(Stoe & Cie, 1992*a*). Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*-76 (Sheldrick, 1976). Molecular graphics: *PLUTON*93 (Spek, 1993). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Unusual C-4a Hydroxylated Decahydroquinolone

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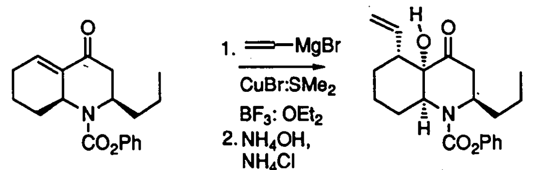
Abstract

The crystal structure and the relative stereochemistry of the four asymmetric centers of an unusual C-4a hydroxylated decahydroquinolone, phenyl 1,2α,3,4,4aα,5β,6,7,8,8aα-decahydro-4a-hydroxy-4-oxo-2-propyl-5-vinylquinoline-1-carboxylate, $C_{21}H_{27}NO_4$, are reported. The H and OH groups at the ring juncture are *cis* to each other as are the two H atoms α to the N atom. The vinyl and OH groups are also *cis* to each other. The N atom is sp^2 hybridized.

Comment

The title compound (I) was obtained during our model studies aimed at the synthesis of (±)-gephyrotoxin (Comins & Joseph, 1991; Fujimoto, Kishi & Blount, 1980; Hart & Kanai, 1983; Overman, Lesuisse & Hashimoto, 1983). It was synthesized by the copper-catalyzed addition of vinylmagnesium bromide to the enone (II) at 195 K, and quenching the reaction mixture cold, as shown below. The reaction was completely stereoselective (Comins & Dehghani, 1991). The relative stereochemistry is shown in Fig. 1, which shows that the introduction of the OH group α to the carbonyl occurs from the same face as the vinyl substituent, the ring juncture is *cis*, and both H atoms α to the N atom are *cis*. The N atom is sp^2 hybridized; the sum of the three bond angles around the N atom is 359.8°.



(II) (I)

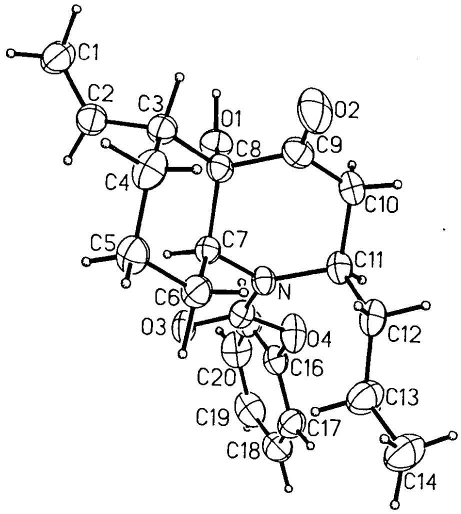


Fig. 1. Displacement ellipsoid plot (30% probability ellipsoids) showing the numbering scheme and the relative configurations of the four asymmetric centers (C3, C7, C8, C11). For clarity, atom C15 (which is attached to N) and the phenyl carbon C21 are not labeled.

Experimental

Crystal data

$C_{21}H_{27}NO_4$
$M_r = 357.45$
Monoclinic
$P2_1/n$
$a = 13.764\ (5)$ Å
$b = 7.787\ (7)$ Å
$c = 18.047\ (9)$ Å
$\beta = 92.83\ (3)°$
$V = 1932\ (2)$ Å^3
$Z = 4$

$D_x = 1.23$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10\text{-}15°$
$\mu = 0.079$ mm^{-1}
$T = 298$ K
Plate
0.62 × 0.43 × 0.25 mm
Colorless

Data collection

Siemens *R*3*m*/μ diffractometer
ω scans
Absorption correction: none
2775 measured reflections
2529 independent reflections
1722 observed reflections $[|F_o| \geq 4\sigma(|F_o|)]$

$R_{\rm int} = 0.034$
$\theta_{\rm max} = 22.5°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 19$
2 standard reflections monitored every 48 reflections
intensity variation: 2.4%

Refinement

Refinement on *F*
$R = 0.048$
$wR = 0.050$
$S = 1.40$
1722 reflections
336 parameters
$w = 1/[\sigma^2(F_o) + 0.00028F_o^2]$
$(\Delta/\sigma)_{\rm max} = 0.06$

$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: 2.0 (3) × 10^{-6} (secondary)
Atomic scattering factors from *SHELXTL* (Sheldrick, 1985)

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	$U_{\rm eq}$
C(1)	0.2982 (3)	0.1915 (5)	0.5463 (2)	0.073 (2)
C(2)	0.2266 (3)	0.1819 (4)	0.5904 (2)	0.058 (1)
C(3)	0.1481 (2)	0.3151 (4)	0.5944 (2)	0.052 (1)
C(4)	0.0524 (3)	0.2512 (5)	0.5573 (2)	0.067 (1)
C(5)	0.0031 (2)	0.1169 (5)	0.6034 (2)	0.066 (1)
C(6)	−0.0170 (2)	0.1881 (4)	0.6802 (2)	0.057 (1)
C(7)	0.0767 (2)	0.2517 (4)	0.7189 (2)	0.044 (1)
C(8)	0.1344 (2)	0.3791 (4)	0.6739 (2)	0.045 (1)
C(9)	0.0856 (2)	0.5554 (4)	0.6752 (2)	0.056 (1)
C(10)	0.0700 (3)	0.6234 (4)	0.7508 (2)	0.060 (1)
C(11)	0.0208 (2)	0.4975 (4)	0.8025 (2)	0.051 (1)
N	0.0618 (2)	0.3226 (3)	0.7937 (1)	0.044 (1)
C(12)	−0.0902 (3)	0.5019 (5)	0.7923 (2)	0.057 (1)
C(13)	−0.1426 (3)	0.3877 (5)	0.8431 (2)	0.082 (2)
C(14)	−0.2527 (3)	0.4026 (6)	0.8359 (2)	0.091 (2)
O(1)	0.2260 (1)	0.3987 (3)	0.7148 (1)	0.057 (1)
O(2)	0.0642 (2)	0.6356 (3)	0.6196 (1)	0.094 (1)
C(15)	0.0946 (2)	0.2265 (4)	0.8517 (2)	0.047 (1)
O(3)	0.1271 (2)	0.0821 (3)	0.8489 (1)	0.057 (1)
O(4)	0.0849 (2)	0.3085 (3)	0.9181 (1)	0.067 (1)
C(16)	0.1244 (2)	0.2261 (4)	0.9816 (2)	0.050 (1)
C(17)	0.0631 (3)	0.1732 (5)	1.0345 (2)	0.062 (1)
C(18)	0.1004 (3)	0.0973 (5)	1.0987 (2)	0.073 (2)
C(19)	0.1980 (3)	0.0768 (5)	1.1095 (2)	0.080 (2)
C(20)	0.2578 (3)	0.1327 (5)	1.0572 (2)	0.075 (2)
C(21)	0.2227 (2)	0.2084 (4)	0.9927 (2)	0.061 (1)

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

C(1)—C(2)	1.299 (5)	C(2)—C(3)	1.502 (5)
C(3)—C(4)	1.532 (5)	C(3)—C(8)	1.539 (4)
C(4)—C(5)	1.517 (5)	C(5)—C(6)	1.530 (5)
C(6)—C(7)	1.519 (4)	C(7)—C(8)	1.529 (4)
C(7)—N	1.481 (4)	C(8)—C(9)	1.529 (4)
C(8)—O(1)	1.436 (3)	C(9)—C(10)	1.489 (5)
C(9)—O(2)	1.205 (4)	C(10)—C(11)	1.534 (5)
C(11)—N	1.486 (4)	C(11)—C(12)	1.531 (5)
N—C(15)	1.347 (4)	C(12)—C(13)	1.490 (5)
C(13)—C(14)	1.519 (5)	C(15)—O(3)	1.213 (4)
C(15)—O(4)	1.369 (4)	O(4)—C(16)	1.401 (4)
C(16)—C(17)	1.368 (5)	C(16)—C(21)	1.365 (5)
C(17)—C(18)	1.377 (5)	C(18)—C(19)	1.358 (6)
C(19)—C(20)	1.355 (5)	C(20)—C(21)	1.371 (5)
C(1)—C(2)—C(3)	124.0 (3)	C(2)—C(3)—C(4)	111.1 (3)
C(2)—C(3)—C(8)	113.0 (2)	C(4)—C(3)—C(8)	111.8 (3)
C(3)—C(4)—C(5)	112.5 (3)	C(4)—C(5)—C(6)	110.6 (3)
C(5)—C(6)—C(7)	110.4 (3)	C(6)—C(7)—C(8)	114.7 (2)
C(6)—C(7)—N	112.9 (2)	C(8)—C(7)—N	109.9 (2)
C(3)—C(8)—C(7)	112.1 (2)	C(3)—C(8)—C(9)	112.3 (2)
C(7)—C(8)—C(9)	109.5 (2)	C(3)—C(8)—O(1)	111.6 (2)
C(7)—C(8)—O(1)	105.2 (2)	C(9)—C(8)—O(1)	105.8 (2)
C(8)—C(9)—C(10)	114.6 (3)	C(8)—C(9)—O(2)	122.8 (3)
C(10)—C(9)—O(2)	122.5 (3)	C(9)—C(10)—C(11)	114.7 (2)
C(10)—C(11)—N	109.8 (3)	C(10)—C(11)—C(12)	112.4 (3)
N—C(11)—C(12)	113.0 (3)	C(7)—N—C(11)	120.7 (2)
C(7)—N—C(15)	116.4 (2)	C(11)—N—C(15)	122.7 (2)
C(11)—C(12)—C(13)	115.0 (3)	C(12)—C(13)—C(14)	114.4 (3)
N—C(15)—O(3)	126.4 (3)	N—C(15)—O(4)	112.2 (3)
O(3)—C(15)—O(4)	121.4 (3)	C(15)—O(4)—C(16)	116.9 (2)
O(4)—C(16)—C(17)	118.7 (3)	O(4)—C(16)—C(21)	120.6 (3)
C(17)—C(16)—C(21)	120.6 (3)	C(16)—C(17)—C(18)	119.9 (4)
C(17)—C(18)—C(19)	119.8 (4)	C(18)—C(19)—C(20)	119.5 (3)
C(19)—C(20)—C(21)	122.0 (3)	C(16)—C(21)—C(20)	118.3 (3)

Diffractometer software was provided by Siemens Analytical X-ray Instruments Inc. The structure was solved and refined using *SHELXTL* (Sheldrick, 1985). Positional and isotropic displacement parameters were refined for all H atoms except H(6*B*) and H(14*B*).

The authors wish to express their appreciation to the National Institutes of Health (grant GM 34442) for financial support of this research. Financial support from the National Science Foundation (grant CHE 8307022) for upgrading the X-ray diffractometer from $P\bar{1}$ to *P*3/*F* is also gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71744 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1094]

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2,3-Dihydro-6-hydroxy-1,3-dimethyl-7-propyl-9-(2-thienylmethyl)pyrimido[2,1-*f*]purine-4,8(1*H*,9*H*)-dione

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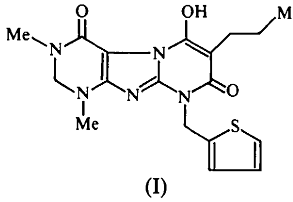
Abstract

The molecular structure of $C_{18}H_{21}N_5O_3S$ comprises an almost planar purine ring fused to a reduced pyrimidine ring. An intramolecular O···O distance of 2.492 (3) Å indicates the presence of hydrogen bonding.

Comment

The present compound (I) belongs to a series of substituted 2,3-dihydro-6-hydroxypyrimido[2,1-*f*]-purine-4,8(1*H*,9*H*)-diones having anti-inflammatory activity in the adjuvant-induced arthritis rat model. Crystal structure analysis has been carried out to show the effect of substituents on the molecular geometry and conformation.



(I)

The almost planar purine ring is fused to the reduced pyrimidine ring with dihedral angles of 4.4 (1) (between planes *A* and *B*) and 3.6 (1)° (between planes *B* and *C*). Only atom C2 of the reduced pyrimidine ring *A* deviates significantly from the best plane of the remaining ring atoms. The lengthening of the bond O13—C4 [1.265 (5) Å] from the normal C=O distance may be a result of the intramolecular O14···O13 hydrogen bonding. Atom C9 is bonded to three N atoms. The bond lengths indicate a double bond to N10 [1.313 (4) Å] and single bonds to N5 [1.394 (5) Å] and N9 [1.346 (3) Å]. The endocyclic angle around N9 is greater than those around N1 and N3. All these structural features are comparable to those in 2,2-dimethyl-1,2,3,4-tetrahydrobenzimidazo[3,2-*a*]pyrimid-4-one (Bird, Nyburg & Parkins, 1991). The conformation of the side chain relative to the fused ring system is described by the torsion angles about the bonds C7—C15 and C15—C16. The thiophene ring geometry is comparable to that found in 4-(4,6-dimethyl-2-pyridyl)-2-thiophene carboxamide (Rodier, Robert & Le Baut, 1992). The dihedral angle between the fused ring plane and the thiophene ring plane is 115.5 (2)°.

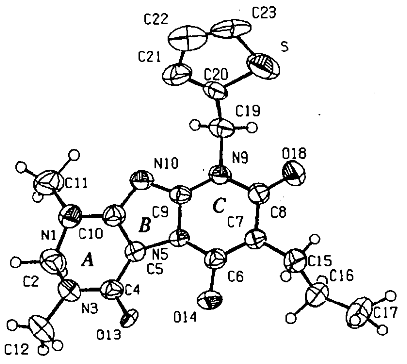


Fig. 1. A view of the molecule with 50% probability anisotropic displacement ellipsoids for the non-H atoms and atomic numbering scheme.

Experimental

The compound was synthesized and supplied by Dr James Kaminski, Pharmaceutical Research Division, New Jersey, USA. Crystals were obtained by slow evaporation from chloroform/methanol (1:1) solution.

Crystal data

$C_{18}H_{21}N_5O_3S$
$M_r = 387.4$
Monoclinic
$P2_1/a$
$a = 11.426$ (1) Å
$b = 16.090$ (1) Å
$c = 11.359$ (1) Å
$\beta = 118.37$ (1)°
$V = 1837.5$ (3) Å^3
$Z = 4$

$D_x = 1.401$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 58$–61°
$\mu = 1.77$ mm^{-1}
$T = 296$ K
Plate
$0.9 \times 0.7 \times 0.3$ mm
Colourless