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6-Acetonyldihydroavicine

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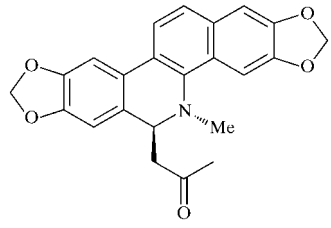
The title compound, 1-(5-methyl-5,6-dihydro[1,3]dioxolo[4′,5′:-4,5]benzo[*c*][1,5]dioxolo[4,5-*j*]phenanthridin-6-yl)acetone, C_{23}-$H_{19}NO_5$, isolated from the stem bark of *Zanthoxylum rhoifolium*, crystallizes as a racemate in space group $P\overline{1}$. The structure shows two aromatic ring systems, each terminated by a five-membered dioxole ring, coupled by an N-containing ring. The core of the molecule is almost planar; the planes of the two ring systems form an angle of 18.42 (6)°. The packing shows the molecules parallel to each other and about 3.5 Å apart with graphite-type interactions. The *N*-methyl and acetone groups, which are *anti* with respect to one another, lie out of the plane and pack in spaces between neighbouring molecules.

Comment

Zanthoxylum rhoifolium (Rutaceae), locally called 'mamica-de-cadela, mamica-de-porca, jujevê', is a plant that grows in South America (Brazil, Uruguay, Paraguay and Argentina). It has been used in Brazilian folk medicine as teas or infusions against a variety of diseases (Tin-Wa *et al.*, 1974). Its medicinal properties may be related to its alkaloid composition (Tin-Wa *et al.*, 1974; Odebiyl & Sofowora, 1979; Lenfeld *et al.*, 1981; Nowick, 1983; Cushman *et al.*, 1984). As a continuation of our chemical studies on Rutaceae plants (Morel *et al.*, 1997), we now report the structure determination of a dihydrobenzophenanthridine alkaloid, 6-acetonyldihydroavicine, (I), isolated from *Z. rhoifolium*. This alkaloid, which has been previously isolated from *Zanthoxylum tetraspermum* (Nissanka *et al.*, 2001), was found together with three other known benzophenantridine alkaloids, namely 6-acetonyldihydronitidine, (II), 6-acetonyldihydrochelerythrine, (III) (Decaudain *et al.*, 1974; Waterman & Khalid, 1981; Desai *et al.*, 1967), and xanthoxyline, (IV) (Morel *et al.*, 1997). All were identified by mass and $^1H/^{13}C$ multidimensional NMR spectroscopic methods. To determine whether compounds (I), (II) and (III) were artifacts from the extraction and isolation procedure, the same plant material was extracted with MeOH at room temperature, followed by extraction under neutral conditions (absence of acetone). Using this procedure, alkaloids (I), (II) and (III) were still present.



(I)

The single-crystal X-ray study of (I) confirms that the compound exists as a racemate, as suggested by its low specific rotary power, $[\alpha]_D^{25} = -1°$ (*c* 0.35, MeOH). The structure (Fig. 1) shows two planar systems, consisting of aromatic rings with attached five-membered dioxole rings (C1–C13 and C16–C24), bent at an angle of 18.42 (6)° to each other, coupled by the N-containing ring (Table 1). The N-containing ring adopts a screw–boat form, with Cremer & Pople (1975) puckering values of $\theta = 68.2°$ and $\varphi = 329.1°$, and a puckering amplitude $Q = 0.417$ Å. The near planarity of the core of the molecule gives rise to a graphite-type packing arrangement. The molecules form sheets parallel to the $(1\overline{1}1)$ plane, spaced 3.533 (6) Å apart, staggered so that the two groups (C25 and C26/C27/O29/C28) that are out of the plane fit in spaces between the rings, packed above and below. There is a C8—H8*B*···O29 hydrogen-bonding interaction (Table 2).

The antimicrobial activity of alkaloids (I) and (II) was evaluated by means of direct bioautography in a thin-layer chromatography bioassay. Alkaloids (I) and (II) show a strong activity against the two Gram-positive bacteria *Staphylococcus aureus* (ATCC 6538p) and *Staphylococcus epidermidis* (ATCC 12228), and the three Gram-negative bacteria

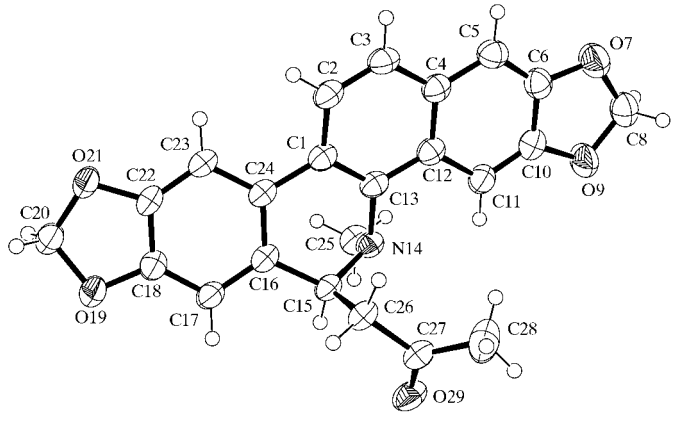


Figure 1
View of the molecule of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids for non-H atoms. H atoms are represented by spheres of arbitrary size.

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Klebsiela pneumoniae (ATCC 10031), *Salmonella setubal* (ATCC 19196) and *Escherichia coli* (ATCC 11103). Both were inactive against *Micrococcus luteus* (ATCC 9341).

Experimental

Zanthoxylum rhoifolium was collected in March 1998 in the town of Jaguari, Rio Grande do Sul, Brazil, and was identified by Professor Ana Zélia Silva. The voucher specimen (No. 1150) is in the Herbário Ático Seabra of the Federal University of Maranhão. The compounds were extracted from the bark with methanol. The crude extract was dissolved in water, acidified and washed with diethyl ether. The aqueous solution was basified and partitioned with *n*-hexane and diethyl ether. The products were isolated by column and thin-layer chromatography of the organic fractions. Complete details of the purification and antibacterial assay are given in the _exptl_special_details section of the deposited CIF.

Crystal data

$C_{23}H_{19}NO_5$
M_r = 389.39
Triclinic, $P\overline{1}$
a = 8.2525 (7) Å
b = 8.2653 (6) Å
c = 13.9594 (6) Å
α = 94.191 (6)°
β = 93.879 (6)°
γ = 105.293 (6)°
V = 912.25 (10) Å^3
Z = 2
D_x = 1.419 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 8.9–27.1°
μ = 0.83 mm^{-1}
T = 213 (2) K
Needle, colorless
0.25 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan with 5 reflections using the *ABSPSI* routine in *PLATON* (Spek, 1995)
T_{min} = 0.864, T_{max} = 0.921
3809 measured reflections
3107 independent reflections
2287 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 65.0°
$h = -1 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.125
S = 1.04
3107 reflections
267 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 0.1711P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0064 (8)

H atoms were constrained to geometric positions, with distances fixed at 0.99 (CH), 0.98 (CH_2), 0.94 (aromatic H) or 0.97 Å (CH_3). The isotropic displacement parameters of the H atoms were set at 150% of those of the parent atoms for CH_3 groups and at 120% for the other groups. The methyl H atoms were located in regions of highest electron density and the methyl groups were allowed to rotate while maintaining a tetrahedral geometry.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *HELENA* (Spek, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °).

C1—C24	1.475 (3)	N14—C15	1.472 (3)
C6—O7	1.373 (3)	C16—C24	1.400 (3)
C6—C10	1.400 (3)	C18—O19	1.379 (2)
O7—C8	1.424 (3)	C18—C22	1.381 (3)
C8—O9	1.425 (3)	O19—C20	1.432 (2)
O9—C10	1.375 (3)	C20—O21	1.426 (3)
C13—N14	1.431 (2)	O21—C22	1.377 (2)
N14—C25	1.466 (2)		
C13—N14—C25	111.69 (15)	N14—C15—C26	108.82 (16)
C13—N14—C15	112.94 (15)	C16—C15—C26	113.55 (16)
C25—N14—C15	112.83 (16)	C27—C26—C15	109.83 (16)
N14—C15—C16	112.70 (16)		
C24—C1—C13—N14	−0.4 (3)	C15—C16—C24—C1	−0.2 (3)
C1—C13—N14—C15	−33.1 (2)	C13—C1—C24—C16	17.8 (3)
C13—N14—C15—C16	48.3 (2)	C15—C26—C27—C28	126.3 (2)
N14—C15—C16—C24	−32.5 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8B···O29^{i}	0.98	2.42	3.372 (3)	164

Symmetry code: (i) $1-x, -y, 1-z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1384). Services for accessing these data are described at the back of the journal.

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