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The Antifungal Agent 8-Ethyl-5,8-dihydro-5-oxo-2-(1-pyrrolidinyl)pyrido[2,3-*d*]-pyrimidine-6-carboxylic Acid (Piromidic Acid)

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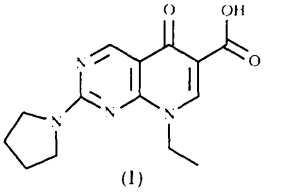
Abstract

The structure of the title compound, $C_{14}H_{16}N_4O_3$, was determined by single-crystal X-ray methods. The molecule is planar within ±0.15 Å except for the C atoms of the pyrrolidine ring and the *N*-ethyl group, which is displaced by −1.246 (3) Å from the mean plane. There is a significant difference between the two N—C bond lengths in the pyridine ring with the N1—C10 bond to the ring junction being longer by 0.039 (4) Å than N1—C2. The N—C bond lengths in the pyrimidine ring range from 1.306 (4) to 1.373 (3) Å; similar structural features have been reported for pipemidic acid. The *N*-ethyl group is approximately perpendicular to the plane of the pyrido–pyrimidinone moiety; the C2—N1—C11—C12 torsion angle is −93.2 (3)°. A single intramolecular hydrogen bond is observed between the H atom of the carboxylic acid group and the O atom of the ketone [O16···H—O15 2.525 (3) Å and 154 (1)°].

Comment

The title compound has been used as an antimicrobial agent in the treatment of urinary tract infections suspected to be caused by gram negative bacteria. Although the mechanism is not known exactly, it is known that the quinolones inhibit a subunit of DNA gyrase in bacteria (Timmers & Sternglanz, 1978). The crystal structures of the antibacterial quinoline agents nalidixic acid (Achari & Neidle, 1976), aminooxolinic acid (Czugler *et al.*, 1976), oxolinic acid (Cygler & Huber, 1985), pipemidic acid (Fonseca *et al.*, 1986) and cinoxacin (Rosales *et al.*, 1985) have been determined by X-ray analysis. We report here the structure of the title compound, (I).



(I)

The molecule contains a pyrrolidine ring joined to a pyrido–pyrimidine ring system. The dihedral angle between the least-squares planes is 7.46 (8)°. The substituents on the pyridine ring at N1, C3 and C4 are the same as those supported by the pyridine rings in nalidixic acid (Huber *et al.*, 1980), oxolinic acid (Cygler & Huber, 1985), aminooxolinic acid (Czugler *et al.*, 1976), pipemidic acid (Fonseca *et al.*, 1986), cinoxacin (Rosales *et al.*, 1985) and silver pefloxacin (Baenziger *et al.*, 1986). The geometric parameters for these substituents in the title compound are similar to those observed in the antibacterial quinolone compounds. The C4=O16 bond length of 1.261 (3) Å is in good agreement with that observed in oxolinic acid [1.259 (3) Å], nalidixic acid [1.261 (8) Å] and pefloxacin [1.254 (5) Å], while it is longer than that observed in pipemidic acid [1.237 (3) Å] and cinoxacin [1.248 (3) Å].

The pyrido–pyrimidinone moiety in the title compound is practically planar with a dihedral angle of 1.09 (6)° between the pyrimidine and pyridine rings. The N—C bond lengths in the pyrimidine ring range from 1.306 (4) to 1.373 (3) Å; this significant difference is also observed in pipemidic acid. The *N*-ethyl substituent in the title compound is almost perpendicular to the pyridine ring, and is slightly rotated about the C—N bond away from the carboxylic acid group. The C2—N1—C11—C12 torsion angle is −93.2 (3)°, in good agreement with values of −102.3 (2), −97.5, −97.3 (3) and −90.0° in oxolinic, aminooxolinic, pipemidic and nalidixic acid, respectively.

Cygler & Huber (1985) have presented a report on a group of highly active antibacterial agents, all presenting a strong intramolecular hydrogen bond between an O atom of the carboxylic acid group and the O atom of an adjacent carbonyl group. Timmers & Sternglanz (1978) suggested that oxolinic and nalidixic acid may exert their antibacterial activity by forming a complex *in situ* involving the 4-keto O atom and the ionized 3-carboxylic acid with a divalent cation in the metalloprotein involved in DNA replication. All members in this quinolone family have the 4-oxopyridine-3-carboxylic

acid moiety in common. The title compound also has a single intramolecular hydrogen bond, as depicted in Fig. 1 [O16···H—O15 2.525 (3) Å and 154 (1)°].

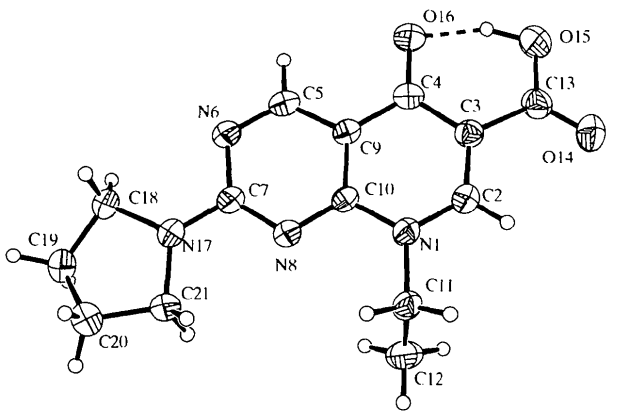


Fig. 1. The molecular structure of the title compound showing the numbering scheme. Displacement ellipsoids are drawn at 40% probability. The dashed line shows the intramolecular hydrogen bonding.

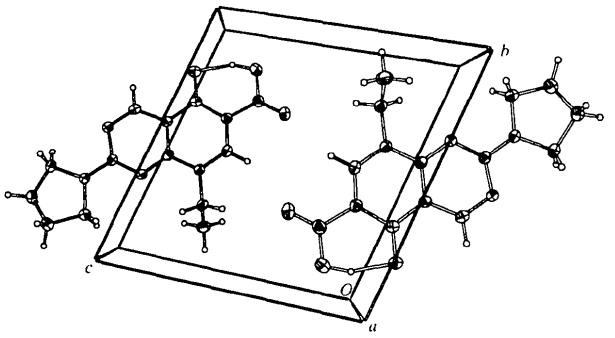


Fig. 2. The packing of the title compound.

Experimental

The title crystals were grown from chloroform/acetone (6:4) solution at room temperature.

Crystal data

$C_{14}H_{16}N_4O_3$
M_r = 288.31
Triclinic
$P\bar{1}$
a = 7.123 (1) Å
b = 10.149 (1) Å
c = 10.223 (2) Å
α = 103.33 (1)°
β = 109.79 (2)°
γ = 92.43 (2)°
V = 670.8 (3) Å^3
Z = 2
D_x = 1.427 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 2.2–12.8°
μ = 0.103 mm^{-1}
T = 293 (2) K
Needle
0.6 × 0.4 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2507 measured reflections
2362 independent reflections
1296 reflections with $I > 2\sigma(I)$

R_{int} = 0.014
θ_{max} = 25°
h = −8 → 8
k = 0 → 12
l = −12 → 11
3 standard reflections
frequency: 120 min
intensity decay: <1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.144
S = 1.056
2362 reflections
194 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.147 e Å^{-3}
$\Delta\rho_{min}$ = −0.219 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.346 (3)	C7—N8	1.343 (3)
N1—C10	1.385 (3)	N8—C10	1.325 (3)
N1—C11	1.486 (3)	C9—C10	1.409 (3)
C2—C3	1.367 (3)	C11—C12	1.498 (4)
C3—C4	1.438 (3)	C13—O14	1.204 (3)
C3—C13	1.477 (4)	C13—O15	1.329 (3)
C4—O16	1.261 (3)	N17—C21	1.469 (3)
C4—C9	1.431 (3)	N17—C18	1.469 (3)
C5—N6	1.306 (3)	C18—C19	1.507 (4)
C5—C9	1.398 (3)	C19—C20	1.503 (4)
N6—C7	1.373 (3)	C20—C21	1.519 (4)
C7—N17	1.330 (3)		
C2—N1—C10	119.2 (2)	C5—C9—C4	123.5 (2)
C2—N1—C11	120.2 (2)	C10—C9—C4	122.0 (2)
C10—N1—C11	120.6 (2)	N8—C10—N1	117.5 (2)
N1—C2—C3	124.5 (2)	N8—C10—C9	123.3 (2)
C2—C3—C4	119.6 (2)	N1—C10—C9	119.2 (2)
C2—C3—C13	118.8 (2)	N1—C11—C12	112.3 (2)
C4—C3—C13	121.6 (2)	O14—C13—O15	120.3 (2)
O16—C4—C9	122.1 (2)	O14—C13—C3	124.5 (3)
O16—C4—C3	122.5 (2)	O15—C13—C3	115.2 (2)
C9—C4—C3	115.4 (2)	C7—N17—C21	123.2 (2)
N6—C5—C9	125.0 (2)	C7—N17—C18	124.2 (2)
C5—N6—C7	114.8 (2)	C21—N17—C18	112.5 (2)
N17—C7—N8	117.6 (2)	N17—C18—C19	102.6 (2)
N17—C7—N6	115.9 (2)	C20—C19—C18	104.5 (2)
N8—C7—N6	126.4 (2)	C19—C20—C21	104.2 (2)
C10—N8—C7	115.9 (2)	N17—C21—C20	102.7 (2)
C5—C9—C10	114.5 (2)		

All H atoms were placed in idealized positions and included as riding atoms (except for those of methyl and OH groups) with fixed isotropic displacement parameters in the structure-factor calculations.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal*3.2 (Hall *et al.*, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX* (McArdle, 1995). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1074). Services for accessing these data are described at the back of the journal.

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Structure and Conformation of Photosynthetic Pigments and Related Compounds. XI.† 5,10,15,20-Tetrabutylbacteriochlorin

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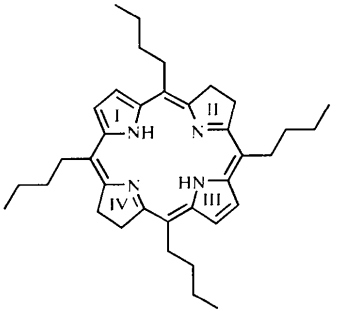
Abstract

The structure of the title compound, $C_{36}H_{50}N_4$, is the first example of a tetra-*meso*-substituted free-base bacteriochlorin (2,3,12,13-tetrahydroporphyrin). While general structural characteristics are similar to other hydroporphyrins, the present structure presents one of the few examples of a hydroporphyrin with a planar macrocycle conformation.

Comment

Bacteriochlorins are the main photoactive chromophores of photosynthetic bacteria (Scheer, 1989). They are distinguished from their parent porphyrins by a higher degree of saturation, *i.e.* they constitute 2,3,12,13-tetrahydroporphyrins. Despite their importance, few crystal structures of bacteriochlorins have been published, notably those of methyl bacteriopheophorbide a (Barkigia *et al.*, 1981, 1989; Barkigia & Gottfried, 1994) and three synthetic bacteriochlorins (Barkigia *et al.*, 1984, 1991; Waditschatka *et al.*, 1985). Renewed interest in this class of compounds arose from current studies on the conformation flexibility of tetrapyrroles (Barkigia *et al.*, 1988), which is believed to allow a modulation of the physicochemical chromophore properties *in vivo*; see Senge (1992) for a general review. No structure of tetra-*meso*-substituted free-base bacteriochlorin was known and so we performed a structure determination of the title compound, (I), as a basis for further theoretical studies.



(I)

The general structural characteristics are typical for a tetrahydroporphyrin. This includes the Cβ—Cβ single bond in the reduced pyrrole ring [C7—C8 = 1.512 (2) Å *versus* C2—C3 = 1.374 (2) Å], a slightly smaller Cα—N—Cα angle in ring II [109.0 (1)°], localization of the pyrrole H atoms at the pyrrole rings, and core expansion compared with the respective porphyrins; see Barkigia & Gottfried (1994) for a detailed description of bacteriochlorin characteristics. For example, the core size (defined as the vector length from the geometric centre of the four N atoms to the N atoms) is 2.149 (5) Å in the title compound compared with 2.059 (6) Å in the parent porphyrin. The structural differences between the pyrrole and pyrroline quadrants are smaller in the title compound than, for example, in bacteriopheophorbide a. The macrocycle exhibits a planar conformation. The average deviation of the 24 macrocycle atoms from their least-squares plane is 0.018 (2) Å. The largest deviations are observed for the Cβ atoms C2 and C3, which are displaced from the least-squares plane of the four N atoms by 0.06 (1) and 0.07 (1) Å, respectively. The tilt of the pyrrole rings is minimal; ring I is tilted by 2.0 (1)° and the reduced ring II by 0.40 (5)° against the N_4 plane. In contrast to other bacteriochlorin structures, the title compounds packs in the crystal without formation of π stacks. Instead, the molecules pack in a '—|—|'-type arrangement. The packing, unit-cell parameters and coordinate positions for the non-H atoms are very similar to those of the parent 5,10,15,20-

† Part X: Senge & Smith (1997). *Acta Cryst.* C**53**, 1314–1318.