03 \times 0.21$ and $0.35 \times 0.04 \times 0.23$ mm, which are coated by a commercial quick set adhesive "Aron Alpha" were used for collecting x-ray intensity data. Oscillation and Weissenberg photographs were taken for a preliminary x-ray investigation of the crystals. The cell dimensions were obtained with the use of a diffractometer and CuK_{α} radiation. The Weissenberg photographs showed absences of $h00$, $0k0$ and $00l$ for h, k and l odd respectively. The density was measured by floating the crystals in a water-saturated solution of zinc chloride mixture.

The three-dimensional intensity data were collected on a Rigaku Denki automatic four-circle diffractometer, using Ni-filtered Cuk_{α} radiation operated in the ω-2θ scanning mode. The 1451 independent reflections within a sphere of radius $2\sin\theta/\lambda = 1.123$ ($2\theta < 120°$) were measured, of which 1252 reflections had intensities significantly above the background. A scaling on intensity was made for the crystals and the usual Lorentz and polarization corrections were applied, but no corrections were made for absorption or extinction.

3. Crystal Data

$C_{14}H_{19}O_9Br$, F. W. 411.24
Orthorhombic
$a = 14.245 \pm 0.002$, $b = 23.239 \pm 0.001$, $c = 5.632 \pm 0.002\mathrm{A}$, $U = 1864.4\mathrm{A}^3$
$D_{-m} = 1.44\ \mathrm{cm}^{-3}$, $D_x = 1.465\ \mathrm{g\ cm}^{-3}$, $Z = 4$
Systematic absences,
h00 with $h = 2n+1$, 0k0 with $k = 2n+1$, 001 with $1 = 2n+1$.
Space group $p2^1 2^1 2^1$.

4. Determination of the Structure

The heavy atom vectors, Br-Br, were identified on the threedimensional Pattersonn function. The heavy atom Fourier map obtained by using Br phase reveals a part of the structure. with the aid of the minimum function, which was synthesized on the basis of the coordinates of the Br atom, several sites were selected as possible locations of atoms. After several cyclic procedures of least-squares refinement followed by the synthesis of an electron density map, were carried out, the approximate locations of all the C and O atoms were established, the R index being at 0.327 at this stage. Further refinement by the block-diagonal least-square method gave $R = 0.160$ after three cycles with anisotropic thermal factors Br, C and O atoms. The final R index was 0.088, with all hydrogen atoms included. The final parameters are given in Table 1 and 2. The atomic scattering factors for Br, C, O and H atoms were taken from the International Table for x-ray Crystallography[2]. The anomalous dispersion terms were ignored.

Table 1. Final fractional atomic coordinates and thermal parameters of non-hydrogen atoms. Temparature facter=exp $[-(B_{11}h^2+B_{22}K^2+B_{33}1^2+B_{12}hK+B_{23}K1)]$. The estimated standard deviations are in parentheses.

Atom	x	y	z	B(11)	B(22)	B(33)	B(12)	B(13)	B(23)
Br	0.1188(27)	0.2294(18)	0.1019(19)	0.0866(11)	0.0028(0)	0.0085(1)	0.0058(4)	−0.0063(7)	0.0034(1)
C (1)	0.3902(175)	0.1738(124)	0.0975(131)	0.0468(69)	0.0020(27)	0.0052(7)	0.0041(26)	0.0033(50)	0.0022(7)
C (2)	0.2917(184)	0.1115(142)	0.0789(117)	0.0604(87)	0.0028(3)	0.0028(6)	−0.0013(30)	0.0094(41)	0.0009(7)
C (3)	0.1551(158)	0.0881(112)	0.1636(114)	0.0419(64)	0.0015(2)	0.0042(6)	−0.0074(23)	−0.0019(40)	−0.0004(6)
C (4)	0.3192(171)	0.0969(126)	0.2542(117)	0.0519(75)	0.0021(2)	0.0032(5)	−0.0066(25)	−0.0004(41)	0.0016(6)
C (5)	0.3880(184)	0.1591(120)	0.2605(116)	0.0550(73)	0.0017(2)	0.0038(6)	0.0003(27)	−0.0003(46)	0.0003(6)
C (6)	0.5784(232)	0.1646(129)	0.3433(154)	0.0967(118)	0.0015(2)	0.0077(9)	−0.0018(32)	−0.0256(66)	−0.0006(8)
O (2)	0.1173(130)	0.1120(108)	0.0043(81)	0.0531(51)	0.0043(3)	0.0030(4)	−0.0039(26)	−0.0030(31)	−0.0002(6)
O (3)	0.1440(107)	0.0277(76)	0.1528(83)	0.0386(41)	0.0017(1)	0.0058(4)	−0.0000(16)	0.0012(30)	−0.0007(4)
O (4)	0.1350(102)	0.0871(82)	0.3288(78)	0.0309(37)	0.0023(1)	0.0043(4)	0.0011(16)	−0.0001(27)	0.0014(4)
O (5)	0.5214(107)	0.1745(89)	0.1765(82)	0.0503(47)	0.0023(2)	0.0039(4)	−0.0031(17)	0.0035(26)	0.0009(5)
O (6)	0.6529(152)	0.2225(86)	0.3442(95)	0.0941(74)	0.0016(1)	0.0067(5)	−0.0026(24)	−0.0125(43)	−0.0013(5)
C (21)	0.1995(233)	0.1095(179)	−0.0878(147)	0.0822(123)	0.0044(4)	0.0046(7)	−0.0095(44)	−0.0073(60)	−0.0007(10)
C (22)	−0.0059(211)	0.1087(238)	−0.1560(160)	0.0589(96)	0.0077(8)	0.0044(8)	−0.0008(51)	−0.0010(53)	0.0015(14)
O (21)	0.4064(131)	0.1081(188)	−0.1025(114)	0.0356(53)	0.0118(7)	0.0057(6)	−0.0027(38)	0.0100(40)	−0.0011(12)
C (31)	−0.0851(185)	0.0030(130)	0.1567(113)	0.0614(81)	0.0020(2)	0.0035(5)	0.0050(30)	−0.0095(43)	−0.0011(7)
C (32)	−0.0774(253)	−0.0598(151)	0.1550(148)	0.1033(130)	0.0025(3)	0.0057(8)	−0.0031(41)	0.0141(68)	−0.0014(9)
O (31)	−0.2603(118)	0.0315(103)	0.1589(139)	0.0397(49)	0.0026(2)	0.0154(10)	0.0053(20)	0.0048(43)	−0.0027(9)
C (41)	0.2149(190)	0.0507(144)	0.4037(125)	0.0648(92)	0.0028(3)	0.0036(6)	−0.0058(31)	−0.0012(46)	0.0022(8)
C (42)	0.0026(171)	0.0446(188)	0.4676(155)	0.0357(69)	0.0048(5)	0.0060(9)	0.0025(33)	0.0070(45)	0.0061(12)
O (41)	0.4131(136)	0.0342(133)	0.4085(131)	0.0520(58)	0.0054(3)	0.0118(9)	0.0057(29)	0.0021(40)	0.0077(10)
C (61)	0.8774(189)	0.2362(158)	0.3987(146)	0.0536(74)	0.0031(3)	0.0065(8)	0.0012(33)	0.0095(53)	−0.0044(10)
C (62)	0.8959(237)	0.2965(149)	0.3889(208)	0.0920(111)	0.0020(3)	0.0148(15)	−0.0069(37)	−0.0314(90)	−0.0041(12)
O (61)	0.9230(152)	0.2001(118)	0.4471(133)	0.0761(70)	0.0034(3)	0.0116(9)	−0.0010(27)	−0.0205(52)	−0.0014(9)

Table 2. Hydrogen atom parameters and their estimated standard deviations.

Atom		x	y	z
H	(1)	0 650(143)	0.184(106)	0.036(109)
H	(2)	0.432(130)	0.077(108)	0.052(110)
H	(3)	−0.009(127)	0.113(109)	0.183(115)
H	(4)	0.494(134)	0.074(112)	0.264(116)
H	(5)	0.260(132)	0.186(111)	0.290(112)
H	(62)	0.743(128)	0.146(110)	0.316(114)
H	(61)	0.606(134)	0.131(106)	0.339(111)
H	(221)	−0.160(132)	0.099(104)	−0.121(110)
H	(222)	−0.061(132)	0.168(108)	−0.194(110)
H	(223)	−0.000(124)	0.041(110)	−0.157(116)
H	(321)	−0.224(125)	−0.112(107)	0.122(113)
H	(322)	0.011(125)	−0.068(107)	0.121(113)
H	(323)	−0.107(139)	−0.071(107)	0.224(108)
H	(421)	−0.131(132)	0.016(105)	0.428(106)
H	(422)	−0.103(141)	0.078(105)	0.488(108)
H	(423)	0.070(131)	0.008(106)	0.499(110)
H	(621)	0.746(126)	0.324(109)	0.420(113)
H	(622)	1.026(124)	0.311(108)	0.419(114)
H	(623)	0.988(129)	0.327(110)	0.321(115)

5. Description of the Structure and Discussion

An ORTEP drawing (Johnson, 1965) along the c-axis showing the thermal ellipsoids of variation with 50% probability surfaces for all nonhydrogen atoms is

Table 3. Least-squares planes in tetra-O-acetyl-α-D-glucopyranosyl bromide.
Equation of plane; AX+BY+CZ+D=0, where X, Y, Z are in A.

		Atoms in plane	Distance from best plane		Given constant
Pyranose ring	1	C(1)		−0.041	A=−0.9539
		C(2)		0.047	B= 0.2921
		C(4)		−0.029	C= 0.0684
		C(5)		0.029	D= 0.7800
			O(3)	0.704	
			O(5)	−0.663	
			Br	1.798	
			O(2)	0.914	
			O(3)	0.343	
			O(4)	0.966	
			C(6)	−0.875	
			O(6)	−0.881	
Acetates	2	O(2)		0.000	A=−0.0181
		C(21)		−0.002	B=−0.9990
		C(22)		0.000	C= 0.0389
		O(21)		0.000	D= 2.6107
	3	O(3)		0.002	A=−0.0381
		C(31)		−0.008	B= 0.0079
		C(32)		0.002	C=−0.9992
		O(31)		0.003	D= 2.2037
	4	O(4)		−0.004	A=−0.2727
		C(41)		0.018	B=−0.8153
		C(42)		−0.005	C=−0.5106
		O(41)		−0.008	D= 4.2466
	5	O(6)		−0.006	A= 0.6301
		C(61)		0.034	B=−0.2304
		C(62)		−0.012	C=−0.7415
		O(61)		−0.014	D= 2.5044

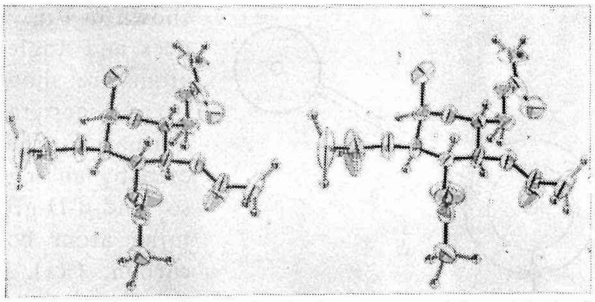


Fig. 1. A stereoscopic view of tetra-O-acetyl-α-D-glucopyranosyl bromide looking down the c-axis

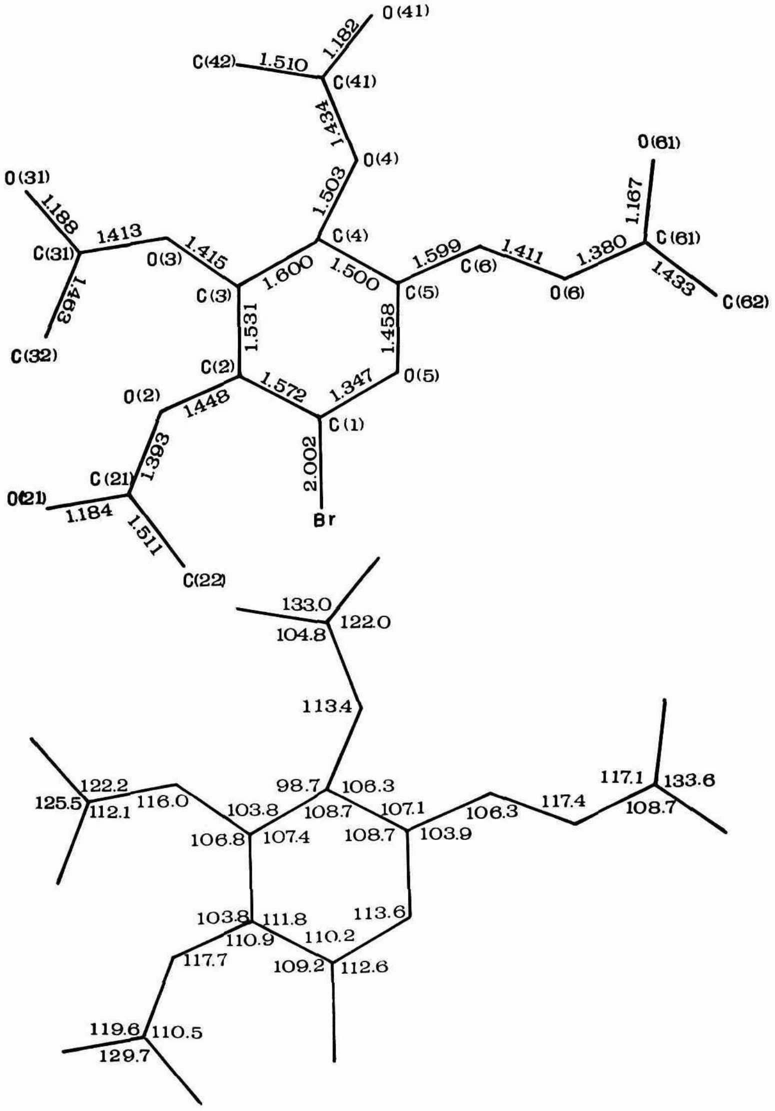


Fig. 2. Bond distances and angles of tetra-O-acetyl-α-D-glucopyranosyl bromide.

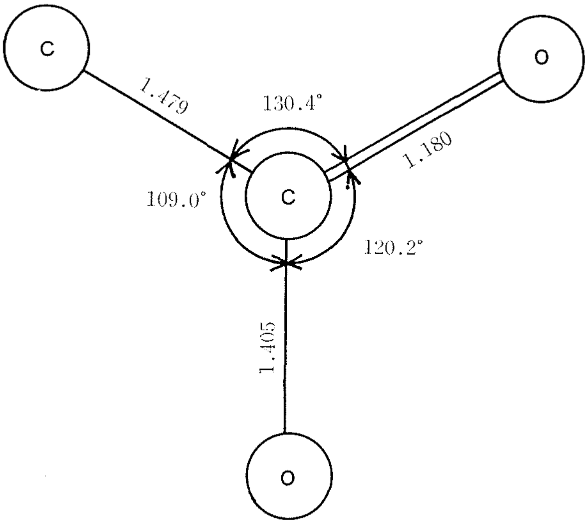


Fig. 3. The average bond distances and angles for the acetate groups.

shown in Fig. 1. The bond distances and angles of nonhydrogen atoms are shown in Fig. 2.

Glucopyranose ring has the normal $^4C_1$ conformation as expected by analogy with α-D-glucose[3] and β-D-glucose[4,5]. The bromine atom bonded to the ring carbon, C(1), occupies the axial position, whereas all acetate groups occupy the equatorial position and are planar within the experimental error. The Br-C(1) bond length is slightly longer than the average in parafinic, olefinic and aromatic bromides. However, this is similar to the average in acetyl bromide by electron diffraction[6]. The ring carbon-oxygen bonds are unequal: C(1)-O(5) = 1.347 A(σ = 0.015 A), C(5)-O(5) = 1.458 A(σ = 0.014 A). According to Arnott and Scott[7], the average valeus for C(1)-O(5) and C(5)-O(5) are 1.429 and 1.436 A respectively, thus the discrepancies here are much more pronounced. Similar observations for the discrepancies have been reported in previous investigations of sugars [8,9]. The mean C-C bond length is 1.550 A($\langle\sigma\rangle$ = 0.016 A), and that of the C-O bond is 1.444 A($\langle\sigma\rangle$ = 0.015 A). The average bond lengths and bond angles for the acetate groups are shown in Fig. 3.

The ring C-H bond lengths, except C(1)-H(1) bond (1.72 A, λ = 0.11 A) lie in the range of 1.03-1.18 A and those of the methyl groups are in the range of 0.72-1.55 A.

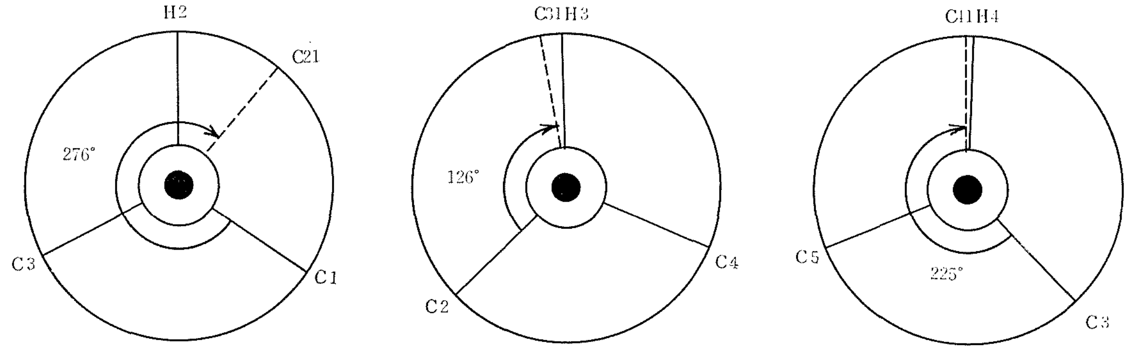
The mean interior and exterior ring angles are 110.0°($\langle\sigma\rangle$ = 0.9°) and 106.3°($\langle\sigma\rangle$ = 0.8°), respectively. The mean angle at the oxygen atom linked to the acetate group is 116.1°($\langle\sigma\rangle$ = 0.9°). The angles Me-C(Ac)-O for all acetate groups are 109.0°($\langle\sigma\rangle$ = 1.1°), much less than 120° as one might expect. Similar distortions of this bond angle were also observed in 3′-O-acetyl-4-thiothymidine[10], and β-D, 1–4 xylobiose hexaacetate[9].

Least-square plane of the glucopyranose ring is formed by the four carbon atoms: C(1), C(2), C(4), C(5). The deviation of those atoms from the plane is within 0.047 A (Table 3). Acetyl groups should be planar. Actually the deviations of their atoms from their least-square planes are very small without the primary acetyl group attached to C(6) of the glucose unit (Table 3). Dihedral angles between the planes of the glucopyranose ring and acetyl groups are listed in Table 4.

Table 4. Dihedral angles between the planes

Between the planes	Dihedral angles (deg.)
1 and 2	105.7
1 and 3	91.6
1 and 4	90.7
1 and 5	135.9
2 and 3	92.6
2 and 4	36.9
2 and 5	79.0
3 and 4	59.0
3 and 5	44.3
4 and 5	66.7

The planes of the secondary acetyl groups attached to C(2), C(3) and C(4) of the glucose unite are approximately pe-



O2→C2 O3→C3 O4→C4

Fig. 4. Orientation of acetate groups (Newman projection) at O(2), O(3) and O(4) positions in tetre-O-acetyl-α-D-glucopyranosyl bromide.

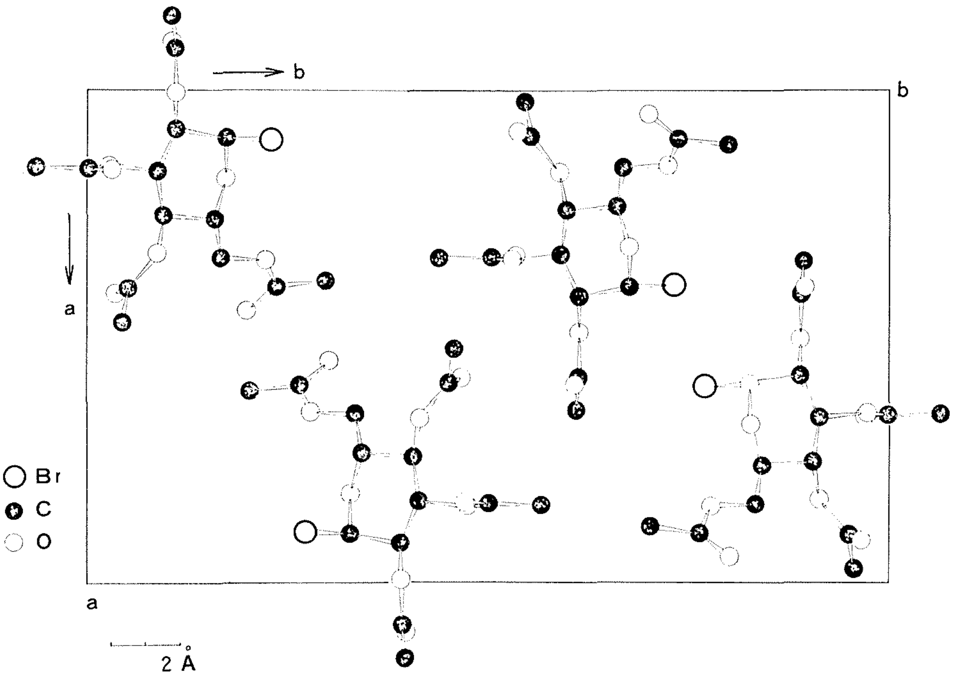


Fig. 5. The crystal structure viewed along the c-axis.

rpendicular to the plane of the glucose ring. However that of C(6) position is rather at parallel angle. These results coincide with the dichroism of the stretching-vibration component of the carbonyl groups[11]. Furthermore, by studying oriented cellulose triacetate, the main C=O stretching shows that, by a polarized infrared radiation, the component of the secondary acetyl group actually lies approximately perpendicular to the fiber axis and that of the primary one is parallel to it[12].

The orientation of the secondary acetate group with respect to the glncopyra-

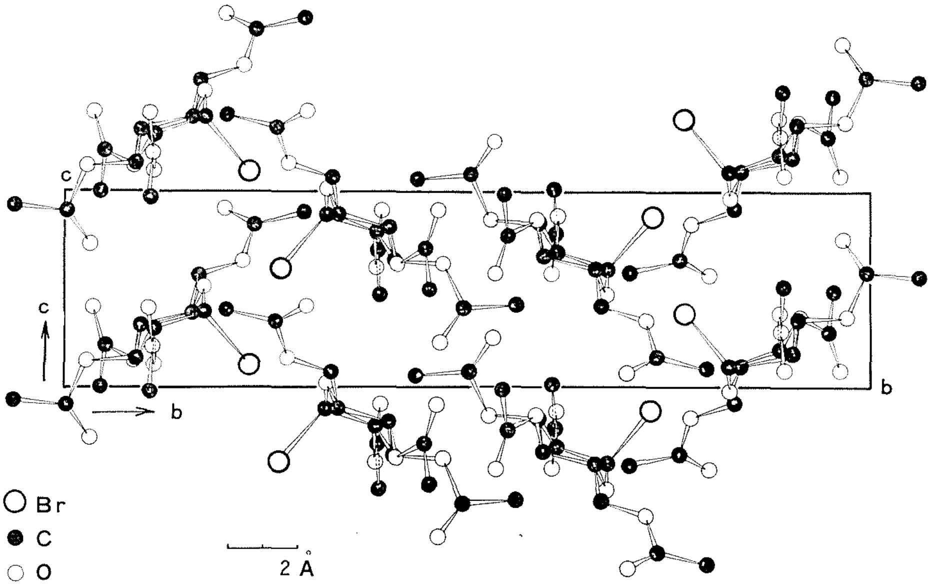


Fig. 6. The crystal structure viewed along the a-axis

Table 5. Distances, angles and their standard deviations of van der Waals contacts between carbonyl oxygen atom and methyl group or brome atom and the glucose ring hydrogen atom.

The asymmetric units are denoted as follows:

Coordinates			Notation	Coordinates			Nortation
x	y	z	i	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$	iv
$1+x$	y	z	ii	$\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$	v
$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$	iii	$-x$	$-y$	$-\frac{1}{2}+z$	vi

O(Carbonyl)	H(Me)	C(Me)	d(O ··· C)	d(O ··· H)	∠(O ··· H-C)	∠(C=O ··· H)
O(21, i)	H(C 221, ii)	C(22, ii)	3.396(20)Å	2.416(111)Å	151.7(8.6)°	175.1(2.8)°
O(31, i)	H(C 423, vi)	C(42, vi)	3.524(21)	3.014(111)	117.7(7.2)	106.7(2.3)
O(41, i)	H(C 421, ii)	C(42, ii)	3.434(20)	2.610(108)	127.7(7.0)	169.7(2.5)
O(41, i)	H(C 223, v)	C(22, v)	3.486(21)	2.057(117)	148.9(7.2)	118.5(3.4)
C(61, i)	H(C 621, iv)	C(62, iv)	3.542(25)	2.685(114)	130.5(7.5)	144.6(2.6)
Br	**H**	**C**	**d(Br ··· C)**	**d(Br ··· H)**	**∠(Br ··· H-C)**	**∠(C-Br ··· H)**
Br(i)	H(C1, iii)	C (1, iii)	3.844(13)Å	2.806(110)Å	113.9(5.0)°	112.8(2.2)°

nose ring is shown in the Newman projection of Fig. 4. In the acetyl group attached to C(2) of the glucose unit, the carbonyl carbon, C(21)-O(2) bond makes a dihedral angle of 40° with respect to C(2)-H(2) bond. On the other hand, C(31)-O(3) and C(41)-O(4) bonds are approximately in a coplanar position with C(3)-H(3) and C(4)-H(4), respectively.

There is, of course, no hydrogen bonding in the crystal structure (Fig. 5 and 6). However there are several short van der walls contacts between the carbonyl oxygens and the methyl hydrogens, bromine atoms and the glucopyranose ring hydrogen atoms: H(1) (Table 5). These van der walls contacts dominate the intermolecular packing in this crystal.

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