C2	1.00	−0.014 (02)	−0.175 (02)	0.4367 (05)	4.1 (7)
C5	1.00	0.172 (02)	0.202 (02)	0.3969 (05)	4.4 (7)
C6	1.00	0.257 (02)	0.379 (02)	0.4185 (06)	7.1 (9)
C9	1.00	0.3135 (14)	0.3121 (14)	0.3082 (05)	4.6 (6)
C10	1.00	0.461 (02)	0.326 (02)	0.2956 (05)	7.6 (8)
C11	1.00	0.5649 (14)	0.435 (02)	0.2581 (05)	8.1 (9)
C12	1.00	0.522 (02)	0.5394 (14)	0.2344 (05)	6.8 (9)
C13	1.00	0.376 (02)	0.529 (02)	0.2443 (06)	8 (1)
C14	1.00	0.2692 (14)	0.414 (02)	0.2818 (05)	6.7 (7)
F14	0.15 (1)	−0.092 (10)	−0.362 (08)	0.361 (02)	9.0
F15	0.15 (1)	−0.069 (10)	−0.458 (12)	0.436 (03)	9.0
F16	0.15 (1)	−0.266 (07)	−0.414 (11)	0.424 (04)	9.0

Table 2. *Selected geometric parameters* (Å, °)

F11—C1	1.37 (2)	N8—C5	1.35 (2)
F12—C1	1.25 (3)	N8—C9	1.45 (1)
F13—C1	1.29 (2)	C1—C2	1.54 (2)
F61—C6	1.31 (2)	C5—C6	1.55 (2)
F62—C6	1.32 (2)	C9—C10	1.37 (2)
F63—C6	1.35 (2)	C9—C14	1.40 (2)
N3—N4	1.40 (1)	C10—C11	1.38 (2)
N3—C2	1.29 (2)	C11—C12	1.38 (2)
N4—C5	1.27 (1)	C12—C13	1.36 (3)
N7—C2	1.33 (1)	C13—C14	1.40 (2)
N4—N3—C2	110.1 (9)	N4—C5—N8	127 (1)
N3—N4—C5	113 (1)	N4—C5—C6	118 (1)
C5—N8—C9	128.3 (9)	N8—C5—C6	115 (1)
F11—C1—F12	104 (2)	F61—C6—F62	110 (1)
F11—C1—F13	104 (1)	F61—C6—F63	109 (1)
F11—C1—C2	106 (1)	F61—C6—C5	113 (2)
F12—C1—F13	113 (2)	F62—C6—F63	106 (2)
F12—C1—C2	113 (1)	F62—C6—C5	111 (1)
F13—C1—C2	115 (1)	F63—C6—C5	107 (1)
C2—C1—F14	116 (3)	N8—C9—C10	119 (1)
C2—C1—F15	112 (3)	N8—C9—C14	122 (1)
C2—C1—F16	112 (5)	C10—C9—C14	118 (1)
F14—C1—F15	102 (6)	C9—C10—C11	122 (2)
F14—C1—F16	110 (6)	C10—C11—C12	118 (2)
F15—C1—F16	104 (6)	C11—C12—C13	122 (1)
N3—C2—N7	132 (1)	C12—C13—C14	119 (2)
N3—C2—C1	113 (1)	C9—C14—C13	120 (1)
N7—C2—C1	115 (1)		

The structure was solved using direct methods (*MITHRIL*; Gilmore, 1984) in the space group $P3_2$ (No. 145) which requires two molecules in the asymmetric unit; the two molecules found were clearly related by a twofold axis at $(\frac{2}{3},y,\frac{1}{2})$. Space group $P3_2$ has equivalent 3_2 axes at $(\frac{2}{3},\frac{1}{3},z)$ and $(0,0,z)$. A change to space group $P3_221$ (No. 154) was implied, but its 3_2 axes were no longer equivalent; the added twofold axes pass through $(0,0,z)$. The solution of the present structure in $P3_221$ was achieved in two steps. First, x and y coordinates were reduced by $\frac{2}{3}$ and $\frac{1}{3}$, respectively, moving the known twofold axis to $(0,y-\frac{1}{3},\frac{1}{2})$, placing the molecules around the 3_2 axis at $(0,0,z)$, but requiring a z translation of $-\frac{1}{6}$ to bring the molecules to valid equivalent positions in $P3_221$. The known twofold axis was now at $(0,y-\frac{1}{3},\frac{1}{3})$, which may be redesignated as $(0,x,\frac{1}{3})$ which is acceptable in $P3_221$ and requires only one molecule per asymmetric unit. Data collection and cell refinement: CAD-4 software. Data reduction: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1985). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *CIF* (Hall, Allen & Brown, 1991).

The CAD-4 diffractometer was funded by the SERC which is also thanked for funding the Chemical Databank Services used for cystallographic literature searches.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl-α-D-galacturonic Acid Methyl Ester

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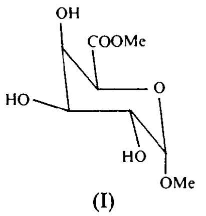
Abstract

The structure of methyl methyl-α-D-galacturonoate monohydrate, $C_8H_{14}O_7.H_2O$, has been redetermined. The sugar ring has the expected $^4C_1$ conformation. The orientation of the methoxy group is *gauche-trans* and

the methyl ester group is nearly planar and lies equatorial to the ring.

Comment

D-Galacturonic acid is widely distributed among homo- and heteropolysaccharides and may occur either as free acid or the methyl ester. For example, this acid is present in pectins (Aspinall, 1970), in certain gums and mucilages (Smith & Montgomery, 1959), and in capsular polysaccharides of the genus *Klebsiella* (Nimmich, 1968). The physical and biological properties of these polymers are greatly influenced by conformational parameters and interactions with divalent cations, especially Ca^{2+} (Gould, Gould, Rees & Scott, 1975). We now report the X-ray crystal and molecular structure redetermination of methyl-α-D-galacturonic acid methyl ester, (I), as part of a program involving structural studies of sugar carboxylate anions.



(I)

The title compound was synthesized as described by Matsuhiro, Zanlungo & Dutton (1981). In an earlier short communication (Hjortås, Larsen, Mo & Thanomkul, 1974) the atomic coordinates were not reported. A fragment search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) found five related structures: calcium sodium α-D-galacturonate hexahydrate (Hjortås, Larsen & Thanomkul, 1974; Gould, Gould, Rees & Scott, 1975; Thanomkul, Hjortås & Sørum, 1976); strontium sodium α-D-galacturonate hexahydrate (Gould, Gould, Rees & Scott, 1975); tetrakis(tryptophan methyl ester) α-galacturonic acid β-galacturonic acid trihydrochoride dihydrate (Gould, Taylor, Varvill & Walkinshaw, 1986); methyl 1,2,3,4-tetra-*O*-acetyl-β-D-galactopyranuronate (Nimgirawath, James & Stevens, 1975); and strontium 4-*O*-(4-deoxy-β-L-*threo*-hex-4-enosyl)-α-D-galacturonate 4.5-hydrate (Gould, Gould, Rees & Wight, 1976). Bond lengths and valence angles in the present study agree well with those reported.

The orientation of the methoxy group is *gauche-trans*; the O5—C1—O1—C8 and C2—C1—O1—C8 torsion angles are +64.5 (2) and −173.9 (2)°, respectively. The pyranose ring has the $^4C_1$ chair conformation with very little distortion from ideality. The Cremer & Pople (1975) ring puckering parameters are $Q = 0.570(2)$ Å, $\varphi_2 = -6.6(6)°$ and $\theta_2 = 2.1(2)°$. The methyl ester group is nearly planar and lies equatorial to the ring, with O5—C5—C6—O6 and O5—C5—C6—O7 torsion angles of 2.4 (3) and −176.9 (1)°, respectively. The crystal packing is governed by a complex three-dimensional pattern of hydrogen bonds (Fig. 2 and Table 3). The molecules are stacked along the short *a* axis and are connected by H—O3···O5, H—O3···O6 and H1—O1*W*···O3 hydrogen bonds. Columns of these stacks are held together through the O1*W* water molecule which, by donating a hydrogen bond to the O2 hydroxyl group and accepting an O4—H bond, constitutes an important cohesive factor along the *b* axis; further stabilization derives from the O2 hydroxyl group which donates a hydrogen bond to a symmetry related O4 hydroxyl group. The hydrophobic interactions involving the methoxy and methyl ester groups are governed by van der Waals forces.

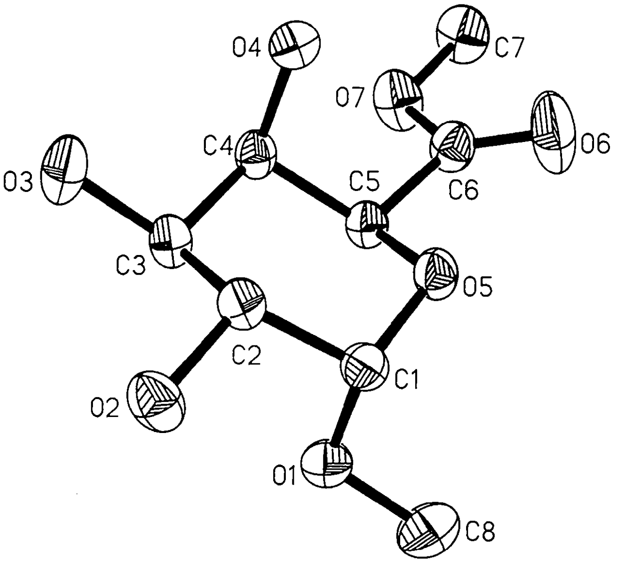


Fig. 1. A view of the molecule showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels.

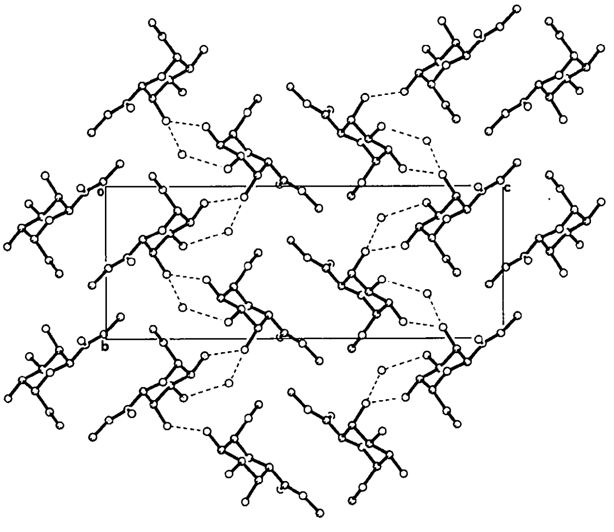


Fig. 2. A view of the crystal packing along the *a* axis.

Experimental

Crystal data

$C_8H_{14}O_7.H_2O$
$M_r = 240.21$
Orthorhombic
$P2_12_12_1$
$a = 6.496$ (1) Å
$b = 7.993$ (1) Å
$c = 20.831$ (3) Å
$V = 1081.5$ (3) Å^3
$Z = 4$
$D_x = 1.475$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 29 reflections
$\theta = 14.0–17.0°$
$\mu = 0.1254$ mm^{-1}
$T = 295$ K
Prism
0.8 × 0.4 × 0.2 mm
Colourless
Crystal source: ethyl acetate

Data collection

Profile data from ω scans
Absorption correction: none
2882 measured reflections
2746 independent reflections
2239 observed reflections [$F > 4\sigma(F_o)$]
$R_{\rm int} = 0.0153$

$\theta_{\rm max} = 35°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 33$
3 standard reflections monitored every 97 reflections intensity variation: 8.0%

Refinement

Refinement on F
$R = 0.0443$
$wR = 0.0610$
$S = 1.12$
2239 reflections
210 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.0017F_o^2]$
$(\Delta/\sigma)_{\rm max} = 0.123$

$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A and 2.3.1 for C and O and Table 2.2C for H)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	−0.0816 (3)	−0.3400 (2)	0.31994 (7)	0.0271 (4)
C2	0.1106 (3)	−0.2665 (2)	0.28853 (7)	0.0267 (4)
C3	0.2542 (2)	−0.1944 (2)	0.33898 (7)	0.0278 (4)
C4	0.1374 (2)	−0.0709 (2)	0.38205 (7)	0.0255 (3)
C5	−0.0545 (3)	−0.1554 (2)	0.40831 (7)	0.0260 (3)
C6	−0.1886 (3)	−0.0371 (2)	0.44721 (8)	0.0317 (4)
C7	−0.1885 (4)	0.1465 (3)	0.5357 (1)	0.0442 (6)
C8	−0.1942 (4)	−0.5667 (3)	0.3826 (1)	0.0485 (7)
O1	−0.0227 (2)	−0.4783 (2)	0.35647 (6)	0.0333 (4)
O2	0.2192 (2)	−0.3891 (2)	0.25242 (6)	0.0351 (4)
O3	0.4172 (2)	−0.1115 (2)	0.30653 (7)	0.0392 (4)
O4	0.0710 (2)	0.0727 (2)	0.34777 (6)	0.0335 (4)
O5	−0.1819 (2)	−0.2163 (2)	0.35785 (5)	0.0285 (3)
O6	−0.3658 (3)	−0.0098 (3)	0.4369 (1)	0.0658 (7)
O7	−0.0804 (2)	0.0327 (2)	0.49369 (6)	0.0416 (4)
O1*W*	0.3581 (3)	0.2932 (2)	0.30783 (7)	0.0419 (4)

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.527 (2)	C4—O4	1.419 (2)
C1—O1	1.395 (2)	C5—C6	1.520 (2)
C1—O5	1.423 (2)	C5—O5	1.423 (2)
C2—C3	1.519 (2)	C6—O6	1.191 (3)
C2—O2	1.423 (2)	C6—O7	1.320 (2)
C3—C4	1.534 (2)	C7—O7	1.444 (3)
C3—O3	1.420 (2)	C8—O1	1.427 (3)
C4—C5	1.520 (2)		
O1—C1—O5	111.9 (1)	C5—C4—O4	106.9 (1)
C2—C1—O5	110.2 (1)	C4—C5—O5	111.3 (1)
C2—C1—O1	108.3 (1)	C4—C5—C6	112.7 (1)
C1—C2—O2	111.5 (1)	C6—C5—O5	105.9 (1)
C1—C2—C3	110.6 (1)	C5—C6—O7	110.4 (2)
C3—C2—O2	108.8 (1)	C5—C6—O6	124.9 (2)
C2—C3—O3	107.8 (1)	O6—C6—O7	124.7 (2)
C2—C3—C4	110.2 (1)	C1—O1—C8	112.7 (2)
C4—C3—O3	110.3 (1)	C1—O5—C5	112.4 (1)
C3—C4—O4	112.1 (1)	C6—O7—C7	116.8 (2)
C3—C4—C5	109.3 (1)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	A	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4	H4O	O1$W^{\rm i}$	0.81 (3)	2.698 (2)	1.94 (4)	155 (4)
O2	H2O	O4$^{\rm ii}$	1.03 (3)	2.829 (2)	1.84 (3)	159 (3)
O1*W*	H1*W*	O3$^{\rm iii}$	0.75 (2)	2.896 (2)	2.32 (3)	134 (3)
O1*W*	H2*W*	O2$^{\rm iv}$	0.97 (3)	2.931 (2)	1.99 (4)	162 (3)
O3	H3O	O5$^{\rm v}$	1.08 (4)	2.937 (2)	2.05 (5)	137 (4)
O3	H3O	O6$^{\rm v}$	1.08 (4)	3.166 (3)	2.24 (5)	143 (4)

Symmetry codes: (i) x, y, z; (ii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $x, y+1, z$; (v) $x+1, y, z$.

The intensities were corrected for crystal decay. Lorentz and polarization corrections were applied. The structure was solved by direct methods and refined by full-matrix least-squares methods. At an intermediate stage in the refinement a difference map revealed maxima consistent with the positions of the H atoms, which were included in the subsequent cycles of refinement. Data collection: *R3m/V Software* (Siemens, 1990). Cell refinement: *R3m/V Software*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *PARST* (Nardelli, 1983). Molecular geometry calculations: *PARST*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1060). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Chloro-4-methoxy-6-methyl-1,3,5-triazine

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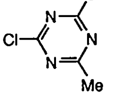
Abstract

Molecules of the title compound, $C_5H_6ClN_3O$, lie on crystallographic mirror planes. Within these planes molecules are linked into zigzag chains by N···Cl intermolecular interactions of 3.139 (3) Å. Molecules in adjacent planes are rotated by 180° but lie almost directly above one another; the interplanar spacing is 3.283 (2) Å. Ring angles at the N atoms are substantially more acute than those at the C atoms.

Comment

The 3-methoxy-5-methyl-1,3,5-triazine system is found in a number of commercially important sulfonylurea herbicides, such as Metsulfuron Methyl and Thifensulfuron (Cremlyn, 1991). Only one crystal structure containing this system has been reported (Lotz, Kiel & Gattow, 1991), and this is of poor quality. The title compound, (I), is also relevant to the recent interest in chlorotriazines, such as cyanuric chloride (Pascal & Ho, 1992; Maginn, Compton, Harding, Brennan & Docherty, 1993), which show N···Cl intermolecular contacts.



(I)

The molecule possesses crystallographic C_s symmetry. The ring C—N bond lengths vary from 1.320 (3) to 1.346 (3) Å and the mean bond length of 1.336 (7) Å is identical to those in aminochloromethoxy-1,3,5-triazines (Glowka & Iwanicka, 1991). As found in other triazines (Glowka & Iwanicka, 1991, and references therein), the ring angles at the N atoms are substantially more acute [112.3 (2)–114.6 (2)°], and those at the C atoms [124.7 (2)–128.4 (2)°] more obtuse, than the ideal value of 120°. A correlation between the C—Cl bond distance and the corresponding endocyclic N—C—N bond angle has been suggested (Glowka & Iwanicka, 1991) and our data fit this relationship.

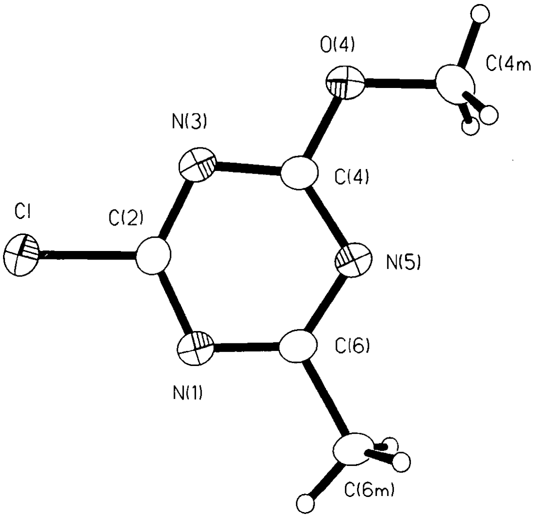


Fig. 1. A view of the molecule with the atom-numbering scheme. Except for two symmetry-related H atoms in each methyl group, all atoms lie on a crystallographic mirror plane. Displacement ellipsoids are plotted at the 30% probability level.

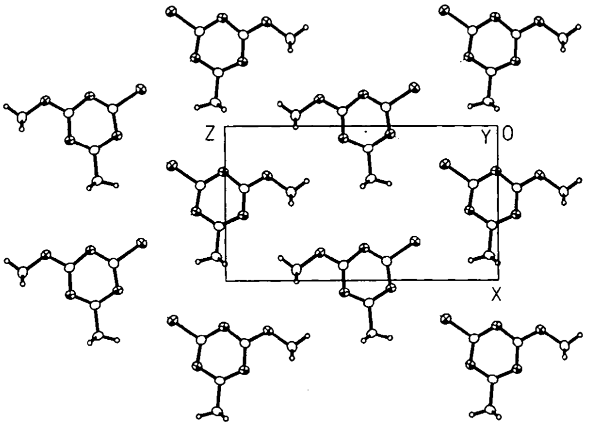


Fig. 2. A view of a plane of molecules at $y = \frac{1}{4}$ linked into zigzag chains by N···Cl intermolecular interactions of 3.139 (3) Å. Molecules in adjacent planes are rotated through 180° by the symmetry operation ($1 - x$, $\frac{1}{2} + y$, $-z$) but lie almost directly above each other with an interplanar spacing of 3.283 (2) Å.

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