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(3*R*,6*S*,7*R*,8*R*,9*S*,9a*S*)-Methyl 6,9-diacetoxy-7,8-diazidoperhydro-5-oxothiazolo[3,2-*a*]azepine-3-carboxylate

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Key indicators

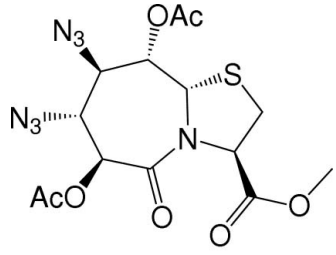
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.002 Å
R factor = 0.023
wR factor = 0.057
Data-to-parameter ratio = 12.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The absolute configuration has been determined for the bicyclic title compound, $C_{14}H_{17}N_7O_7S$, an intermediate in the synthesis of fixed chiral bis(1,2-aminohydroxy) compounds. In the crystal structure, the chair conformation of the seven-membered lactam ring exhibits four axial heteroatom substituents. The fused five-membered thiazolidine ring prevents inversion of the seven-membered iduronic acid ring derivative to the thermodynamically more favourable chair conformation with four equatorial substitutions.

Comment

1,2-Amino alcohols find application as chiral auxiliaries, where the heteroatoms form a complex with a metal reaction centre (Ager *et al.*, 1996). Two vicinal amino alcohol units are the starting material in the syntheses of bis(oxazolines), which provide high enantioselectivities in a number of transformations (Gant & Meyers, 1994). We present a precursor of a bis(1,2-amino alcohol), a novel class of ligands with two amino alcohol units attached to a seven-membered lactam ring.



(I)

The title compound, (I) (Fig. 1), was prepared from the starting material (3*R*,6*S*,7*S*,8*S*,9*S*,9a*S*)-methyl octahydro-6,7,8,9-tetrahydroxy-5-oxothiazolo[3,2-*a*]azepine-3-carboxylate, which is obtained by condensation of D-γ-mannuronolactone with the methyl ester of L-cysteine (Tremmel & Geyer, 2002). The bond lengths and angles (Table 1) are within normal ranges. Activation and subsequent substitution of NaN_3 for the two hydroxy groups in positions 7 and 8 inserts the N-termini in the molecule. Finally, the acetylation of the remaining hydroxy groups was performed with acetic acid anhydride.

In contrast to the conformation observed in the crystalline state, the seven-membered lactam ring shows dynamics between a chair and a twist–boat conformation in solution. The coupling constants between the protons 6, 7 and 8 represent the typical values for dynamic systems of about 5–8 Hz. The NOE experiments also indicate a more flexible structure of (I) in solution.

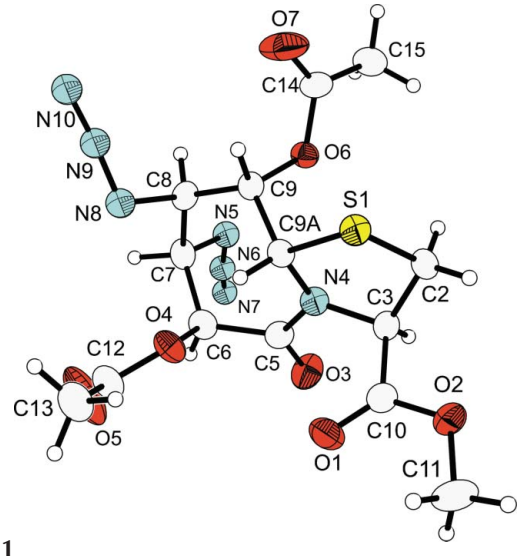


Figure 1
A view of (I), with 50% probability displacement ellipsoids.

Experimental

The reaction of (3*R*,6*S*,7*R*,8*R*,9*S*,9a*S*)-methyl 6,9-dihydroxy-7,8-diazidooctahydro-5-oxothiazolo[3,2-*a*]azepine-3-carboxylate (1.88 g, 5.48 mmol) with an excess of acetic acid anhydride (4 ml) was carried out in dry pyridine (30 ml) overnight at room temperature. After removal of the solvent, colourless crystals were obtained by recrystallization from ethyl acetate (yield 2.2 g, 5.26 mmol, 95%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.60 (*d*, $^3J_{9aH,9H}$ = 1.23 Hz, 1H, 9a-H), 5.53 (*d*, $^3J_{6H,7H}$ = 7.41 Hz, 1H, 6-H), 5.32 (*dd*, $^3J_{3H,2'H}$ = 6.93 Hz, $^3J_{3H,2H}$ = 2.40 Hz, 1H, 3-H), 5.13 (*dd*, $^3J_{9H,9aH}$ = 1.23 Hz, $^3J_{9H,8H}$ = 3.57 Hz, 1H, 9-H), 4.23 (*dd*, $^3J_{7H,6H}$ = 7.41 Hz, $^3J_{7H,8H}$ = 6.17 Hz, 1H, 7-H), 3.91 (*dd*, $^3J_{8H,7H}$ = 6.24 Hz, $^3J_{8H,9H}$ = 3.64 Hz, 1H, 8-H), 3.78 (*s*, 3H, CO_2CH_3), 3.35 (*dd*, $^3J_{2'H,3H}$ = 6.93 Hz, $^2J_{2'H,2H}$ = 11.53 Hz, 1H, 2′-H), 3.14 (*dd*, $^2J_{2H,2'H}$ = 11.60 Hz, $^3J_{2H,3H}$ = 2.47 Hz, 1H, 2-H), 2.23 (*s*, 3H, CH_3), 2.18 (*s*, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.61 (CO), 169.49 (CO), 169.29 (CO), 164.43 (5-C), 74.86 (9-C), 73.84 (6-C), 64.89 (3-C), 63.09 (8-C), 59.33 (7-C), 58.90 (9a-C), 53.22 (CH_3), 31.44 (2-C), 21.07, 20.85 (CH_3).

Crystal data

$C_{14}H_{17}N_7O_7S$
M_r = 427.41
Orthorhombic, $P2_12_12_1$
a = 8.6418 (4) Å
b = 11.8765 (6) Å
c = 18.2755 (12) Å
V = 1875.69 (18) Å^3
Z = 4
D_x = 1.514 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26411 reflections
θ = 2–26°
μ = 0.23 mm^{-1}
T = 193 (2) K
Block, colourless
0.6 × 0.3 × 0.2 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: none
27463 measured reflections
3765 independent reflections
3473 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 26.2°
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.057
S = 1.03
3765 reflections
298 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0035 (8)
Absolute structure: Flack (1983), with 1222 Friedel pairs
Flack parameter: −0.02 (5)

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.8038 (15)	C5—C6	1.526 (2)
S1—C9*A*	1.8228 (13)	C6—C7	1.527 (2)
C2—C3	1.517 (2)	C7—C8	1.527 (2)
C3—N4	1.4577 (17)	C8—C9	1.5374 (19)
N4—C5	1.3559 (18)	C9—C9*A*	1.5202 (19)
N4—C9*A*	1.4766 (17)		
C2—S1—C9*A*	92.81 (6)	C5—C6—C7	114.79 (12)
C3—C2—S1	103.49 (9)	C8—C7—C6	117.34 (12)
N4—C3—C2	106.24 (11)	C7—C8—C9	119.82 (12)
C5—N4—C3	118.59 (11)	C9*A*—C9—C8	116.94 (11)
C5—N4—C9*A*	124.36 (11)	N4—C9*A*—S1	105.54 (9)
C3—N4—C9*A*	114.48 (10)	C9—C9*A*—S1	110.99 (9)
N4—C5—C6	118.50 (12)		
N4—C5—C6—O4	−58.52 (15)	N5—C7—C8—C9	−75.46 (15)
C5—C6—C7—N5	47.00 (15)	C7—C8—C9—O6	78.73 (15)
O4—C6—C7—C8	47.55 (16)	N8—C8—C9—C9*A*	75.08 (14)
C6—C7—C8—N8	−76.07 (15)	O6—C9—C9*A*—N4	−52.54 (14)

Methyl groups were refined with idealized geometry [C—H = 0.98 Å, H—C—H = 109.5° and U_{iso}(H) = 1.5U_{eq}(C)], with torsion angles refined to fit the electron density. All other H atoms were located and refined isotropically. The resulting C—H bond lengths are in the range 0.941 (17)–1.034 (17) Å.

Data collection: *X-AREA* (Stoe & Cie, 2003; cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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