

10-Hydroxy-9-methoxy-5,6,13,13a-tetrahydro[1,3]dioxolo[4,5-g]isoquino[3,2-a]-isoquinolin-8-one

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Key indicators

Single-crystal X-ray study
 $T = 295\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.052
 wR factor = 0.113
 Data-to-parameter ratio = 7.2

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

In the title compound, 8-oxotetrahydrothalifendine, $\text{C}_{19}\text{H}_{17}\text{NO}_5$, the dihydropyrido and pyrido moieties adopt the intermediate conformations of envelope–screw-boat and envelope–twist, respectively. The dihedral angle between the two benzene rings is $37.16(8)^\circ$. In the crystal structure, the molecules translated by a unit along the c axis are linked by three weak $\text{C}-\text{H}\cdots\text{O}$ intermolecular interactions to form a molecular chain. Along the a axis, the adjacent chains related by screw symmetry are connected by a strong $\text{O}-\text{H}\cdots\text{O}$ and a weak $\text{C}-\text{H}\cdots\text{O}$ intermolecular interaction to form layers parallel to the bc plane.

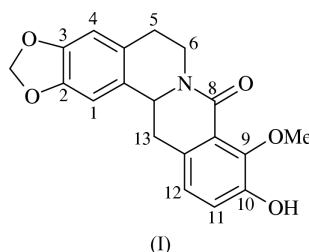
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Comment

Protoberberine alkaloids found in many plants exhibit pharmacological activities (Schmeller & Wink, 1998; Simeon *et al.*, 1989). The crystal structures of berberine salts [chloride, bromide, iodide, sulfate, hydrogen sulfate, azide, thiocyanate (Abadi *et al.*, 1984; Kariuki & Jones, 1995; Man *et al.*, 2001), jatrorrhizine (Ghosh *et al.*, 1993), 8-cyano-8*H*-berberine (Man *et al.*, 2001), isocorypalmine (Ribár *et al.*, 1992), canadine (Sakai & Taira, 1987) and capaurine (Shimanouchi *et al.*, 1969) have been reported. In the present study, the structure of the title compound, (I), has been investigated.



The molecular structure of (I), with the atomic numbering scheme, is shown in Fig. 1. The dihydropyrido moiety adopts an intermediate form between envelope and screw boat conformations, with puckering parameters Q , θ and φ (Cremer & Pople, 1975) of $0.511(3)\text{ \AA}$, $116.1(3)^\circ$ and $250.8(3)^\circ$, respectively. The pyrido moiety exhibits an intermediate form between envelope and twist conformations, with the corresponding values of $0.513(3)\text{ \AA}$, $67.3(3)^\circ$ and $276.4(3)^\circ$, respectively. The dioxolane ring is in an envelope form, with Q of $0.119(2)\text{ \AA}$ and φ of $143.4(4)^\circ$. The dihedral angle between the least-squares planes through the two benzene rings is $37.16(8)^\circ$, which is comparable to those of isocorypalmine [$33.81(5)^\circ$; Ribár *et al.*, 1992] and of 8-cyano-8*H*-berberine [$37.69(5)^\circ$; Man *et al.*, 2001]. This value is much higher than

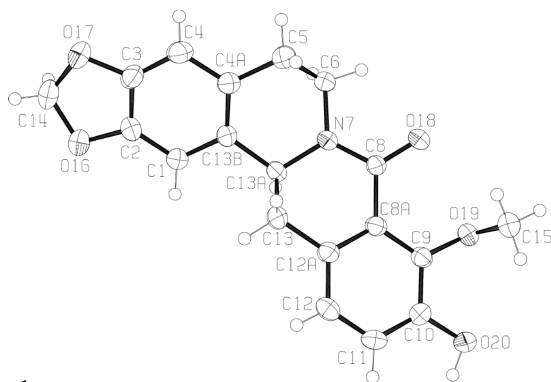


Figure 1
The molecular structure of the title compound, showing 50% probability displacement ellipsoids.

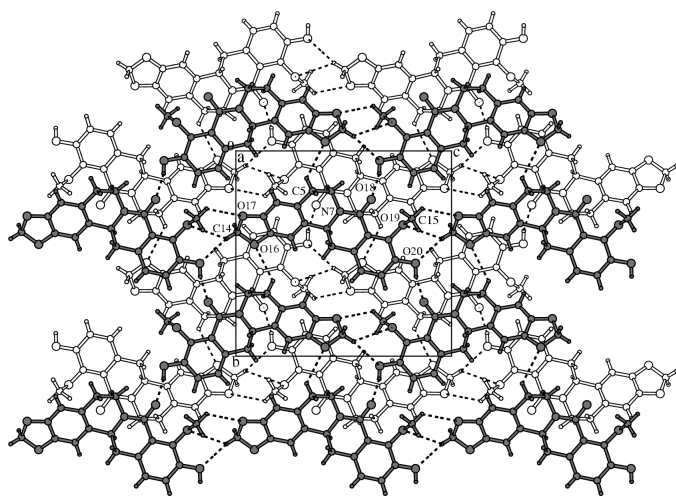


Figure 2
Packing diagram of the title compound, viewed down the *a* axis. The molecular layers at the front and at the back are displayed with filled and open bonds, respectively.

those of the other above-mentioned berberine structures [range 4.24 (3)–14.96 (3)°]. The methoxy group at C9 is nearly perpendicular to the attached benzene ring, with a torsion angle C10–C9–O19–C15 of –86.1 (3)°.

In the crystal structure, the molecules translated by a unit along the *c* axis are linked by weak C14–H14B···O19ⁱⁱⁱ, C14–H14B···O20ⁱⁱⁱ [symmetry code: (iii) *x*, *y*, *z* – 1] and C15–H15C···O17^{iv} [symmetry code: (iv) *x*, *y*, 1 + *z*] interactions to form a molecular chain (Fig. 2 and Table 2). Along the *a* axis, adjacent chains related by screw symmetry are connected by a strong O20–H20···O18ⁱ [symmetry code: (i) –*x*, $\frac{1}{2}$ + *y*, $\frac{3}{2}$ – *z*] and a weak C5–H5B···O16ⁱⁱ [symmetry code: (ii) –*x*, $y - \frac{1}{2}$, $\frac{1}{2}$ – *z*] hydrogen bond to form layers (Fig. 2) parallel to the *bc* plane.

Experimental

The title compound was isolated from the stems of *Coscinium fenestratum*. Crystals were obtained by recrystallizing the ethyl acetate/dichloromethane crude extract from a solvent mixture of dichloromethane/methanol. M.p. 481–483 K. The ¹H and ¹³C NMR results confirmed that the title compound is 8-oxotetrahydro-

thalifendine, as previously reported (Pinho *et al.*, 1992; Gentry *et al.*, 1998).

Crystal data

C₁₉H₁₇NO₅
M_r = 339.34
 Orthorhombic, *P*2₁2₁2₁
a = 8.0217 (7) Å
b = 13.5313 (12) Å
c = 14.2383 (12) Å
V = 1545.5 (2) Å³
Z = 4
D_x = 1.458 Mg m^{–3}

Mo *K*α radiation
 Cell parameters from 1481 reflections
 θ = 2.5–20.4°
 μ = 0.11 mm^{–1}
T = 295 (2) K
 Rod, colorless
 0.16 × 0.11 × 0.09 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.986, *T_{max}* = 0.991
 9913 measured reflections

2104 independent reflections
 1771 reflections with *I* > 2σ(*I*)
R_{int} = 0.041
 θ_{max} = 28.0°
h = –10 → 10
k = –13 → 17
l = –17 → 18

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.053
wR (*F*²) = 0.113
S = 1.12
 2104 reflections
 294 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.153P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.24 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.33 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å).

C2–O16	1.375 (4)	C9–O19	1.379 (3)
C3–O17	1.381 (3)	C10–O20	1.368 (3)
C6–N7	1.459 (3)	C14–O16	1.415 (5)
N7–C8	1.352 (3)	C14–O17	1.422 (5)
N7–C13A	1.480 (3)	C15–O19	1.436 (4)
C8–O18	1.237 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O20–H20···O18 ⁱ	0.88 (4)	1.84 (4)	2.702 (3)	165 (3)
C5–H5B···O16 ⁱⁱ	0.91 (4)	2.72 (4)	3.352 (4)	128 (3)
C14–H14B···O19 ⁱⁱⁱ	0.88 (4)	2.81 (4)	3.449 (4)	130 (3)
C14–H14B···O20 ⁱⁱⁱ	0.88 (4)	2.50 (4)	3.366 (5)	170 (3)
C15–H15C···O17 ^{iv}	0.96 (4)	2.66 (4)	3.325 (4)	127 (3)

Symmetry codes: (i) –*x*, $\frac{1}{2}$ + *y*, $\frac{3}{2}$ – *z*; (ii) –*x*, $y - \frac{1}{2}$, $\frac{1}{2}$ – *z*; (iii) *x*, *y*, *z* – 1; (iv) *x*, *y*, 1 + *z*.

The Friedel pairs were merged for the refinement. The absolute configuration could not be determined, thus an arbitrary choice of enantiomers has been made. All H atoms were located from a difference Fourier map and both positional and isotropic displacement parameters were refined, except for H14A; as the C14–H14A bond was too long (1.24 Å), it was restrained to a reasonable distance of 1.09 Å. The ranges of C–H and O–H bond lengths are 0.88 (4)–1.03 (3) and 0.88 (4) Å, respectively.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SHELXTL* (Bruker, 2000) and *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and

MOLSCRIPT (Kraulis, 1991); software used to prepare material for publication: *PLATON* (Spek, 1990) and *SHELXL97*.

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