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The Crystal Structure of Methyl 3,4-*O*-Isopropylidene-β-L-*erythro*-pentopyranosid-2-ulose

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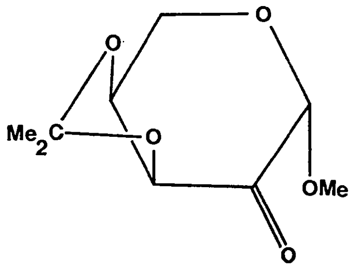
The crystal structure of methyl 3,4-*O*-isopropylidene-*β*-L-*erythro*-pentopyranosid-2-ulose, $C_9O_5H_{14}$, has been determined by direct methods and refined by least-squares calculations to $R=0·043$ for 868 observed intensities. The crystals are orthorhombic, space group $P2_12_12_1$, with $a=6·876$ (2), $b=7·921$ (2), $c=18·774$ (4) Å, $Z=4$. The pyranosidulose ring is in the *C*1 conformation, strained by the presence of the carbonyl group in position 2 and the 1,3-dioxolane ring bridging C(3) and C(4). There is evidence for transannular shortening between the pyranose ring oxygen O(5) and C(2) bonded to the carbonyl oxygen O(2).

Introduction

The glycosidulose $C_9O_5H_{14}$ (I) was prepared by Burton, Overend & Williams (1965). The X-ray analysis of this compound was undertaken at the suggestion of Professor W. G. Overend to determine the effect of the polar carbonyl group =O(2) at the C(2) position on the geometry of the pyranosidulose ring and to examine the possibility of transannular interaction with the carbonyl group O(2) and the ring oxygen O(5) which would result in shortening of the distance C(2)···O(5).



(I)

Experimental

A sample of crystals from diisopropyl ether regrown for X-ray analysis by sublimation at 70 °C under 2 mm Hg was supplied by Racz (1974). Unit cell and space group data were obtained from Weissenberg photographs. Accurate cell parameters were determined by least-squares calculations from 20 *θ*-values measured on a Hilger–Watts Y290 automatic four-circle diffractometer with Cu $K\alpha_1$ radiation. Intensities were measured on the same instrument employing the ω–2θ mode with a scan rate of 0·01° s^{-1} and a scan width of 0·9° in 90 steps. The background was counted for 13·5 s on either side of the extreme position for each reflexion. Reference reflexions were measured after every 50 reflexions.

Crystals mounted on glass fibres with conventional adhesives deteriorated after some time in the X-ray beam. A stable mounting was achieved by inserting a dry crystal into a thin-walled 0·3 mm diameter glass capillary tube of the type used in protein crystallography. Reference reflexions for this crystal showed no significant fluctuation with time.

1216 independent intensities were measured, of which 868 were classified as observed with $I_0(hkl) > 3\sigma I_0(hkl)$. Lp corrections were applied but no absorption correction. Crystal data is given in Table 1.

Table 1. *Crystal data*

Molecular formula	$C_9O_5H_{14}$
F.W.	202
Crystal system	Orthorhombic
Habit/form	Prismatic, elongated along **b**
Space group	$P2_12_12_1$
a	6·876 (2) Å
b	7·921 (2)
c	18·774 (4)
V	1022·52 Å^3
Z	4
D_c	1·312 g cm^{-3}
$F(000)$	432
μ(Cu $K\alpha$)	10·46 cm^{-1}
λ(Cu $K\alpha_1$)	1·54051 Å
Crystal size	(0·3 mm)^3
ω axis	b

Structure determination and refinement

Normalized structure factors were calculated using the *K*-curve method (Karle, Hauptman & Christ, 1958) and the 118 reflexions with $|E|>1·50$ were used as input to the program *MULTAN* (Germain, Main & Woolfson, 1971). Eight phase sets were produced and an *E* map calculated with the set having the lowest R_{Karle} (17·86) and highest absolute figure of merit, FOM (1·23) revealed 14 high peaks in stereochemically feasible positions.

This model was refined by full-matrix least-squares calculations with a modified version of Cruickshank & Smith's program using all the 1216 measured reflexions. A secondary extinction correction (Zachariasen, 1963, 1967) was applied during the final cycles. After completion of anisotropic refinement the five non-methyl H atoms were located on a difference map. The nine methyl H atoms were located on a second difference map after several further refinement cycles, although H(63) still appeared somewhat disordered. Refinement was completed after several further cycles with anisotropic temperature factors for C and O and isotropic for H atoms. The final R values were 0·043 for the 868 observed relexions, 0·079 for all 1216 reflexions and corresponding weighted $R=0{\cdot}090$.* Relative weights were calculated from:

$$\omega=[1-\{\exp\,-(a\sin^2\theta/\lambda^2)\}](b+|F_o|+c|F_o|^2)^{-1}$$

where $a=40$, $b=60$ and $c=0{\cdot}01$. The mean value of $\omega(|F_o|-|F_c|)^2$ was approximately constant over ranges of $|F_o|$ and $\sin\theta/\lambda$ in the final cycle. The value for the coefficient of secondary extinction was $2{\cdot}2\times10^{-5}$. Scattering factors used were those of Hanson, Herman, Lea & Skilman (1964).

Final positional and thermal parameters are listed in Table 2 with the numbering scheme of Fig. 1. Fig. 2 is a stereo view of the molecule.

Discussion

Bond lengths and angles are given in Table 3, torsion angles in Table 4.

The C–C bond lengths range from 1·487 to 1·521 Å with a mean value of 1·507 Å which is lower than expected. None of the C–C bond lengths is significantly different from the mean. The C–O bond lengths range from 1·408 to 1·442 Å, mean value 1·423 Å which is close to the expected value.

The mean value of the C–O bond lengths in the

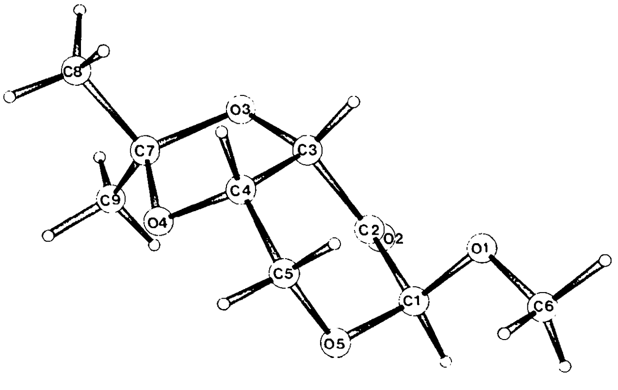


Fig. 1. Atom numbering scheme.

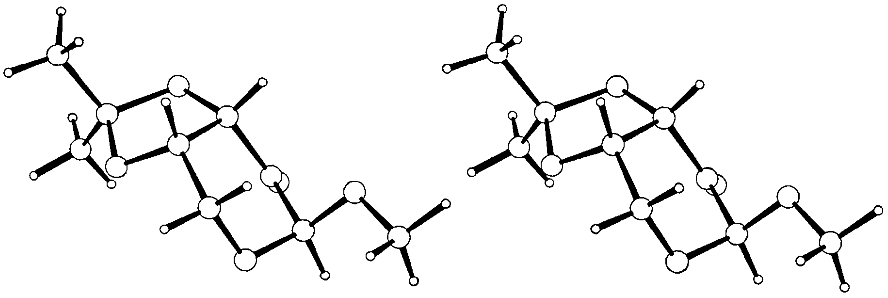


Fig. 2. Stereo view of the molecule.

Table 2. *Atomic parameters*

(*a*) Refined positional and thermal parameters ($\times10^4$) for non-H atoms with e.s.d.'s in parentheses. Anisotropic temperature factor is of the form:

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2klb^*c^*U_{23}+2lkc^*a^*U_{31}+2hka^*b^*U_{12})\right].$$

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{13}$	$2U_{23}$
C(1)	0·5598 (6)	0·9688 (6)	0·8159 (2)	606 (22)	744 (22)	640 (20)	−100 (43)	−60 (36)	−16 (37)
C(2)	0·4186 (6)	0·8935 (6)	0·8685 (2)	498 (19)	650 (21)	851 (26)	−12 (35)	86 (37)	−245 (41)
C(3)	0·5100 (6)	0·7860 (5)	0·9266 (2)	587 (20)	685 (22)	566 (18)	−135 (37)	137 (34)	−271 (35)
C(4)	0·6687 (6)	0·6741 (5)	0·8976 (2)	481 (18)	723 (21)	533 (16)	−31 (38)	79 (30)	−127 (33)
C(5)	0·7855 (7)	0·7479 (6)	0·8367 (3)	531 (22)	738 (24)	844 (25)	127 (40)	128 (38)	−52 (45)
O(5)	0·6686 (5)	0·8355 (4)	0·7859 (1)	730 (17)	777 (16)	568 (13)	−0 (33)	148 (26)	−116 (25)
O(1)	0·6743 (5)	1·0819 (4)	0·8557 (1)	738 (18)	683 (15)	677 (14)	−271 (29)	−14 (29)	677 (14)
O(2)	0·2460 (5)	0·9140 (6)	0·8622 (3)	455 (17)	1143 (28)	1493 (34)	176 (37)	80 (39)	301 (58)
O(3)	0·3752 (5)	0·6709 (4)	0·9564 (2)	780 (19)	746 (17)	715 (15)	−122 (32)	585 (29)	−251 (28)
O(4)	0·5565 (4)	0·5329 (4)	0·8735 (1)	630 (16)	669 (15)	561 (13)	−7 (27)	205 (23)	−157 (23)
C(6)	0·8025 (10)	1·1816 (8)	0·8137 (3)	835 (34)	808 (30)	905 (33)	−316 (61)	99 (59)	160 (54)
C(7)	0·4098 (6)	0·5066 (5)	0·9257 (2)	623 (21)	687 (22)	482 (16)	−60 (39)	162 (32)	−72 (31)
C(8)	0·4762 (10)	0·3887 (9)	0·9837 (3)	908 (36)	988 (38)	644 (23)	−116 (68)	25 (51)	273 (51)
C(9)	0·2312 (9)	0·4441 (8)	0·8897 (3)	745 (31)	927 (33)	744 (27)	−292 (57)	36 (50)	−13 (54)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31209 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2 (*cont.*)

(*b*) Refined positional and isotropic thermal parameters for H atoms with e.s.d.'s in parentheses.

$U^2_{\rm iso}$ is the isotropic temperature factor in the expression $B_{\rm iso} = 8\pi^2 U^2_{\rm iso}$

	x	y	z	$U^2_{\rm iso} \times 10^4$
H(1)	0·4966 (84)	1·0245 (68)	0·7714 (26)	611 (148)
H(3)	0·5620 (98)	0·8645 (76)	0·9620 (32)	713 (168)
H(4)	0·7679 (56)	0·6419 (51)	0·9386 (19)	241 (91)
H(51)	0·8852 (99)	0·8315 (81)	0·8589 (31)	643 (170)
H(52)	0·8429 (78)	0·6474 (61)	0·8145 (24)	404 (118)
H(61)	0·7619 (93)	1·2203 (79)	0·7709 (35)	694 (182)
H(62)	0·9064 (98)	1·1151 (74)	0·7952 (30)	585 (16)
H(63)	0·8593 (141)	1·2841 (116)	0·848 (45)	1115 (271)
H(81)	0·3737 (86)	0·3919 (67)	1·0287 (27)	627 (137)
H(82)	0·5973 (82)	0·4380 (64)	0·9971 (24)	442 (128)
H(83)	0·5169 (120)	0·2760 (10)	0·9639 (38)	811 (246)
H(91)	0·2445 (121)	0·3357 (119)	0·8614 (43)	951 (254)
H(92)	0·1898 (96)	0·5191 (86)	0·8549 (36)	633 (182)
H(93)	0·1292 (117)	0·4215 (95)	0·9211 (37)	826 (213)

Table 3. *Bond lengths* (Å) *and angles* (°)

(*a*) Non-hydrogen atoms. Standard deviations are in parentheses.

C(1)–C(2)	1·508 (6)	C(5)–O(5)–C(1)	113·3 (3)
C(2)–C(3)	1·521 (6)	O(5)–C(1)–C(2)	107·9 (3)
C(3)–C(4)	1·507 (5)	O(5)–C(1)–O(1)	113·0 (3)
C(4)–C(5)	1·515 (6)	C(2)–C(1)–O(1)	105·3 (3)
C(5)–O(5)	1·427 (5)	C(1)–O(1)–C(6)	113·9 (4)
C(1)–O(5)	1·411 (5)	C(1)–C(2)–O(2)	121·2 (5)
C(1)–O(1)	1·408 (5)	C(3)–C(2)–O(2)	123·6 (5)
C(6)–O(1)	1·423 (6)	C(2)–C(3)–O(3)	111·9 (3)
C(2)–O(2)	1·204 (5)	C(5)–C(4)–O(4)	110·4 (3)
C(3)–O(3)	1·415 (5)	C(3)–O(3)–C(7)	108·3 (3)
C(7)–O(3)	1·442 (5)	O(3)–C(7)–O(4)	105·1 (3)
C(4)–O(4)	1·432 (5)	C(7)–O(4)–C(4)	106·2 (3)
C(7)–O(4)	1·422 (4)	O(4)–C(4)–C(3)	100·5 (3)
C(7)–C(8)	1·505 (7)	C(4)–C(3)–O(3)	103·8 (3)
C(7)–C(9)	1·487 (7)	O(3)–C(7)–C(8)	108·7 (4)
C(1)–C(2)–C(3)	115·2 (3)	O(3)–C(7)–C(9)	110·2 (4)
C(2)–C(3)–C(4)	111·6 (3)	C(8)–C(7)–C(9)	112·0 (4)
C(3)–C(4)–C(5)	115·5 (4)	C(8)–C(7)–O(4)	112·0 (4)
C(4)–C(5)–O(5)	113·3 (4)	C(9)–C(7)–O(4)	108·7 (4)

(*b*) Hydrogen atoms. Standard deviations are in parentheses.

C(1)–H(1)	1·04 (5)	O(5)—C(5)–H(51)	109 (3)
C(3)–H(3)	0·98 (6)	O(5)—C(5)–H(52)	110 (3)
C(4)–H(4)	1·06 (4)	C(4)—C(5)–H(51)	107 (3)
C(5)–H(51)	1·04 (6)	C(4)—C(5)–H(52)	103 (3)
C(5)–H(52)	0·98 (5)	H(51)–C(5)–H(52)	115 (5)
C(6)–H(61)	0·91 (7)	O(1)—C(6)–H(61)	119 (4)
C(6)–H(62)	0·95 (7)	O(1)—C(6)–H(62)	111 (4)
C(6)–H(63)	1·11 (9)	O(1)—C(6)–H(63)	108 (5)
C(8)–H(81)	1·10 (6)	H(61)–C(6)–H(62)	95 (5)
C(8)–H(82)	0·95 (6)	H(61)–C(6)–H(63)	112 (6)
C(8)–H(83)	1·01 (8)	H(62)–C(6)–H(63)	111 (6)
C(9)–H(91)	1·01 (9)	C(7)—C(8)–H(81)	110 (3)
C(9)–H(92)	0·93 (7)	C(7)—C(8)–H(82)	102 (3)
C(9)–H(93)	0·93 (8)	C(7)—C(8)–H(83)	112 (4)
O(5)–C(1)–H(1)	103 (3)	H(81)–C(8)–H(82)	110 (4)
C(2)–C(1)–H(1)	115 (3)	H(81)–C(8)–H(83)	119 (5)
O(1)–C(1)–H(1)	113 (3)	H(82)–C(8)–H(83)	103 (6)
O(3)–C(3)–H(3)	113 (4)	C(7)—C(9)–H(91)	117 (5)
C(4)–C(3)–H(3)	111 (4)	C(7)—C(9)–H(92)	111 (4)
C(2)–C(3)–H(3)	106 (3)	C(7)—C(9)–H(93)	113 (4)
O(4)–C(4)–H(4)	113 (2)	H(91)–C(9)–H(92)	102 (6)
C(5)–C(4)–H(4)	108 (2)	H(91)–C(9)–H(93)	103 (6)
C(3)–C(4)–H(4)	110 (2)	H(92)–C(9)–H(93)	110 (7)

Table 4. *Selected torsion angles* (°)

The torsion angle for the chain of atoms *A–B–C–D* is the angle required to bring the plane *A–B–C* into coincidence with plane *B–C–D* when viewed along the bond from *B* to *C*. A clockwise rotation is positive.

O(5)–C(1)–C(2)–C(3)	56
C(1)–C(2)–C(3)–C(4)	−42
C(2)–C(3)–C(4)–C(5)	34
C(3)–C(4)–C(5)–O(5)	−42
C(4)–C(5)–O(5)–C(1)	58
C(5)–O(5)–C(1)–C(2)	−64
C(1)–O(2)–C(2)–C(3)	−177
O(2)–C(3)–C(2)–C(1)	−178
C(3)–C(1)–C(2)–O(2)	−178
O(5)–C(1)–O(1)–C(6)	70
C(2)–C(1)–O(1)–C(6)	−173
O(5)–C(1)–C(2)–O(2)	−122
O(2)–C(2)–C(1)–O(1)	118
C(3)–C(2)–C(1)–O(1)	−65
C(5)–O(5)–C(1)–O(1)	52
O(2)–C(2)–C(3)–C(4)	136
O(2)–C(2)–C(3)–O(3)	20
C(2)–C(3)–O(3)–C(7)	101
C(2)–C(3)–C(4)–O(4)	−85
C(3)–C(4)–O(4)–C(7)	−40
C(4)–O(4)–C(7)–O(3)	29
O(4)–C(7)–O(3)–C(3)	−5
C(7)–O(3)–C(3)–C(4)	−20
O(3)–C(3)–C(4)–O(4)	36
C(3)–O(3)–C(7)–C(8)	115
C(3)–O(3)–C(7)–C(9)	−122
C(4)–O(4)–C(7)–C(8)	−89
C(4)–O(4)–C(7)–C(9)	147
C(5)–C(4)–C(3)–O(3)	155
C(5)–C(4)–O(4)–C(7)	−162
O(5) C(5)–C(4)–O(4)	72
C(1)–C(2)–C(3)–O(3)	−158

five-membered 1,3-dioxolane ring is 1·428 Å, individual differences all being $<3\sigma$ from this value. Atoms C(3), O(3), C(7) and O(4) are roughly planar, C(4) being out of this plane.

In the pyranosidulose ring the bond C(1)–O(5) is less than C(5)–O(5) by about 3σ and the link C(1)–O(1) is shorter by 3σ than the mean C–O bond length, results apparently in agreement with the proposals of Kim & Jeffrey (1967) for pyranose monosaccharides.

The pyranosidulose ring is a strained *C*1 chair with conformation 1*a*2*e*3*e*4*a*. Distortions in the geometry of this ring are best assessed by comparison with the geometry of a hypothetical ideal unstrained pyranose ring with C–C = 1·525, C–O = 1·430 Å, valence angles on C atoms = 109·5° and that on the ring O atom = 113·3° quoted by Kim & Jeffrey (1967). On this basis C(1)–O(5) is short at significance level 4σ and C(1)–C(2), C(3)–C(4) are both short at the 3σ level. Apart from the C(1)–O(5)–C(5) angle which is normal, all the other internal valence angles in this ring are abnormal, C(2)–C(1)–O(5) being low and the rest high. As expected the presence of the carbonyl group results in an approximately planar configuration about atom C(2) which is 0·027 Å from the plane defined by C(1), O(2) and C(3). The resulting ring torsion angle C(1)–C(2)–C(3)–C(4) of −41·77° is ~14° less than the nor-

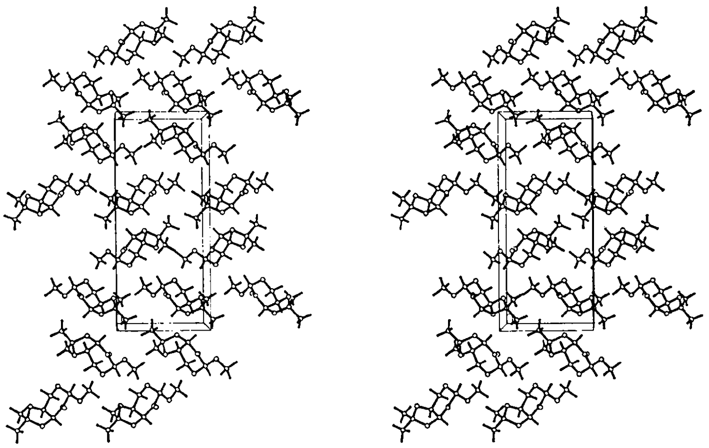

Fig. 3. Stereo view showing the packing of the molecules.

mal value (Kim & Jeffrey, 1967). Although the carbonyl oxygen O(2) has markedly anisotropic thermal parameters, as might be expected the smallest r.m.s. vibration component is approximately in the plane defined by atoms C(1), C(2), C(3) and O(2) and along the C(2)=O(2) bond direction. The ring is further strained to accommodate the 1,3-dioxolane ring, the torsion angle C(2)–C(3)–C(4)–C(5) being ~22° less and C(3)–C(4)–C(5)–O(5) ~14° less than normal. The substituent at C(3) thus has a quasi equatorial disposition and that at C(4) a quasi axial disposition compared with the unstrained pyranose ring substituents. The ring valence angles about C(3) and C(4) are consequently increased. To further investigate the effects of strain on the geometry of the pyranosidulose ring the transannular distances between next nearest neighbours are tabulated in Table 5, together with the corresponding distances for the hypothetical unstrained pyranose ring. This reveals a shortening of the distance C(2)···O(5) = 2·360 (5) Å compared with 2·414 Å (hypothetical), difference 11σ. In *β*-DL-arabinose (Kim & Jeffrey, 1967) this distance is 2·423 Å, difference 13σ. The observed transannular shortening is consistent with the concept of a weak interaction between $\delta(-)$ and $\delta(+)$ charges on O(5) and C(2) respectively (Overend, 1975). The overall opening up of the ring results in significant increases in all other transannular distances except C(1)···C(5) which is short at the 3σ level.

The mean C–H distance is 1·00 Å, mean O–C–H, C–C–H and H–C–H angles 111, 110 and 108° respectively, there being no significant deviations from these mean values.

Table 5. *Transannular distances compared with those calculated for an ideal unstrained pyranose ring*

	Distances (Å)		
Atoms	Ideal value	This structure	Difference
C(2)···O(5)	2·414	2·360 (5)	-11σ
C(3)···C(5)	2·471	2·556 (6)	$+14\sigma$
C(1)···C(3)	2·471	2·556 (6)	$+14\sigma$
C(4)···O(5)	2·414	2·455 (5)	$+8\sigma$
C(1)···C(5)	2·389	2·371 (6)	-3σ
C(2)···C(4)	2·471	2·505 (5)	$+7\sigma$

Table 6. *Selected intermolecular distances* (Å)

H(93)···H(63$^{\mathrm{i}}$)	2·55	O(4)···O(1$^{\mathrm{iv}}$)	3·68
O(2)····H(51$^{\mathrm{ii}}$)	2·57	O(4)···C(6$^{\mathrm{iv}}$)	3·44
C(9)····H(63$^{\mathrm{i}}$)	2·96	C(9)···C(6$^{\mathrm{i}}$)	3·89
C(2)····H(61$^{\mathrm{iii}}$)	3·20		

Symmetry code: The first atom is that in the asymmetric unit, the second is the generated atom.

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

Table 6 lists some of the shorter intermolecular contacts, all of which correspond to weak van der Waals interactions. Fig. 3 is a stereo view showing the packing of the molecules.

Computations were carried out on the University of London CD6600 computer using the Birkbeck College Crystallographic Program Library.

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