Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-hydroxyimino-α-D-*erythro*-pyranoside methanol solvate

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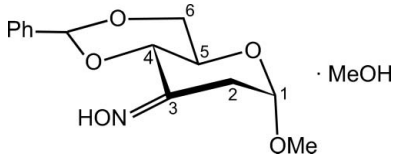
Received 14 November 2007; accepted 15 November 2007

Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.005 Å; R factor = 0.048; wR factor = 0.128; data-to-parameter ratio = 9.8.

The title compound, $C_{14}H_{17}NO_5\cdot CH_3OH$, is a methyl- and benzylidene-protected precursor for the synthesis of the amino sugar daunosamine (3-amino-2,3,6-trideoxy-L-*lyxo*-hexose). The configuration is determined by the stereochemistry of the starting material. The bond lengths and angles are normal and the molecule has the preferred $^4C_1$ conformation (*cf.* the standard carbohydrate atomic numbering). One methanol molecule per asymmetric unit acts both as a hydrogen-bond acceptor and donor for the oxime group. This pattern is enlarged by the twofold axis of the space group to a homodromic cycle supported by σ-cooperativity *via* the oxime N—O bond.

Related literature

The title compound was prepared according to the procedure described by Horton & Weckerle (1975).



Experimental

Crystal data

$C_{14}H_{17}NO_5\cdot CH_4O$
M_r = 311.33
Monoclinic, $C2$
a = 21.8696 (12) Å
b = 4.7001 (2) Å
c = 16.0494 (8) Å
β = 109.009 (3)°
V = 1559.74 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 200 (2) K
0.40 × 0.05 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
6634 measured reflections
2006 independent reflections
1238 reflections with $I > 2\sigma(I)$
R_{int} = 0.073

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.128
S = 1.04
2006 reflections
205 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O8—H88···O9	0.84	1.80	2.641 (3)	175
O9—H89···N1^{i}	0.84	2.08	2.873 (4)	157

Symmetry code: (i) $-x+2, y, -z+1$.

Data collection: *COLLECT* (Nonius 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor 1997); data reduction: *DENZO* (Otwinowski & Minor 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

The authors thank Anna Zangl for experimental support, and Richard Betz and Tobias Kerscher for helpful remarks.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LN2001).

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 doi:10.1107/S1600536807059521

supplementary materials

Acta Cryst. (2007). E**63**, o4765 [**doi:10.1107/S1600536807059521**]

Methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-hydroxyimino-*α*-D-*erythro*-pyranoside methanol solvate

M. Davies, S. Goette, P. Klüfers and T. Schwarz

Comment

The title compound, (I), was prepared in the course of the synthesis of the aminosugar daunosamine (3-amino-2,3,6-trideoxy-*L*-*lyxo*-hexose).

The molecular structure shows the pyranoside in its preferred $^4C_1$ chair conformation (Fig. 1). In the crystal structure, two pyranoside and two methanol molecules form a hydrogen-bond-connected cluster, the methanol molecules acting both as a hydrogen-bond donor and acceptor, whereas the nitrogen atom of the oxime group is a hydrogen-bond acceptor und the oxime's hydroxyl group is a donor. The central hydrogen-bonded motif thus is a 10-membered ring of donor and acceptor atoms with the shape of a pseudo-hexagon (Fig. 2).

Experimental

The title compound was prepared upon the reaction of hydroxylamine and methyl 2-deoxy-*D*-*erythro*-hex-3-ulose-4*O*,6*O*-benzylidene- α-pyranoside in methanol. Colourless crystals were obtained by cooling the solution to 277 K [m.p. 478–479 K (decomp.)].

Refinement

All H atoms were located initially in a difference map, then their positions were optimized geometrically and refined as riding on their parent atoms with one common refined isotropic displacement parameter for the methyl H atoms and one parameter for the remaining H atoms. The methyl and hydroxy H atoms were allowed to rotate about the axes of their respective groups.

Figures

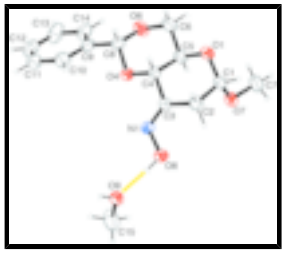

Fig. 1. The molecular structure of (I), with atom labels and anisotropic displacement ellipsoids (drawn at the 50% probability level) for non-H atoms. The hydrogen bond to the methanol molecule is drawn as a yellow bar.

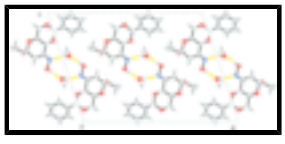

Fig. 2. The packing of (I), viewed along [0 1 0]. The hydrogen bonds are drawn as yellow bars.

Methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-hydroxyimino-α-D-*erythro*-\ pyranoside methanol solvate

Crystal data

$C_{14}H_{17}NO_5 \cdot CH_4O$	$F_{000} = 664$
$M_r = 311.33$	$D_x = 1.326$ Mg m^{-3}
Monoclinic, *C*2	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: C 2y	Cell parameters from 8876 reflections
a = 21.8696 (12) Å	θ = 3.1–27.5º
b = 4.7001 (2) Å	μ = 0.10 mm^{-1}
c = 16.0494 (8) Å	*T* = 200 (2) K
β = 109.009 (3)º	Needle, colourless
V = 1559.74 (13) Å^3	0.40 × 0.05 × 0.05 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	1238 reflections with $I > 2\sigma(I)$
Radiation source: rotating anode	$R_{int} = 0.073$
Monochromator: MONTEL, graded multilayered X-ray optics	$\theta_{max} = 27.6$º
T = 200(2) K	$\theta_{min} = 3.7$º
CCD; rotation images; thick slices scans	*h* = −28→28
Absorption correction: none	*k* = −6→6
6634 measured reflections	*l* = −20→20
2006 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.048$	H-atom parameters constrained
$wR(F^2) = 0.128$	$w = 1/[\sigma^2(F_o^2) + (0.0692P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max} < 0.001$
2006 reflections	$\Delta\rho_{max} = 0.18$ e Å^{-3}
205 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Refinement. Due to the absence of significant anomalous scattering the absolute structure factor is meaningless. Thus, Friedel opposites were merged. The absolute structure is determined by the stereochemistry of the starting material.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.82189 (10)	0.8533 (6)	0.73526 (14)	0.0475 (6)
O4	0.98051 (9)	0.5771 (5)	0.74614 (12)	0.0403 (6)
O6	0.97148 (11)	0.5728 (7)	0.88686 (14)	0.0604 (8)
O7	0.76006 (10)	0.5196 (6)	0.63550 (15)	0.0513 (6)
O8	0.87819 (10)	0.5175 (7)	0.48398 (13)	0.0506 (7)
H88	0.9010	0.4539	0.4550	0.057 (3)*
N1	0.91647 (11)	0.5482 (7)	0.57293 (15)	0.0395 (7)
C1	0.78439 (16)	0.7958 (8)	0.6454 (2)	0.0448 (9)
H1	0.7472	0.9315	0.6274	0.057 (3)*
C2	0.82390 (14)	0.8336 (9)	0.5833 (2)	0.0472 (8)
H21	0.7993	0.7539	0.5248	0.057 (3)*
H22	0.8302	1.0392	0.5755	0.057 (3)*
C3	0.88860 (14)	0.6914 (7)	0.6164 (2)	0.0374 (7)
C4	0.92304 (13)	0.7422 (8)	0.7127 (2)	0.0387 (8)
H4	0.9350	0.9480	0.7211	0.057 (3)*
C5	0.87757 (14)	0.6750 (8)	0.7645 (2)	0.0443 (8)
H5	0.8643	0.4706	0.7562	0.057 (3)*
C6	0.91267 (17)	0.7332 (11)	0.8605 (2)	0.0607 (11)
H61	0.9224	0.9388	0.8696	0.057 (3)*
H62	0.8853	0.6770	0.8963	0.057 (3)*
C7	0.71604 (17)	0.4730 (10)	0.6834 (3)	0.0647 (12)
H71	0.6869	0.6366	0.6755	0.110 (7)*
H72	0.7404	0.4498	0.7461	0.110 (7)*
H73	0.6907	0.3008	0.6614	0.110 (7)*
C8	1.01113 (16)	0.6450 (8)	0.8370 (2)	0.0475 (9)
H8	1.0199	0.8542	0.8426	0.057 (3)*
C9	1.07425 (15)	0.4886 (8)	0.8695 (2)	0.0456 (8)
C10	1.11891 (16)	0.5232 (11)	0.8264 (2)	0.0598 (10)
H10	1.1085	0.6407	0.7756	0.057 (3)*
C11	1.17843 (17)	0.3908 (10)	0.8557 (2)	0.0600 (11)
H11	1.2088	0.4198	0.8257	0.057 (3)*
C12	1.19364 (18)	0.2166 (10)	0.9285 (2)	0.0601 (11)
H12	1.2341	0.1209	0.9483	0.057 (3)*
C13	1.14973 (19)	0.1827 (11)	0.9724 (3)	0.0706 (13)
H13	1.1603	0.0653	1.0233	0.057 (3)*
C14	1.09005 (16)	0.3177 (10)	0.9433 (2)	0.0556 (10)
H14	1.0601	0.2924	0.9743	0.057 (3)*
O9	0.95366 (10)	0.3482 (5)	0.39429 (15)	0.0450 (6)
H89	0.9861	0.4391	0.3918	0.110 (7)*
C15	0.9600 (2)	0.0630 (10)	0.3752 (4)	0.0866 (16)

H151	0.9493	0.0391	0.3114	0.110 (7)*
H152	0.9305	−0.0522	0.3960	0.110 (7)*
H153	1.0046	0.0013	0.4048	0.110 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0450 (11)	0.0520 (14)	0.0465 (12)	0.0088 (12)	0.0165 (10)	−0.0091 (12)
O4	0.0380 (10)	0.0493 (14)	0.0300 (10)	0.0059 (11)	0.0063 (8)	−0.0017 (10)
O6	0.0576 (14)	0.090 (2)	0.0361 (12)	0.0198 (16)	0.0187 (11)	0.0043 (15)
O7	0.0430 (12)	0.0505 (17)	0.0638 (15)	0.0044 (13)	0.0223 (11)	−0.0119 (14)
O8	0.0441 (11)	0.0719 (18)	0.0323 (11)	0.0110 (14)	0.0078 (9)	−0.0057 (13)
N1	0.0359 (12)	0.0500 (18)	0.0298 (13)	0.0004 (14)	0.0067 (11)	−0.0022 (14)
C1	0.0428 (17)	0.047 (2)	0.0451 (19)	0.0067 (17)	0.0147 (15)	−0.0061 (17)
C2	0.0454 (17)	0.050 (2)	0.0454 (18)	0.0123 (19)	0.0133 (15)	0.0045 (18)
C3	0.0349 (15)	0.0388 (18)	0.0399 (18)	0.0002 (15)	0.0141 (14)	0.0006 (16)
C4	0.0357 (15)	0.0407 (19)	0.0392 (18)	0.0024 (15)	0.0117 (14)	−0.0027 (15)
C5	0.0453 (18)	0.049 (2)	0.0401 (18)	0.0090 (17)	0.0162 (15)	−0.0016 (17)
C6	0.058 (2)	0.083 (3)	0.045 (2)	0.018 (2)	0.0227 (17)	−0.004 (2)
C7	0.053 (2)	0.062 (3)	0.090 (3)	−0.003 (2)	0.038 (2)	−0.015 (2)
C8	0.0493 (19)	0.054 (2)	0.0320 (17)	0.0026 (17)	0.0034 (15)	−0.0049 (16)
C9	0.0452 (17)	0.050 (2)	0.0336 (16)	0.0003 (18)	0.0016 (14)	−0.0079 (17)
C10	0.058 (2)	0.078 (3)	0.0384 (18)	0.017 (2)	0.0083 (16)	0.008 (2)
C11	0.051 (2)	0.074 (3)	0.049 (2)	0.013 (2)	0.0084 (17)	−0.004 (2)
C12	0.051 (2)	0.055 (2)	0.061 (2)	0.002 (2)	−0.0012 (19)	0.001 (2)
C13	0.056 (2)	0.074 (3)	0.068 (3)	−0.004 (2)	0.000 (2)	0.027 (2)
C14	0.0479 (19)	0.062 (3)	0.049 (2)	−0.006 (2)	0.0046 (16)	0.009 (2)
O9	0.0444 (12)	0.0445 (14)	0.0494 (13)	−0.0022 (12)	0.0196 (10)	−0.0060 (12)
C15	0.065 (3)	0.046 (3)	0.159 (5)	−0.004 (2)	0.050 (3)	−0.024 (3)

Geometric parameters (Å, °)

O1—C5	1.426 (4)	C6—H62	0.9900
O1—C1	1.433 (4)	C7—H71	0.9800
O4—C4	1.425 (4)	C7—H72	0.9800
O4—C8	1.429 (3)	C7—H73	0.9800
O6—C8	1.400 (4)	C8—C9	1.500 (5)
O6—C6	1.431 (4)	C8—H8	1.0000
O7—C1	1.392 (5)	C9—C10	1.378 (5)
O7—C7	1.431 (4)	C9—C14	1.378 (5)
O8—N1	1.407 (3)	C10—C11	1.380 (5)
O8—H88	0.8400	C10—H10	0.9500
N1—C3	1.260 (4)	C11—C12	1.376 (6)
C1—C2	1.528 (4)	C11—H11	0.9500
C1—H1	1.0000	C12—C13	1.372 (6)
C2—C3	1.497 (4)	C12—H12	0.9500
C2—H21	0.9900	C13—C14	1.388 (5)
C2—H22	0.9900	C13—H13	0.9500
C3—C4	1.501 (4)	C14—H14	0.9500

C4—C5	1.523 (4)	O9—C15	1.392 (5)
C4—H4	1.0000	O9—H89	0.8400
C5—C6	1.506 (4)	C15—H151	0.9800
C5—H5	1.0000	C15—H152	0.9800
C6—H61	0.9900	C15—H153	0.9800
C5—O1—C1	111.6 (2)	H61—C6—H62	108.4
C4—O4—C8	109.0 (2)	O7—C7—H71	109.5
C8—O6—C6	111.6 (3)	O7—C7—H72	109.5
C1—O7—C7	112.3 (3)	H71—C7—H72	109.5
N1—O8—H88	109.5	O7—C7—H73	109.5
C3—N1—O8	112.4 (2)	H71—C7—H73	109.5
O7—C1—O1	111.3 (3)	H72—C7—H73	109.5
O7—C1—C2	108.0 (3)	O6—C8—O4	111.0 (3)
O1—C1—C2	112.0 (3)	O6—C8—C9	110.7 (3)
O7—C1—H1	108.5	O4—C8—C9	108.5 (3)
O1—C1—H1	108.5	O6—C8—H8	108.9
C2—C1—H1	108.5	O4—C8—H8	108.9
C3—C2—C1	112.7 (3)	C9—C8—H8	108.9
C3—C2—H21	109.0	C10—C9—C14	118.7 (3)
C1—C2—H21	109.0	C10—C9—C8	119.4 (3)
C3—C2—H22	109.0	C14—C9—C8	122.0 (3)
C1—C2—H22	109.0	C9—C10—C11	121.3 (4)
H21—C2—H22	107.8	C9—C10—H10	119.3
N1—C3—C2	127.9 (3)	C11—C10—H10	119.3
N1—C3—C4	118.9 (3)	C12—C11—C10	119.8 (4)
C2—C3—C4	113.2 (3)	C12—C11—H11	120.1
O4—C4—C3	112.7 (3)	C10—C11—H11	120.1
O4—C4—C5	109.5 (3)	C13—C12—C11	119.3 (4)
C3—C4—C5	109.4 (2)	C13—C12—H12	120.4
O4—C4—H4	108.4	C11—C12—H12	120.4
C3—C4—H4	108.4	C12—C13—C14	120.8 (4)
C5—C4—H4	108.4	C12—C13—H13	119.6
O1—C5—C6	109.0 (3)	C14—C13—H13	119.6
O1—C5—C4	109.8 (3)	C9—C14—C13	120.0 (4)
C6—C5—C4	108.4 (3)	C9—C14—H14	120.0
O1—C5—H5	109.9	C13—C14—H14	120.0
C6—C5—H5	109.9	C15—O9—H89	109.5
C4—C5—H5	109.9	O9—C15—H151	109.5
O6—C6—C5	108.4 (3)	O9—C15—H152	109.5
O6—C6—H61	110.0	H151—C15—H152	109.5
C5—C6—H61	110.0	O9—C15—H153	109.5
O6—C6—H62	110.0	H151—C15—H153	109.5
C5—C6—H62	110.0	H152—C15—H153	109.5
C7—O7—C1—O1	63.5 (3)	C3—C4—C5—C6	−178.9 (3)
C7—O7—C1—C2	−173.1 (3)	C8—O6—C6—C5	59.1 (4)
C5—O1—C1—O7	63.2 (3)	O1—C5—C6—O6	−174.7 (3)
C5—O1—C1—C2	−57.8 (4)	C4—C5—C6—O6	−55.3 (4)
O7—C1—C2—C3	−75.9 (4)	C6—O6—C8—O4	−63.1 (4)

O1—C1—C2—C3	47.0 (4)	C6—O6—C8—C9	176.3 (3)
O8—N1—C3—C2	−2.8 (5)	C4—O4—C8—O6	62.8 (3)
O8—N1—C3—C4	179.7 (3)	C4—O4—C8—C9	−175.3 (3)
C1—C2—C3—N1	137.9 (4)	O6—C8—C9—C10	177.5 (3)
C1—C2—C3—C4	−44.5 (4)	O4—C8—C9—C10	55.5 (5)
C8—O4—C4—C3	178.2 (3)	O6—C8—C9—C14	−4.8 (5)
C8—O4—C4—C5	−59.8 (3)	O4—C8—C9—C14	−126.8 (4)
N1—C3—C4—O4	−9.8 (4)	C14—C9—C10—C11	0.1 (6)
C2—C3—C4—O4	172.4 (3)	C8—C9—C10—C11	177.9 (4)
N1—C3—C4—C5	−131.8 (3)	C9—C10—C11—C12	1.0 (7)
C2—C3—C4—C5	50.3 (4)	C10—C11—C12—C13	−1.6 (7)
C1—O1—C5—C6	−176.7 (3)	C11—C12—C13—C14	1.1 (7)
C1—O1—C5—C4	64.8 (3)	C10—C9—C14—C13	−0.6 (6)
O4—C4—C5—O1	176.1 (3)	C8—C9—C14—C13	−178.3 (4)
C3—C4—C5—O1	−59.9 (4)	C12—C13—C14—C9	0.0 (7)
O4—C4—C5—C6	57.2 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H88···O9	0.84	1.80	2.641 (3)	175
O9—H89···N1^{i}	0.84	2.08	2.873 (4)	157

Symmetry codes: (i) −*x*+2, *y*, −*z*+1.

Fig. 1

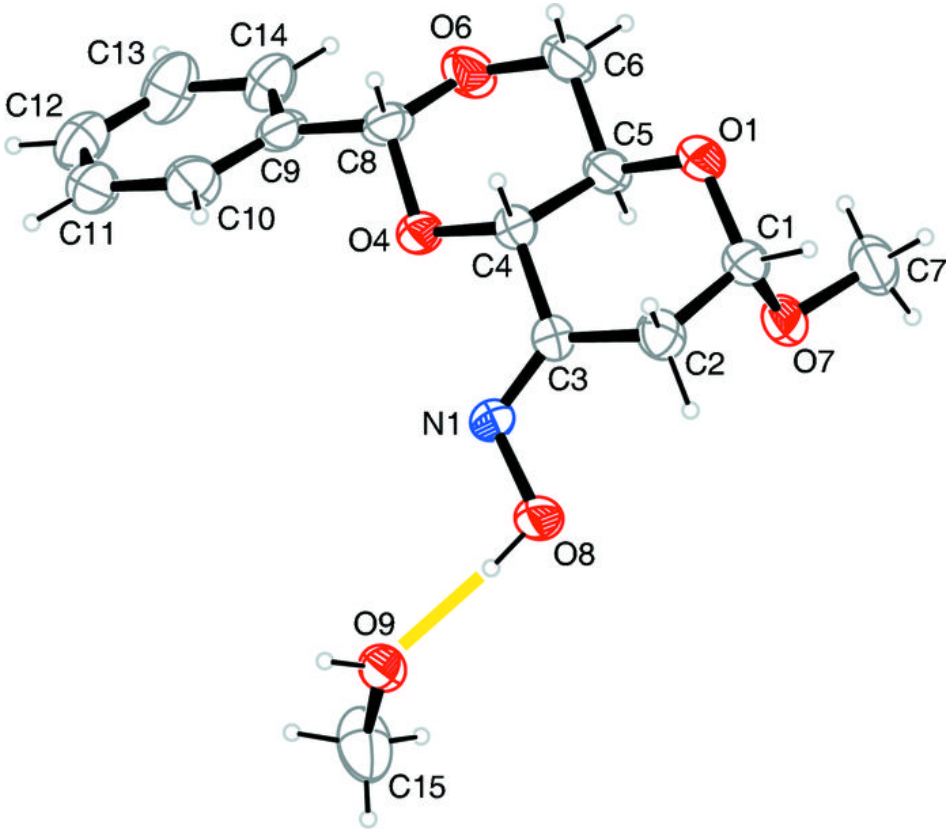
C13
C14
O6
C6
C12
C5
O1
C9
C8
C11
C10
O4
C4
C1
C7
C3
C2
O7
N1
O8
O9
C15

Fig. 2