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8-Acetonyldihydronitidine

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Key indicators

Single-crystal X-ray study
T = 287 K
Mean σ(C–C) = 0.002 Å
R factor = 0.043
wR factor = 0.118
Data-to-parameter ratio = 14.7

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

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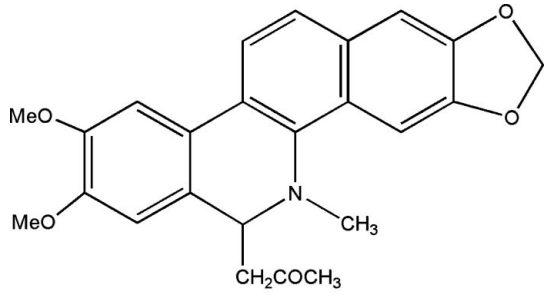
The title compound [systematic name: (*RS*)-13-acetonyl-2,3-dimethoxy-12-methyl-12,13-dihydro-1,3-benzodioxolo[5,6-*c*]-phenanthridine], $C_{24}H_{23}NO_5$, is a benzophenanthridine alkaloid which was isolated from the roots of *Zanthoxylum nitidum*. The molecule contains four six-membered rings and one five-membered ring. The piperidine ring adopts a distorted boat conformation and there is a dihedral angle of 16.90 (5)° between the mean planes of the two benzene rings fused to the piperidine ring.

Comment

The root of *Zanthoxylum nitidum* (Roxb.) DC. is an important traditional Chinese medicine which has been used for the treatment of rheumatoid arthritis, fractures, toothache, burns and as a general analgesic (National Pharmacopoeia Committee, 2005). The main constituent, nitidine, exhibits an antineoplastic, reverse transcriptase inhibitor effect (Zhou *et al.*, 2003). As a derivative of nitidine, 8-acetonyldihydronitidine, (I), showed significant antibacterial and antifungal activity (Nissanka *et al.*, 2001). Our additional investigations of *Z. nitidum* led to the isolation of (I). The structure of (I) was elucidated by spectroscopic analysis, including two-dimensional NMR spectroscopy, and its solid state structure is reported here (Fig. 1 and Table 1).



(I)

The molecule contains four six-membered rings (*A*: C1–C4*A*/C8*A*; *B*: C4*A*–C8*A*; *C*: C5/C6/C9–C14*A*; *D*: C10*A*/C14*A*/C11–C14), and one five-membered ring (C12/C13/O1/C15/O2). Piperidine ring *B* adopts a distorted boat conformation and the dihedral angle between the mean planes of rings *A* and *C* is 16.90 (5)°. The 1,3-dioxolane ring (C12/C13/O1/O2/C15) is also planar, with an r.m.s. deviation from the mean plane of 0.0027 Å.

Experimental

The dried roots of *Zanthoxylum nitidum* (10 kg), were collected in Nanning, Guangxi autonomous area, People's Republic of China, in July 2005. An ethanol extract (600 g) was added to 2% HCl (10 l) and

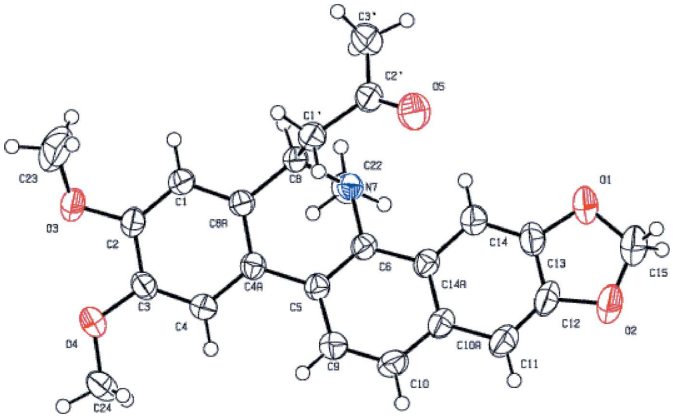


Figure 1
View of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

the aqueous phase extracted with EtOAc (10 l), and made progressively alkaline with aqeuous ammonia (25–28% *w*/*w*) to pH 10 to afford a precipitate (200 g). After filtration, the remaining aqueous phase was extracted with EtOAc (6 l) to afford the crude alkaloid (56 g). This was chromatographed over silica gel (160–200 mesh, 0.8 kg) with eluents of increasing polarity [petrol/acetone/diethylamine (12:1:0.1, 10:1:0.1, 8:1:0.1, 6:1:0.1, 4:1:0.1 and 1:1:0.1), each 2 l] to afford fractions 1–12 according to TLC analysis using the Dragendorff reagent. Fraction 3 (8 g) was applied to a reverse phase silica-gel column and eluted with MeOH–H_2O (4:6-MeOH) to afford the pure title compound, (I) (m.p. 438–440 K). This was further crystallized at room temperature from chloroform to afford colourless prisms. ^{13}C NMR (600 MHz, $CDCl_3$): δ 100.4 (C1), 147.5 (C2), 148.2 (C3), 106.4 (C4), 139.0 (C4*A*), 127.0 (C5), 130.9 (C6), 60.0 (C8), 123.5 (C8a), 119.6 (C9), 110.4 (C10), 127.3 (C10*A*), 123.3 (C11), 148.7 (C12), 149.0 (C13), 104.3 (C14), 123.8 (C14*A*), 148.4 (C1′), 207.9 (C2′), 31.5 (C3′), 101.3 (–OCH_2O–), 42.4 (NCH_3), 56.0 (OCH_3), 56.1 (OCH_3).

Crystal data

$C_{24}H_{23}NO_5$
M_r = 405.43
Monoclinic, $P2_1/n$
a = 11.037 (3) Å
b = 9.560 (3) Å
c = 19.640 (5) Å
β = 93.54 (2)°
V = 2068.5 (9) Å^3
Z = 4
D_x = 1.302 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 287 (2) K
Prism, colourless
0.58 × 0.50 × 0.42 mm

Data collection

Siemens P4 diffractometer
ω scans
Absorption correction: none
4695 measured reflections
4060 independent reflections
2522 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
θ_{max} = 26.0°
3 standard reflections
every 97 reflections
intensity decay: 3.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.118
S = 0.99
4060 reflections
276 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.061P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0067 (9)

Table 1
Selected geometric parameters (Å, °).

O1—C13	1.378 (2)	O5—C2′	1.203 (2)
O2—C12	1.377 (2)	N7—C6	1.433 (2)
O3—C2	1.369 (2)	N7—C8	1.474 (2)
O4—C3	1.368 (2)	C1′—C8	1.527 (2)
C13—O1—C15	105.32 (17)	O5—C2′—C1′	121.28 (18)
C12—O2—C15	105.60 (16)	C6—C5—C9	118.27 (15)
C23—O3—C2	119.86 (17)	C14*A*—C6—N7	117.89 (14)
C3—O4—C24	117.12 (15)	C1—C8*A*—C8	121.18 (15)
C6—N7—C8	112.48 (13)	C10—C9—C5	121.43 (17)
C2—C1—C8*A*	120.43 (16)	C14*A*—C10*A*—C11	120.11 (16)
C2′—C1′—C8	111.97 (15)	C11—C12—C13	122.43 (18)
O3—C2—C1	123.83 (17)	O2—C15—O1	109.83 (17)
C23—O3—C2—C1	−28.3 (3)	C22—N7—C8—C8*A*	77.77 (17)
C8*A*—C1—C2—C3	−1.6 (3)	C4*A*—C8*A*—C8—C1′	−92.87 (18)
C8—C1′—C2′—C3′	61.8 (2)	C14*A*—C10*A*—C10—C9	−0.7 (3)
C1—C2—C3—C4	2.3 (3)	C10*A*—C11—C12—O2	177.42 (17)
C8*A*—C4*A*—C5—C6	−18.0 (2)	C15—O2—C12—C11	−176.8 (2)
C9—C5—C6—C14*A*	−0.8 (2)	C15—O1—C13—C14	178.5 (2)
C8—N7—C6—C5	36.54 (19)	C11—C12—C13—C14	−1.3 (3)
C8—N7—C6—C14*A*	−144.29 (14)	C11—C10*A*—C14*A*—C6	−179.16 (15)
C5—C4*A*—C8*A*—C1	−176.28 (14)	C12—C13—C14—C14*A*	1.0 (3)

H atoms were positioned geometrically (C—H = 0.93–0.98 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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