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Raucaffrinoline

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.005 Å
R factor = 0.040
wR factor = 0.107
Data-to-parameter ratio = 7.6

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

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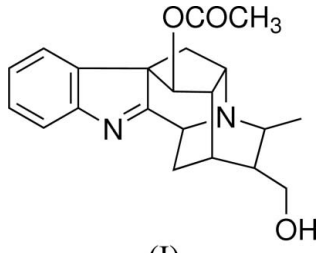
In the crystal structure of the title compound [systematic name: (17*R*,20α,21β)-1,2-didehydro-1-demethyl-19-hydroxy-21-methyl-18-norajmalan-17-yl acetate], $C_{21}H_{24}N_2O_3$, an intermolecular O—H···O hydrogen bond [2.810 (4) Å and 160°] stabilizes the molecular packing as an infinite chain along the [100] direction.

Comment

Bioactive indole alkaloids have been isolated from plant species of the Apocynaceae family, including many belonging to the *Rauvolfia* genus, among which *Rauvolfia serpentina* Benth, from India, has been an important source of reserpine (Stöckigt, 1995). The chemistry of the *Rauvolfia* species has been exhaustively investigated for the presence of indole alkaloids (Siddiqui *et al.*, 1987; Stöckigt, 1995; Court, 1983; Libot *et al.*, 1986). In a research programme on the occurrence of indole alkaloids in Brazilian species of *Rauvolfia*, a phytochemical analysis of the extracts from leaves and bark of *Rauvolfia bahiensis* A. DC. is described.



(I)

Fig. 1 shows the molecular structure of the title compound, (I), with the atomic numbering. The displacement ellipsoids of atoms O1 and O3 are highly anisotropic, indicating probable unresolved disorder in these sites.

The molecule contains an indole unit fused to a quinuclidine unit, forming a cage which can be described by five-, six- and seven-membered rings. The C8–C12 ring has puckering parameters (PP) (Cremer & Pople, 1975) Q = 0.494 (4) Å and φ = 199.1 (5)°, showing a distorted half-chair conformation. The rings N2/C10/C11/C15/C14/C13, N2/C17/C16/C15/C11/C10 and N2/C13/C14/C15/C16/C17 have PP Q (Å), θ (°) and φ (°) averaging 0.858 (4), 88.8 (3) and 160.9 (3), respectively, showing a twist–boat conformation. The ring N2/C10/C9/C8/C7/C13 has PP 0.655 (4), 19.9 (4) and 102.2 (10), respectively, showing a distorted chair conformation. The seven-membered ring C7/C8/C12/C11/C15/C14/C13 has PP Q_2 = 0.703 (4) Å, Q_3 = 0.704 (4) Å, Q = 0.995 (4) Å, φ_2 = 215.5 (3)° and φ_3 = 11.6 (3)°, showing a distorted twist–chair conformation.

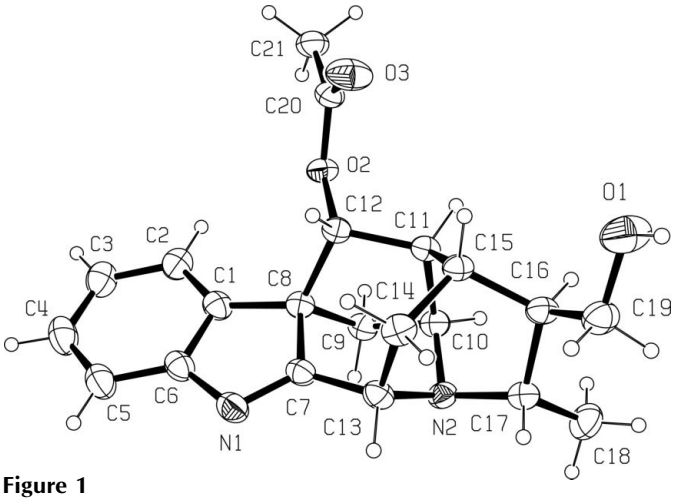


Figure 1
A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

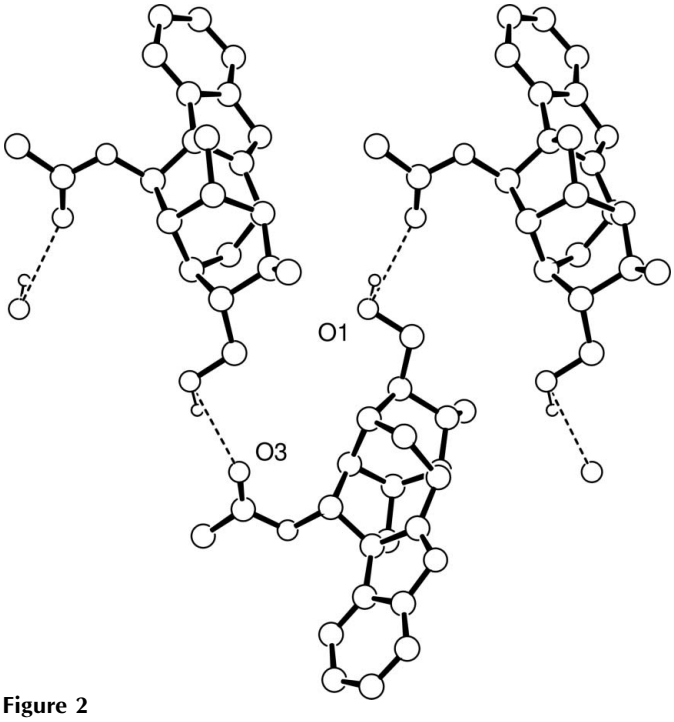


Figure 2
A packing diagram, viewed down the *b* axis; the *a* axis points to the right. Intermolecular O—H···O hydrogen bonds are shown as dashed lines. Only H atoms involved in hydrogen bonds are shown.

The bonds C7—C13, C16—C19 and C20—C21 are shortened by 0.027, 0.029 and 0.05 Å, respectively, compared with the expected formal bond lenghts. The shortening of the C7—C13 and C20—C21 bonds might be ascribed to hyperconjugation. The C7—N1 bond length indicates a double bond and the angles around C7 confirm sp^2 hybridization. We have found two systems of fused rings similar to (I) in the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002), with refcodes JAKFAC ($C_{30}H_{34}N_2O_6$; Li & Cook, 1998) and AJMALN10 ($C_{20}H_{26}N_2O_2$,CH_2Cl_2; Prewo & Stezowski, 1978). The superposition of these structures on that of (I) shows that the average r.m.s. deviation of the eight atoms of the quinuclidine unit is 0.036 Å. The N2—C17—C16—C15 torsion angle (AJMALN10 14.57°; JAKFAC 9.59°) changes due to steric effects caused by different functional groups at positions C17 and C16. Selected geometric parameters are shown in Table 1.

The molecular packing of (I) is stabilized through a hydrogen-bonding network, shown in Fig. 2, with geometric parameters in Table 2. An intermolecular O1—H1···O3^{i} hydrogen bond links neighbouring molecules related by the screw axis, resulting in an infinite one-dimensional chain along the [100] direction.

Experimental

Material from *Rauvolfia bahiensis* A. DC. was collected from Barra do Una, Ilhéus city (Bahia, Brazil), and the aerial parts were air-dried, powdered and extracted with 95% aqueous EtOH. The ethanolic extract from the leaves was submitted to acid/base treatment and fractions corresponding to different pH ranges were purified by repeated separation by preparative thin-layer chromatography, leading to the isolation of thirteen alkaloids, the known alkaloids raucaffrinoline, picrinine, vinorine, normacusine B, norseredamine, seredamine, 10-methoxynormacusine B, norpurpeline, purpeline, 12-methoxy-*N*-methyl-vellosimine, demethoxypurpeline, 12 methoxyaffinisine and 12-methoxy-vellosimine (Kato *et al.*, 2002). The alkaloid raucaffrinoline, (I), was isolated as a brown powder. The spectroscopic data (NMR) and the melting point of raucaffrinoline 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 methanol and hexane (1:9) (m.p. 522–524 K; Libot *et al.*, 1980). Spectroscopic analysis: ^{1}H NMR ($CDCl_3$/TMS 0.01%, 300 MHz, δ, p.p.m.): 7.47 (*d*, 1 H, *J* = 7 Hz, H2), 7.22 (*t*, 1 H, *J* = 7 Hz, H3), 7.38 (*t*, 1 H, *J* = 7 Hz, H4), 7.60 (*d*, 1 H, *J* = 7 Hz, H5), 2.80 (*dd*, 1 H, *J* = 12 and 5 Hz, H9*A*), 1.63 (*dd*, 1 H, *J* = 12 Hz, H9*B*), 3.65 (*m*, 1 H, H10), 2.38 (*t*, 1 H, *J* = 6 Hz, H11), 5.00 (*s*, 1 H, H12), 4.15 (*d*, 1 H, *J* = 10 Hz, H13), 1.94 (*dd*, 1 H, *J* = 15 and 10 Hz, H14*A*), 1.54 (*dd*, 1 H, *J* = 15 and 6 Hz, H14*B*), 2.48 (*m*, 1 H, H15), 1.54 (*dd*, 1 H, *J* = 15 and 6 Hz, H16), 2.52 (*m*, 1 H, H17), 1.27 (*d*, 3 H, *J* = 7 Hz, H18), 3.75 (*dd*, 2 H, *J* = 11 and 6 Hz, H19), 2.17 (*s*, 3 H, H21); ^{13}C NMR ($CDCl_3$/TMS 0.01%, 75.0 MHz, δ, p.p.m.): 136.4.0 (C1), 123.8 (C2), 125.4 (C3), 128.6 (C4), 120.9 (C5), 156.5 (C6), 183.5 (C7), 65.0 (C8), 37.5 (C9), 51.2 (C10), 78.2 (C11), 18.3 (C12), 57.1 (C13), 21.6 (C14), 26.5 (C15), 45.7 (C16), 53.1 (C17), 18.3 (C18), 61.9 (C19), 170.0 (C20), 21.2 (C21).

Crystal data

$C_{21}H_{24}N_2O_3$
M_r = 352.42
Orthorhombic, $P2_12_12_1$
a = 9.436 (1) Å
b = 10.588 (1) Å
c = 17.926 (2) Å
V = 1791.0 (3) Å^3
Z = 4
D_x = 1.307 Mg m^{-3}
Cu $K\alpha$ radiation
μ = 0.71 mm^{-1}
T = 297 (2) K
Block, brown
0.18 × 0.15 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3454 measured reflections
1788 independent reflections
1135 reflections with $I > 2\sigma(I)$
R_{int} = 0.072
θ_{max} = 68.0°
2 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.053P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.107$	$\Delta\rho_{max} = 0.19$ e Å^{-3}
$S = 1.01$	$\Delta\rho_{min} = -0.19$ e Å^{-3}
1788 reflections	Extinction correction: *SHELXL97* (Sheldrick, 1997)
236 parameters	Extinction coefficient: 0.0016 (3)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C19	1.405 (5)	C7—C13	1.493 (5)
O2—C12	1.454 (4)	C9—C10	1.517 (5)
O3—C20	1.207 (5)	C16—C19	1.511 (5)
N1—C7	1.282 (4)	C20—C21	1.469 (6)
N1—C7—C13	125.4 (4)	C13—C7—C8	119.8 (3)
N1—C7—C8	114.8 (3)		
N2—C10—C11—C15	20.2 (4)	N2—C17—C16—C15	22.5 (4)
N2—C13—C14—C15	23.0 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3^{i}	0.82	2.03	2.810 (4)	160

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+2$.

All H atoms were placed in calculated positions and allowed to ride on their parent atoms, with C—H distances in the range 0.93–0.98 Å and an O—H distance of 0.82 Å, and with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms or 1.2U_{eq}(C,O) for all other atoms. Shorter than expected bonds and high displacement components along these bonds are found for the terminal methyl C atoms and the indole ring (Spek, 2003; Hirshfeld, 1976).

Due to poor data quality and the absence of any significant anomalous scatterers in the compound, the absolute configuration could not be determined reliably and the 1279 Friedel pairs were merged before the final refinement. The present configuration is that defined in *Chemical Abstracts* (CAS No. 36285–11-7).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1994); cell refinement: *CAD-4 Software*; 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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