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8-Hydroxy-3,4,5-trimethyl-6-oxo-2,3,4,6-tetrahydroisoquinoline-7-carboxylic acid

Hui Zhao[a] and Hai-Bin Gong[a,b]*

[a]School of Environment and Urban Construction, Wuhan University of Science and Engineering, Wuhan 430073, People's Republic of China, and [b]Xuzhou Central Hospital, Xuzhou 221009, People's Republic of China
Correspondence e-mail: adler_20008@yahoo.com.cn

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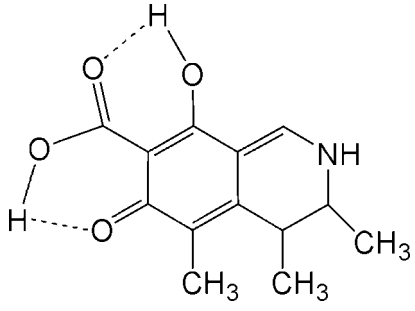
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.008 Å; R factor = 0.068; wR factor = 0.231; data-to-parameter ratio = 8.1.

In the natural product title compound, $C_{13}H_{15}NO_4$, intramolecular O—H···O hydrogen bonds help to establish the conformation.

Related literature

For background, see: Jiao *et al.* (2006); Shen *et al.* (2006).



Experimental

Crystal data

$C_{13}H_{15}NO_4$
M_r = 249.26
Orthorhombic, $P2_12_12_1$
a = 7.287 (1) Å
b = 12.228 (2) Å
c = 13.431 (2) Å
V = 1196.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 (2) K
0.33 × 0.26 × 0.20 mm

Data collection

Bruker APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.967, T_{max} = 0.980
2616 measured reflections
1370 independent reflections
908 reflections with $I > 2\sigma(I)$
R_{int} = 0.062

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.231
S = 1.13
1370 reflections
169 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O1	0.82	1.79	2.522 (6)	147
O3—H3···O2	0.82	1.70	2.456 (7)	152

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2541).

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supplementary materials

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8-Hydroxy-3,4,5-trimethyl-6-oxo-2,3,4,6-tetrahydroisoquinoline-7-carboxylic acid

H. Zhao and H.-B. Gong

Comment

The title compound, (I) (Fig. 1), was isolated from the endophytic fungus Aspergillus terreus (Jiao *et al.*, 2006; Shen *et al.*, 2006).

There exist strong intramolecular hydrogen bonds (Table 1) between the hydroxyl group, carbonyl group and the neighboring carboxyl group. Conversely, the N—H group does not participate in an H bonding interaction.

Experimental

The endophytic fungus Aspergillus terreus was cultured in modified Czapedox media at 298 K for 4 days. The fermentation broth (40 l) was extracted three times with an equal volume of ethyl acetate. The extract was concentrated in vacuo to give a dark brown residue (15 g). The extract was divided into three fractions by column chromatography on silica gel (gradient of chloroform and acetone from 1:0 to 0:1). Fraction 2 (3.1 g) was rechromatographed on silica gel CC (chloroform–acetone from 1:0 to 0:1) to give 3 fractions. Fraction 2–1 (0.6 g) was then subjected to gel filtration on Sephadex LH-20 with chloroform/acetone (1:1 *v*/*v*), followed by recrystallization in methanol to give colourless prisms of (I) (12 mg).

Refinement

Amonalous dispersion was negligible and Friedel pairs were merged before refinement. The H atoms were geometrically placed (C—H = 0.96 Å, N—H = 0.86 Å, O—H = 0.82 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(N, O).

Figures

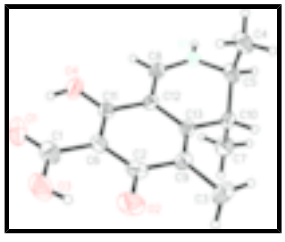

Fig. 1. The molecular structure of (I), showing 30% probability displacement ellipsoids (arbitrary spheres for the H atoms). The H bonds are shown as double-dashed lines.

8-Hydroxy-3,4,5-trimethyl-6-oxo-2,3,4,6-tetrahydroisoquinoline-7-carboxylic acid

Crystal data

$C_{13}H_{15}NO_4$	F_{000} = 528
M_r = 249.26	D_x = 1.383 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation

	λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 1842 reflections
a = 7.287 (1) Å	θ = 3.9–26.1º
b = 12.228 (2) Å	μ = 0.10 mm^{-1}
c = 13.431 (2) Å	T = 293 (2) K
V = 1196.8 (3) $Å^3$	Prism, colourless
Z = 4	0.33 × 0.26 × 0.20 mm

Data collection

Bruker APEX CCD diffractometer	1370 independent reflections
Radiation source: fine-focus sealed tube	908 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.062
T = 293(2) K	θ_{max} = 26.0º
φ and ω scans	θ_{min} = 3.0º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -8 \rightarrow 0$
T_{min} = 0.967, T_{max} = 0.980	$k = -15 \rightarrow 0$
2616 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.122P)^2 + 0.2523P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.068	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.231	$\Delta\rho_{max}$ = 0.23 e $Å^{-3}$
S = 1.13	$\Delta\rho_{min}$ = −0.27 e $Å^{-3}$
1370 reflections	Extinction correction: SHELXTL (Sheldrick, 1997b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
169 parameters	Extinction coefficient: 0.049 (10)
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculat-

ing *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.2486 (9)	0.0956 (5)	0.5965 (3)	0.0960 (17)
O2	0.2630 (9)	0.4173 (4)	0.5363 (3)	0.0953 (17)
O3	0.2521 (10)	0.2633 (5)	0.6536 (3)	0.0976 (17)
H3	0.2547	0.3259	0.6317	0.146*
O4	0.2366 (9)	0.0607 (3)	0.4115 (3)	0.0792 (14)
H4	0.2415	0.0459	0.4710	0.119*
N1	0.2007 (6)	0.1738 (4)	0.1281 (3)	0.0496 (12)
H1A	0.2084	0.1284	0.0794	0.060*
C1	0.2474 (10)	0.1954 (6)	0.5811 (4)	0.0717 (17)
C2	0.2599 (10)	0.3531 (5)	0.4628 (4)	0.0603 (14)
C3	0.2923 (12)	0.5152 (5)	0.3514 (6)	0.093 (3)
H3A	0.3051	0.5334	0.2822	0.140*
H3B	0.4002	0.5379	0.3869	0.140*
H3C	0.1870	0.5519	0.3783	0.140*
C4	−0.0359 (8)	0.3097 (7)	0.1240 (5)	0.080 (2)
H4A	−0.0711	0.2932	0.1913	0.120*
H4B	−0.1044	0.2645	0.0789	0.120*
H4C	−0.0611	0.3853	0.1102	0.120*
C5	0.1633 (8)	0.2883 (6)	0.1112 (4)	0.0622 (16)
H5	0.1943	0.3044	0.0418	0.075*
C6	0.2512 (9)	0.2392 (4)	0.4798 (3)	0.0488 (12)
C7	0.4873 (9)	0.3503 (6)	0.1487 (6)	0.082 (2)
H7A	0.5242	0.2750	0.1509	0.122*
H7B	0.5596	0.3918	0.1949	0.122*
H7C	0.5055	0.3783	0.0826	0.122*
C8	0.2225 (8)	0.1417 (4)	0.2208 (4)	0.0537 (14)
H8	0.2251	0.0669	0.2335	0.064*
C9	0.2687 (9)	0.3954 (4)	0.3621 (4)	0.0581 (14)
C10	0.2846 (8)	0.3595 (4)	0.1765 (4)	0.0544 (15)
H10	0.2463	0.4359	0.1690	0.065*
C11	0.2446 (9)	0.1666 (4)	0.3999 (4)	0.0497 (12)
C12	0.2417 (7)	0.2116 (4)	0.3000 (3)	0.0449 (11)
C13	0.2605 (8)	0.3260 (4)	0.2858 (3)	0.0493 (12)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.115 (4)	0.100 (4)	0.073 (3)	0.007 (4)	0.002 (4)	0.037 (3)
O2	0.122 (4)	0.098 (3)	0.066 (3)	0.004 (4)	−0.007 (3)	−0.034 (3)
O3	0.123 (4)	0.120 (4)	0.050 (2)	−0.003 (5)	−0.007 (3)	−0.004 (2)
O4	0.109 (4)	0.060 (2)	0.069 (2)	−0.011 (3)	0.003 (3)	0.0073 (19)
N1	0.061 (3)	0.056 (2)	0.032 (2)	0.009 (2)	−0.0030 (18)	−0.0085 (19)

C1	0.060 (4)	0.095 (5)	0.060 (3)	0.009 (5)	0.000 (4)	0.000 (3)
C2	0.053 (3)	0.067 (3)	0.061 (3)	−0.001 (4)	−0.007 (3)	−0.011 (3)
C3	0.130 (7)	0.044 (3)	0.105 (5)	−0.011 (4)	−0.009 (6)	0.000 (3)
C4	0.050 (3)	0.119 (6)	0.072 (4)	0.010 (4)	−0.009 (3)	0.011 (5)
C5	0.057 (3)	0.085 (4)	0.044 (3)	0.009 (3)	0.003 (3)	0.011 (3)
C6	0.047 (3)	0.056 (3)	0.044 (3)	0.000 (3)	−0.002 (3)	−0.002 (2)
C7	0.072 (4)	0.099 (5)	0.074 (4)	−0.020 (4)	0.008 (3)	0.025 (4)
C8	0.068 (4)	0.037 (2)	0.057 (3)	0.001 (3)	−0.003 (3)	−0.001 (2)
C9	0.070 (4)	0.042 (3)	0.063 (3)	−0.006 (3)	−0.005 (3)	0.000 (2)
C10	0.061 (4)	0.044 (3)	0.059 (3)	−0.004 (3)	−0.002 (3)	0.015 (2)
C11	0.050 (3)	0.046 (2)	0.053 (2)	0.001 (3)	−0.002 (3)	0.007 (2)
C12	0.040 (2)	0.042 (2)	0.053 (3)	−0.001 (3)	0.001 (3)	0.000 (2)
C13	0.042 (3)	0.050 (3)	0.056 (3)	0.002 (3)	0.001 (3)	0.010 (2)

Geometric parameters (Å, °)

O1—C1	1.238 (9)	C4—H4A	0.9600
O2—C2	1.262 (7)	C4—H4B	0.9600
O3—C1	1.280 (8)	C4—H4C	0.9600
O3—H3	0.8200	C5—C10	1.519 (8)
O4—C11	1.305 (6)	C5—H5	0.9800
O4—H4	0.8200	C6—C11	1.394 (7)
N1—C8	1.316 (6)	C7—C10	1.527 (9)
N1—C5	1.445 (8)	C7—H7A	0.9600
N1—H1A	0.8600	C7—H7B	0.9600
C1—C6	1.462 (8)	C7—H7C	0.9600
C2—C6	1.413 (8)	C8—C12	1.372 (7)
C2—C9	1.450 (8)	C8—H8	0.9300
C3—C9	1.482 (8)	C9—C13	1.331 (7)
C3—H3A	0.9600	C10—C13	1.534 (7)
C3—H3B	0.9600	C10—H10	0.9800
C3—H3C	0.9600	C11—C12	1.451 (7)
C4—C5	1.485 (8)	C12—C13	1.419 (7)
C1—O3—H3	109.5	C11—C6—C1	118.8 (5)
C11—O4—H4	109.5	C2—C6—C1	120.8 (5)
C8—N1—C5	117.4 (4)	C10—C7—H7A	109.5
C8—N1—H1A	121.3	C10—C7—H7B	109.5
C5—N1—H1A	121.3	H7A—C7—H7B	109.5
O1—C1—O3	120.8 (6)	C10—C7—H7C	109.5
O1—C1—C6	121.1 (6)	H7A—C7—H7C	109.5
O3—C1—C6	118.0 (6)	H7B—C7—H7C	109.5
O2—C2—C6	119.2 (5)	N1—C8—C12	124.1 (5)
O2—C2—C9	120.5 (5)	N1—C8—H8	118.0
C6—C2—C9	120.3 (5)	C12—C8—H8	118.0
C9—C3—H3A	109.5	C13—C9—C2	119.2 (5)
C9—C3—H3B	109.5	C13—C9—C3	124.1 (6)
H3A—C3—H3B	109.5	C2—C9—C3	116.6 (5)
C9—C3—H3C	109.5	C5—C10—C7	112.3 (5)
H3A—C3—H3C	109.5	C5—C10—C13	109.4 (4)

H3B—C3—H3C	109.5	C7—C10—C13	109.0 (5)
C5—C4—H4A	109.5	C5—C10—H10	108.7
C5—C4—H4B	109.5	C7—C10—H10	108.7
H4A—C4—H4B	109.5	C13—C10—H10	108.7
C5—C4—H4C	109.5	O4—C11—C6	122.8 (5)
H4A—C4—H4C	109.5	O4—C11—C12	119.1 (4)
H4B—C4—H4C	109.5	C6—C11—C12	118.1 (4)
N1—C5—C4	109.7 (6)	C8—C12—C13	121.3 (4)
N1—C5—C10	110.8 (4)	C8—C12—C11	118.8 (4)
C4—C5—C10	113.7 (6)	C13—C12—C11	119.8 (4)
N1—C5—H5	107.5	C9—C13—C12	121.9 (4)
C4—C5—H5	107.5	C9—C13—C10	124.1 (5)
C10—C5—H5	107.5	C12—C13—C10	113.8 (4)
C11—C6—C2	120.3 (4)		
C8—N1—C5—C4	−83.5 (7)	C2—C6—C11—C12	−1.7 (9)
C8—N1—C5—C10	42.7 (7)	C1—C6—C11—C12	177.8 (6)
O2—C2—C6—C11	178.9 (6)	N1—C8—C12—C13	−7.4 (10)
C9—C2—C6—C11	−2.2 (10)	N1—C8—C12—C11	173.3 (6)
O2—C2—C6—C1	−0.5 (11)	O4—C11—C12—C8	2.8 (9)
C9—C2—C6—C1	178.3 (6)	C6—C11—C12—C8	−175.6 (6)
O1—C1—C6—C11	4.0 (11)	O4—C11—C12—C13	−176.5 (6)
O3—C1—C6—C11	−179.4 (7)	C6—C11—C12—C13	5.0 (8)
O1—C1—C6—C2	−176.5 (7)	C2—C9—C13—C12	0.6 (10)
O3—C1—C6—C2	0.0 (11)	C3—C9—C13—C12	178.6 (7)
C5—N1—C8—C12	−11.1 (9)	C2—C9—C13—C10	−174.6 (6)
O2—C2—C9—C13	−178.3 (7)	C3—C9—C13—C10	3.4 (11)
C6—C2—C9—C13	2.9 (10)	C8—C12—C13—C9	176.1 (6)
O2—C2—C9—C3	3.5 (10)	C11—C12—C13—C9	−4.6 (9)
C6—C2—C9—C3	−175.3 (7)	C8—C12—C13—C10	−8.3 (8)
N1—C5—C10—C7	66.1 (6)	C11—C12—C13—C10	171.1 (5)
C4—C5—C10—C7	−169.8 (5)	C5—C10—C13—C9	−146.2 (6)
N1—C5—C10—C13	−55.1 (6)	C7—C10—C13—C9	90.7 (7)
C4—C5—C10—C13	69.0 (7)	C5—C10—C13—C12	38.3 (7)
C2—C6—C11—O4	180.0 (6)	C7—C10—C13—C12	−84.9 (6)
C1—C6—C11—O4	−0.6 (11)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O1	0.82	1.79	2.522 (6)	147
O3—H3···O2	0.82	1.70	2.456 (7)	152

Fig. 1