C9	0.1931 (2)	0.03067 (7)	0.5709 (2)	3.64 (3)
C10	0.1150 (2)	0.04569 (7)	0.6830 (2)	3.68 (3)
C11	0.2480 (2)	−0.07805 (8)	0.9718 (2)	4.22 (3)
C13	0.4259 (2)	−0.14583 (8)	1.1393 (2)	4.31 (3)
C14*c*	0.5818 (3)	−0.1660 (1)	1.1269 (3)	6.21 (5)
C14*b*	0.3185 (3)	−0.1996 (1)	1.1253 (3)	5.91 (5)
C14*a*	0.4315 (3)	−0.1098 (1)	1.2832 (2)	5.99 (5)
C15	−0.0731 (3)	0.1948 (1)	0.5227 (3)	5.59 (5)
C16	−0.0109 (4)	0.2416 (1)	0.4353 (3)	7.56 (7)
C17	0.0118 (4)	0.2151 (1)	0.2875 (3)	7.50 (7)
C19	0.1708 (4)	0.1419 (1)	0.1859 (3)	7.12 (7)
C20*a*	0.2955 (5)	0.1027 (2)	0.2321 (5)	4.77 (8)
C20*b*	0.2249 (7)	0.0797 (2)	0.1841 (5)	5.9 (1)
C21	0.2784 (3)	0.0490 (1)	0.3303 (2)	5.66 (5)

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

O1—C2	1.379 (2)	C3—C11	1.487 (2)
O1—C9	1.368 (2)	C6—C15	1.519 (2)
O2—C2	1.203 (2)	C8—C21	1.503 (2)
O11—C11	1.204 (2)	C15—C16	1.479 (4)
O12—C11	1.327 (2)	C16—C17	1.513 (4)
O12—C13	1.478 (2)	C19—C20*a*	1.411 (5)
N18—C7	1.363 (2)	C19—C20*b*	1.446 (6)
N18—C17	1.456 (3)	C20*a*—C21	1.499 (4)
N18—C19	1.453 (3)	C20*b*—C21	1.466 (5)
C2—O1—C9	123.5 (1)	C15—C16—C17	110.8 (2)
C11—O12—C13	122.1 (1)	N18—C17—C16	112.3 (2)
C7—N18—C17	121.8 (2)	N18—C19—C20*a*	112.9 (2)
C7—N18—C19	121.4 (2)	N18—C19—C20*b*	117.6 (2)
C17—N18—C19	116.1 (2)	C19—C20*a*—C21	117.8 (3)
O11—C11—O12	125.1 (2)	C19—C20*b*—C21	117.6 (3)
O11—C11—C3	122.6 (2)	C8—C21—C20*a*	110.3 (2)
O12—C11—C3	112.3 (1)	C8—C21—C20*b*	112.8 (3)
O11—C11—C3—C4	25.5 (3)	N18—C7—C6—C15	2.1 (3)
O11—C11—O12—C13	5.8 (3)	C8—C7—N18—C19	8.2 (3)
C17—N18—C19—C20*a*	158.6 (3)	C7—N18—C19—C20*a*	−30.4 (4)
C17—N18—C19—C20*b*	−163.1 (4)	C7—N18—C19—C20*b*	7.9 (5)
C7—C6—C15—C16	−28.1 (3)	N18—C19—C20*a*—C21	47.2 (5)
C6—C15—C16—C17	52.7 (3)	N18—C19—C20*b*—C21	−30.3 (7)
N18—C17—C16—C15	−53.8 (4)	C8—C21—C20*a*—C19	−40.3 (5)
C7—N18—C17—C16	28.4 (4)	C8—C21—C20*b*—C19	34.7 (6)
C16—C17—N18—C19	−160.7 (3)	C7—C8—C21—C20*a*	16.7 (3)
C6—C7—N18—C17	−2.5 (3)	C7—C8—C21—C20*b*	−19.3 (4)
N18—C7—C8—C21	−1.8 (3)		

Most non-H atoms were located by direct methods using the program *SAPI*91 (Fan, 1991). The other non-H atoms and most H atoms were found from difference Fourier maps. The positions of the remaining H atoms, except those attached to atoms C19, C20 and C21, were calculated geometrically. All non-H atoms were refined anisotropically and some H atoms isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 Software. Program(s) used to solve structure: *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1992). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structural Studies of Mitomycins. VIII. Mitomycin D Hydrate, $C_{15}H_{18}N_4O_5.1.5H_2O$

N. HIRAYAMA,[a] H. ARAI[b] AND M. KASAI[b]

[a]*Department of Biological Science and Technology, Tokai University, 317 Nishino, Numazu, Shizouka 410-03, Japan, and* [b]*Pharmaceutical Research Laboratories, Kyowa Hakko Kogyo Co. Ltd, 1188 Shimotogari, Nagaizumi-cho, Suntogun, Shizouka 411, Japan*

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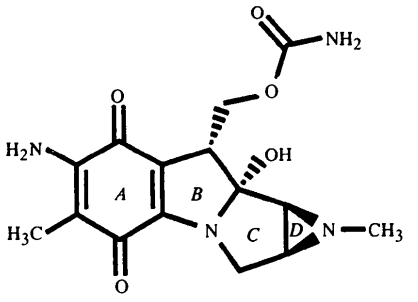
Abstract

The title compound, [1a*S*]-6-amino-1,1a,2,4,7,8,8a,8b-octahydro-8a-hydroxy-1,5-dimethyl-4,7-dioxoazirino[2′,-3′:3,4]pyrrolo[1,2-*a*]indol-7-ylmethyl, is a mitomycin derivative, mitomycins being antitumor antibiotics. The O atoms of the quinone ring deviate significantly from the least-squares plane through the quinone ring.

Comment

Mitomycins are very effective antitumor antibiotics. An understanding of the relationships between the three-dimensional structures and their biological activities is very important when designing better antitumor agents.



(I)

We have undertaken the structural analysis of a series of mitomycins to determine these relationships. The title compound, (I), was isolated from the fermentation broth of *Streptomyces*.

An *ORTEP*II (Johnson, 1976) drawing of the molecule together with the atomic numbering system is shown in Fig. 1. The absolute configuration of the molecule was suggested by referring to that of 7-*p*-bromoanilino-7-demethoxymitomycin B (Hirayama & Shirahata, 1987). The bond lengths are in the range observed in other mitomycins. The exocyclic bond angles around the C5, C7 and C8 atoms are highly asymmetric. The sum of the bond angles around the N4 atom is 354.1 (5)° and indicates that the N atom adopts a planar configuration. The carbamoylmethyl group has an extended conformation. The dihedral angles between the least-squares planes through the rings are as follows: 6.0 (6)° between rings *A* and *B*, 39.3 (5)° between *B* and *C*, and 79.0 (5)° between *C* and *D*. The dihedral angle between ring *A* and the least-squares plane through the carbamoyl group is 73.1 (7)°. The mean deviation of the atoms in ring *A* is 0.017 (6) Å and the deviations of the atoms O5 and O8 from this plane are −0.152 (6) and 0.099 (6) Å, respectively. Significant deviations of the quinone O atoms from the quinone ring are also observed in other mitomycins. In mitomycin C (Arora, 1979) and *N*-(*p*-bromobenzoyl)mitomycin A (Hirayama & Shirahata, 1987), however, the O atoms are located on the same side of the ring. The crystal structure is built up *via* intermolecular O9a—H···N1a($-\frac{3}{2}-x$, $-\frac{1}{2}+y$, $-\frac{7}{4}-z$) hydrogen bonds [O···N 2.750 (7) Å, O—H···N 133°].

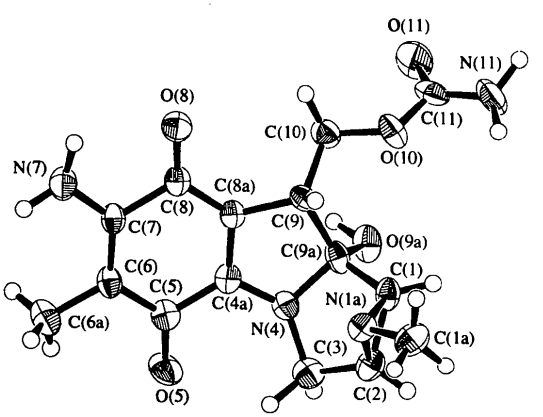


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound showing the atomic numbering. Displacement ellipsoids are shown at the 50% probability level for non-H atoms and the H atoms are shown as small spheres of arbitrary size.

Experimental

The crystals were grown from an aqueous ethanol solution.

Crystal data

$C_{15}H_{18}N_4O_5.1.5H_2O$	Cu $K\alpha$ radiation
M_r = 361.35	λ = 1.54184 Å
Tetragonal	Cell parameters from 25 reflections
$P4_12_12$	θ = 30–35°
a = 9.552 (4) Å	μ = 0.973 mm^{-1}
c = 36.413 (9) Å	T = 293 (2) K
V = 3322 (1) Å^3	Needle
Z = 8	0.3 × 0.15 × 0.15 mm
D_x = 1.45 Mg m^{-3}	Deep violet
D_m not measured	

Data collection

Enraf–Nonius CAD-4 Turbo diffractometer	θ_{max} = 67.9°
$\omega/2\theta$ scans	h = 0 → 11
Absorption correction: none	k = 0 → 8
1903 measured reflections	l = 0 → 41
1903 independent reflections	3 standard reflections
1411 observed reflections [$F > 3\sigma(F)$]	frequency: 60 min
	intensity decay: −2.85%

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.01
R = 0.055	$\Delta\rho_{max}$ = 0.34 e Å^{-3}
wR = 0.067	$\Delta\rho_{min}$ = −0.30 e Å^{-3}
S = 2.33	Extinction correction: none
1411 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
231 parameters	
H atoms: see text	
$w = 1/\sigma^2(F)$	

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

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
O(5)	−0.4781 (4)	−0.0742 (5)	−0.8081 (1)	4.2 (1)
O(8)	−1.0097 (5)	0.0987 (5)	−0.7898 (1)	3.3 (1)
O(9a)	−0.8478 (5)	−0.2965 (5)	−0.8841 (1)	3.4 (1)
O(10)	−1.1184 (5)	−0.1489 (5)	−0.8934 (1)	3.5 (1)
O(11)	−1.2548 (6)	−0.3335 (6)	−0.8780 (1)	5.2 (1)
N(1a)	−0.7187 (6)	0.0300 (6)	−0.9236 (1)	2.7 (1)
N(4)	−0.6867 (6)	−0.1285 (6)	−0.8619 (1)	2.6 (1)
N(7)	−0.8231 (6)	0.1737 (6)	−0.7404 (1)	3.4 (1)
N(11)	−1.2461 (7)	−0.2464 (7)	−0.9362 (2)	4.8 (2)
C(1a)	−0.7380 (8)	0.0945 (8)	−0.9599 (2)	3.8 (2)
C(1)	−0.7855 (7)	−0.1090 (7)	−0.9207 (2)	2.9 (2)
C(2)	−0.6280 (8)	−0.0969 (7)	−0.9234 (2)	3.1 (2)
C(3)	−0.5633 (8)	−0.1257 (7)	−0.8865 (2)	3.3 (2)
C(4a)	−0.7111 (7)	−0.0625 (6)	−0.8301 (2)	2.4 (1)
C(5)	−0.5968 (7)	−0.0253 (7)	−0.8035 (2)	2.8 (2)
C(6a)	−0.5262 (7)	0.1105 (7)	−0.7468 (2)	3.9 (2)
C(6)	−0.6373 (7)	0.0598 (7)	−0.7732 (2)	2.7 (2)
C(7)	−0.7752 (7)	0.0976 (7)	−0.7684 (2)	2.5 (2)
C(8a)	−0.8499 (7)	−0.0313 (6)	−0.8249 (2)	2.3 (1)
C(8)	−0.8914 (7)	0.0512 (7)	−0.7950 (2)	2.5 (2)
C(9a)	−0.8195 (7)	−0.1529 (7)	−0.8817 (2)	2.8 (2)
C(9)	−0.9289 (7)	−0.0631 (7)	−0.8601 (2)	2.4 (1)
C(10)	−1.0670 (7)	−0.1381 (7)	−0.8560 (2)	3.1 (2)
C(11)	−1.2112 (7)	−0.2521 (8)	−0.9008 (2)	3.4 (2)
O(W1)	−0.8424 (6)	−0.1242 (6)	−0.0580 (1)	5.2 (1)
O(W2)	0.0533 (7)	0.053	1/2	11.9 (3)

Table 2. *Geometric parameters (Å, °)*

O(5)—C(5)	1.238 (8)	C(1)—C(2)	1.512 (9)
O(8)—C(8)	1.232 (7)	C(1)—C(9a)	1.516 (8)
O(9a)—C(9a)	1.400 (8)	C(2)—C(3)	1.505 (9)
O(10)—C(10)	1.451 (7)	C(4a)—C(5)	1.501 (9)
O(10)—C(11)	1.353 (8)	C(4a)—C(8a)	1.373 (9)
O(11)—C(11)	1.211 (8)	C(5)—C(6)	1.424 (8)

N(1a)—C(1a)	1.468 (8)	C(6a)—C(6)	1.512 (9)
N(1a)—C(1)	1.477 (8)	C(6)—C(7)	1.377 (9)
N(1a)—C(2)	1.491 (8)	C(7)—C(8)	1.539 (8)
N(4)—C(3)	1.481 (8)	C(8a)—C(8)	1.400 (8)
N(4)—C(4a)	1.338 (7)	C(8a)—C(9)	1.520 (8)
N(4)—C(9a)	1.478 (7)	C(9a)—C(9)	1.563 (9)
N(7)—C(7)	1.332 (7)	C(9)—C(10)	1.508 (9)
N(11)—C(11)	1.335 (9)		
C(10)—O(10)—C(11)	117.4 (6)	N(7)—C(7)—C(6)	124.7 (6)
C(1a)—N(1a)—C(1)	112.8 (5)	N(7)—C(7)—C(8)	113.0 (6)
C(1a)—N(1a)—C(2)	114.8 (5)	C(6)—C(7)—C(8)	122.3 (6)
C(1)—N(1a)—C(2)	61.3 (4)	C(4a)—C(8a)—C(8)	120.3 (6)
C(3)—N(4)—C(4a)	130.8 (6)	C(4a)—C(8a)—C(9)	108.6 (6)
C(3)—N(4)—C(9a)	113.0 (5)	C(8)—C(8a)—C(9)	128.9 (6)
C(4a)—N(4)—C(9a)	110.3 (5)	O(8)—C(8)—C(7)	117.3 (6)
N(1a)—C(1)—C(2)	59.8 (4)	O(8)—C(8)—C(8a)	126.0 (6)
N(1a)—C(1)—C(9a)	114.2 (5)	C(7)—C(8)—C(8a)	116.5 (6)
C(2)—C(1)—C(9a)	107.2 (6)	O(9a)—C(9a)—N(4)	110.5 (5)
N(1a)—C(2)—C(1)	58.9 (4)	O(9a)—C(9a)—C(1)	104.8 (5)
N(1a)—C(2)—C(3)	113.2 (5)	O(9a)—C(9a)—C(9)	116.1 (6)
C(1)—C(2)—C(3)	109.7 (6)	N(4)—C(9a)—C(1)	103.3 (5)
N(4)—C(3)—C(2)	102.5 (6)	N(4)—C(9a)—C(9)	104.0 (5)
N(4)—C(4a)—C(5)	122.9 (6)	C(1)—C(9a)—C(9)	117.5 (6)
N(4)—C(4a)—C(8a)	113.0 (6)	C(8a)—C(9)—C(9a)	101.7 (5)
C(5)—C(4a)—C(8a)	124.2 (6)	C(8a)—C(9)—C(10)	116.4 (5)
O(5)—C(5)—C(4a)	119.3 (6)	C(9a)—C(9)—C(10)	112.0 (5)
O(5)—C(5)—C(6)	124.7 (7)	O(10)—C(10)—C(9)	103.6 (5)
C(4a)—C(5)—C(6)	115.9 (6)	O(10)—C(11)—O(11)	123.9 (7)
C(5)—C(6)—C(6a)	119.0 (6)	O(10)—C(11)—N(11)	109.1 (7)
C(5)—C(6)—C(7)	120.6 (6)	O(11)—C(11)—N(11)	127.1 (7)
C(6a)—C(6)—C(7)	120.4 (6)		
O(10)—C(10)—C(9)—C(8a)	178.1 (5)		
C(9)—C(10)—O(10)—C(11)	156.4 (6)		
O(11)—C(11)—O(10)—C(10)	1 (1)		

All non-H atoms were located by the direct methods using the programs *SAPI*90 (Fan, 1990) and *DIRDIF* (Beurskens *et al.*, 1992). All H atoms except those of water molecules (which were not located) were found from difference Fourier maps. All non-H atoms were refined anisotropically and all H atoms were fixed. One water molecule is located on the twofold axis.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SAPI*90 (Fan, 1990), *DIRDIF* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1992). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acetone 4,4-Dimethyl-5-oxo-2-pyrazolin-3-ylhydrazone

CAL Y. MEYERS,[a] HISHAM G. LUTFI,[a] VERA M. KOLB,[b] YUQING HOU[a] AND PAUL D. ROBINSON[c]

[a]*Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901-4409, USA,* [b]*Department of Chemistry, University of Wisconsin-Parkside, Kenosha, WI 53141-2000, USA, and* [c]*Department of Geology, Southern Illinois University, Carbondale, IL 62901-4324, USA. E-mail: robinson@geo.siu.edu*

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Abstract

The title compound, $C_8H_{14}N_4O$, exhibits an overall molecular coplanarity and trigonal planar geometry of all four N atoms, suggesting resonance interaction extending over eight contiguous atoms. Strong hydrogen bonding between hydrazidic-N donor and carbonyl-O acceptor atoms results in an almost-planar octagonal bridge between two molecules. These dimers are interconnected through a second octagonal bridge of weaker hydrogen bonds between side-chain hydrazine-N donor and ring-N acceptor atoms, leading to an almost-flat linear polymeric structure. The acetone–hydrazone N atom does not participate in hydrogen bonding. From the structure of the title compound, the unequivocal identification of 4,4-dimethyl-5-oxo-2-pyrazolin-3-ylhydrazine, an unexpected byproduct of the reaction of 4,4-dimethylpyrazolidine-3,5-dione with hydrazine, was made.

Comment

We recently prepared 4,4-dimethylpyrazolidine-3,5-dione (1) by refluxing diethyl dimethylmalonate with hydrazine hydrate for 5–8 days (Kolb, Colloton, Robinson, Lutfi & Meyers, 1996) following the methodology reported by Gillis & Izydore (1969) for the preparation of the 4,4-diethyl analog of (1). While Gillis & Izydore did not report the formation of byproducts, our analogous reaction carried out under varying temperatures, produced a mixture of products. Under moderate reaction temperatures, the desired compound (1) was isolated by selective solubility or chromatography. Higher temperatures led to an additional product which could be identified by ^{1}H and ^{13}C NMR only as (3*a*), or *Z* or *E* (3*b*) and which, on recrystallization from acetone, afforded yet another compound identifiable by ^{1}H and ^{13}C only as (4*a*), or *Z* or *E* (4*b*). Further study revealed that (3) was produced when (1) reacted with hydrazine hydrate and that (4) was formed from (3) reacting with acetone. These reactions are summarized in the scheme