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Vallesiachotamine

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.007 Å
R factor = 0.046
wR factor = 0.180
Data-to-parameter ratio = 7.4

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

The title compound, $C_{21}H_{22}N_2O_3$, (2*S*,12β*S*)-methyl 2-[(1*E*)-1-formyl-1-propenyl]-1,2,6,7,12,12b-hexahydroindolo[2,3-α]-quinolizine-3-carboxylic acid, exhibits a rare vallesiachotamane skeleton. Intermolecular hydrogen bonding results in the formation of a chain.

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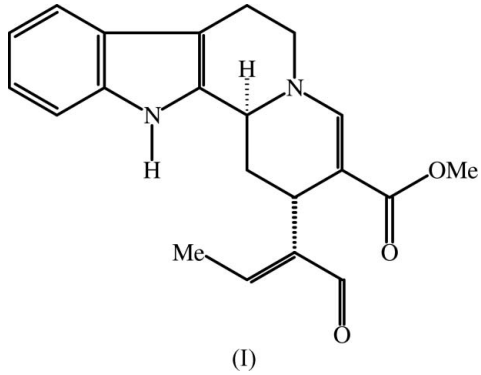
Comment

The genus *Palicourea* Aubl. is a rich source of indole alkaloids that are receiving phytochemical attention because of their biological and chemical diversity (Dusman *et al.*, 2004; Kemmerling, 1996; Morita *et al.*, 1989; Ripperger, 1982; Valverde *et al.*, 1999). As part of our ongoing studies of the phytochemical and biological activities of Rubiaceous plants of the Brazilian Cerrado, we examined *Palicourea rigida* Kunth, a small shrub widely distributed from Mexico to Argentina, which is used in Brazil as a diuretic agent. Two prior studies have been reported on *P. rigida*, but only iridoids (Lopes *et al.*, 2004) and triterpenes (Bolzani *et al.*, 1992) were described. Since Dragendorff analyses indicated the presence of alkaloids in the crude extract of *P. rigida*, we reinvestigated this species to isolate and characterize these compounds. Fractionation using preparative thin-layer chromatography (TLC) on silica gel 60 of the alkaloidal fraction gave vallesiachotamine, (I), a minor bioactive constituent previously isolated from the Peruvian plant *Vallesia dichotoma* (Djerassi *et al.*, 1966), the Asian shrub *Rhazya orientalis* (Evans *et al.*, 1968) and the African plant *Strychnos tricalysioides* (Waterman & Zhong, 1982). It is noteworthy that bioautographic tests on TLC plates with *Staphylococcus aureus*, *Micrococcus luteus* and *Bacillus subtillis* displayed high antibacterial activity for the crude extract of *P. rigida*. The structure of (I) has been identified by spectroscopic data and confirmed by X-ray crystallographic analysis (Fig. 1 and Table 1).



(I)

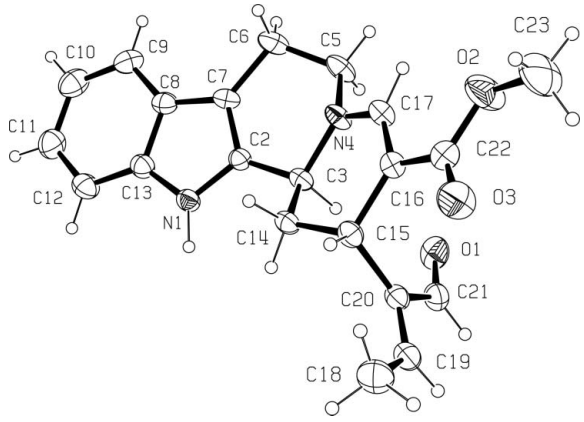


Figure 1
View of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The angle between the least-squares planes through the C17—C16—C22—O3—O2—C23 and C15—C18—C19—C20—C21—O1 residues is 84.0 (2)°. This conformation presumably arises to relieve steric repulsion between the neighbouring aldehyde O1 and ester groups owing to the presence of an intramolecular hydrogen bond, C3—H3···O1 [3.049 (6) Å; Table 2].

According to Cremer & Pople (1975), the N4/C3/C14–C17 ring shows an envelope conformation and the N4/C3/C2/C7/C6/C5 ring shows a distorted chair conformation. The parameters defining these geometries are Q of 0.378 (5) and 0.469 (5) Å, θ of 129.0 (8) and 50.6 (6)°, and φ of 286 (1) and 326.4 (8)°, respectively. The C16—C17 distance of 1.360 (7) Å is consistent with a C=C double bond and the C17—C16—C15 bond angle of 120.7 (4)° confirms the sp^2 character of C17.

We have found no examples of the vallesiachotamane skeleton in the Cambridge Structural Database (Version 5.26; Allen, 2002). Terpene indole alkaloid skeletons structurally related to (I) are javacarboline (Koike *et al.*, 1994) and geissospermine, as the dihydrate (Chiaroni & Riche, 1979).

The molecular packing of (I) (Fig. 2) is stabilized through hydrogen bonds, with geometric parameters in Table 2. An intermolecular N—H···O hydrogen bond links neighbouring molecules, resulting in columns parallel to the [100] direction.

Experimental

The aerial parts of *P. rigida* were collected in Goiania, State of Goiás, Brazil, and air-dried. The ethanol extract of the leaves was submitted to acid/base treatment and fractions corresponding to different pH ranges were purified by repeated preparative TLC separation, leading to the isolation of the alkaloid vallesiachotamine, (I), as a brown powder. The spectroscopic data (NMR and IR) and the melting point of (I) are in complete accordance with those reported in the literature (Djerassi *et al.*, 1966; Solis *et al.*, 1993). Crystals of (I) suitable for single-crystal X-ray diffraction studies were obtained as brown blocks by recrystallization from chloroform and methanol (8:2) (m.p. 523–524 K). ^{1}H NMR ($CDCl_3$/TMS 0.01%, 300 MHz, δ, p.p.m.): 9.36 (*s*, 1H, H21), 8.07 (*s*, 1H, H1), 7.68 (*s*, 1H, H17), 7.48 (*d*, 1H, J = 7.2 Hz, H10), 7.30 (*d*, 1H, J = 7.2 Hz, H11), 7.14 (2H, *m*, H9, H12), 6.67 (*q*, 1H, J = 7.5 Hz, H19), 4.48 (*d*, 1H, J = 11.4 Hz, H3), 4.01 (*d*, 1H, 5.1 Hz, H15), 3.73 (*m*, 2H, H5), 3.60 (*s*, 3H, OCH_3), 2.91 (*m*, 1H, H6*A*), 2.82 (*d*, 1H, H6*B*), 2.18 (*d*, 1H, H14*A*), 2.09 (*d*, 3H, J = 7.5 Hz, H18), 1.92 (*m*, 1H, H14*B*); ^{13}C NMR ($CDCl_3$/TMS 0.01%, 75.0 MHz, δ, p.p.m.): 196.1 (C21), 168.6 (C22), 153.0 (C19), 147.7 (C17), 146.4 (C16), 136.5 (C13), 132.7 (C2), 127.0 (C8), 122.3 (C9), 120.0 (C12), 118.4 (C10), 111.2 (C11), 108.6 (C7), 94.4 (C20), 51.3 (C5), 50.9 (OCH_3), 49.5 (C3), 34.3 (C14), 28.6 (C15), 22.3 (C6), 15.3 (C18); IR (KBr, cm^{-1}) ν_{max}: 3440, 1660 and 1608.

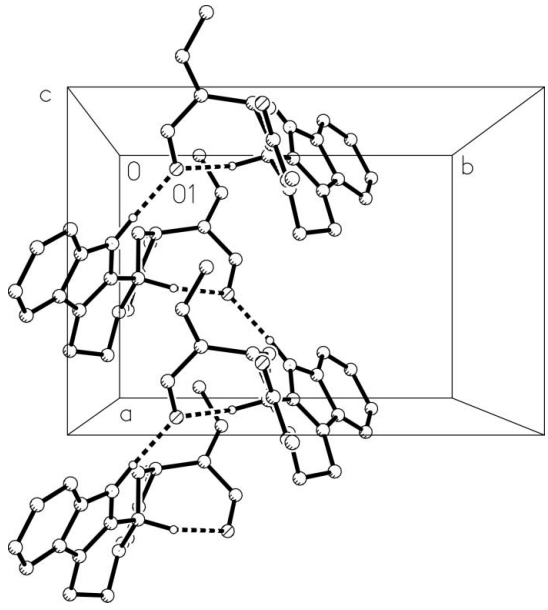


Figure 2
Packing diagram viewed down the *c* axis. Intermolecular N—H···O and intramolecular C—H···O hydrogen bonds are shown as dashed lines. Only the H atoms involved in hydrogen bonds are shown.

Crystal data

$C_{21}H_{22}N_2O_3$
M_r = 350.41
Orthorhombic, $P2_12_12_1$
a = 7.194 (1) Å
b = 9.859 (1) Å
c = 25.995 (6) Å
V = 1843.7 (5) Å^3
Z = 4
D_x = 1.262 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 15.1–30.9°
μ = 0.69 mm^{-1}
T = 297 (2) K
Block, brown
0.18 × 0.15 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non–profiled $\omega/2\theta$ scans
Absorption correction: none
1844 measured reflections
1825 independent reflections
1411 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 67.9°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 11$
$l = -1 \rightarrow 31$
2 standard reflections
frequency: 120 min
intensity decay: < 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.180
S = 1.23
1825 reflections
247 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1038P)^2 + 0.2785P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0035 (9)

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.370 (6)	C3—C14	1.527 (6)
N1—C13	1.379 (6)	C14—C15	1.539 (7)
N4—C3	1.476 (6)	C15—C16	1.520 (7)
N4—C5	1.469 (6)	C15—C20	1.514 (7)
N4—C17	1.330 (6)	C16—C17	1.360 (7)
C2—N1—C13	108.5 (4)	C14—C15—C20	115.9 (4)
C3—N4—C5	115.3 (4)	C16—C15—C20	112.7 (4)
C3—N4—C17	121.4 (4)	C15—C16—C17	120.7 (4)
C5—N4—C17	121.1 (4)	C15—C16—C22	118.3 (5)
N4—C3—C14	109.7 (4)	C17—C16—C22	120.9 (5)
C3—C14—C15	116.4 (4)	N4—C17—C16	125.7 (5)
C14—C15—C16	109.8 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.97 (5)	1.94 (6)	2.877 (5)	163 (5)
C3—H3···O1	1.11 (5)	2.21 (5)	3.049 (6)	131 (3)

Symmetry code: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z$.

All H atoms, except H1 and H3, were positioned geometrically and allowed to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å, and with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and U_{iso}(H) = 1.2U_{eq}(C) for other atoms. The H atoms of atoms N1 and C3 were located in a difference Fourier map and were refined with U_{iso}(H) = 1.2U_{eq}(N,C) (see Table 2 for distances). Due to the absence of any significant anomalous scatterers in (I), the absolute configuration could not be determined and the Friedel pairs were merged before the final refinement. The absolute configuration was confirmed from the chemistry (CAS number 5523-37-5P).

Data collection: *CAD-4*/*PC* (Enraf–Nonius, 1993); cell refinement: *CAD-4*/*PC*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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