N1—C6	1.441 (3)	C7—C8	1.514 (3)
N2—C1	1.350 (3)		
O1—N1—O2	121.5 (2)	N2—C7—C8	113.8 (2)
C1—N2—C7	123.9 (2)	F1—C11—C10	118.7 (3)
C2—C1—C6	115.3 (2)	C10—C11—C12	122.6 (2)
C1—C2—C3	122.3 (2)	C11—C12—C13	118.4 (2)
C1—C6—C5	122.0 (2)		
O1—N1—C6—C5	3.9 (3)	C2—C3—C4—C11	−178.2 (2)
C7—N2—C1—C2	−3.4 (3)	N2—C7—C8—C9	−146.7 (2)
C1—N2—C7—C8	73.9 (2)	F1—C11—C12—C13	178.9 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—HN···O2	0.79 (2)	2.03 (2)	2.624 (2)	132 (2)
N2—HN···O2^{i}	0.79 (2)	2.49 (2)	3.048 (3)	129 (2)

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

H atoms, except for the amino H atom, were placed geometrically 0.95 Å from their parent atoms and a riding model was used with $U(H) = 1.3U_{eq}(C)$. The amino H atom was taken from a difference Fourier map and was refined isotropically.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1990). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976) in *MolEN*. Software used to prepare material for publication: *MolEN*. Hydrogen bonds were calculated with *PARST* (Nardelli, 1995).

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A new 14:15-seco-15-norpregnane derivative from *Mandevilla illustris* Woodson (Apocynaceae)

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Abstract

The structure of a new 14:15-seco-15-norpregnane derivative, 3′-14-epoxy-4′,15-dioxaandrost-5-en-3β-yl acetate, $C_{22}H_{30}O_5$, isolated from the ethyl acetate extract of *Mandevilla illustris* (Apocynaceae), is described. Its chemical substructure contains an unusual 1-methyl-2,5,9-trioxatricyclo[4.2.1.$0^{3,7}$]nonane moiety. Features of the packing include an intermolecular C—H···O contact (C19—H···O5) of 3.230 (7) Å.

Comment

Mandevilla velutina and *M. illustris* (Apocynaceae) are native Brazilian plants, and infusions or alcoholic extracts of their rhizomes are used in popular medicines as anti-inflammatory agents and in the treatment of snakebites. Extracts and different compounds from these plants have been shown to antagonize bradykinin-induced muscle contraction and to have potent inflammatory activity (Calixto *et al.*, 1985; 1987; Calixto, Nicolau, Pizzolatti & Yunes, 1988; Calixto, Nicolau & Yunes, 1988; Calixto *et al.*, 1991). We have previously isolated from *M. velutina*, a compound with a novel pregnane structure, which was named velutinol A and which showed bradykinin antagonist activity (Yunes, Pizzolatti *et al.*, 1993); the structure of velutinol A was confirmed in a previous report (Bento *et al.*, 1996). The isolation from *M. illustris* of a compound named illustrol, (I), with a closely related 14:15-seco-15-norpregnane structure, was subsequently reported (Yunes, Brum *et al.*, 1993). Although alcoholic extracts of *M. illustris* antagonize bradykinin, illustrol was shown to be inactive in isolated rat uterus and isolated guinea pig ileum bradykinin-induced muscle contraction assays (Yunes, Brum *et al.*, 1993).

In this study, we report the crystal structure of the acetylated derivative of illustrol, (II), a new natural compound isolated from *M. illustris*, to define clearly

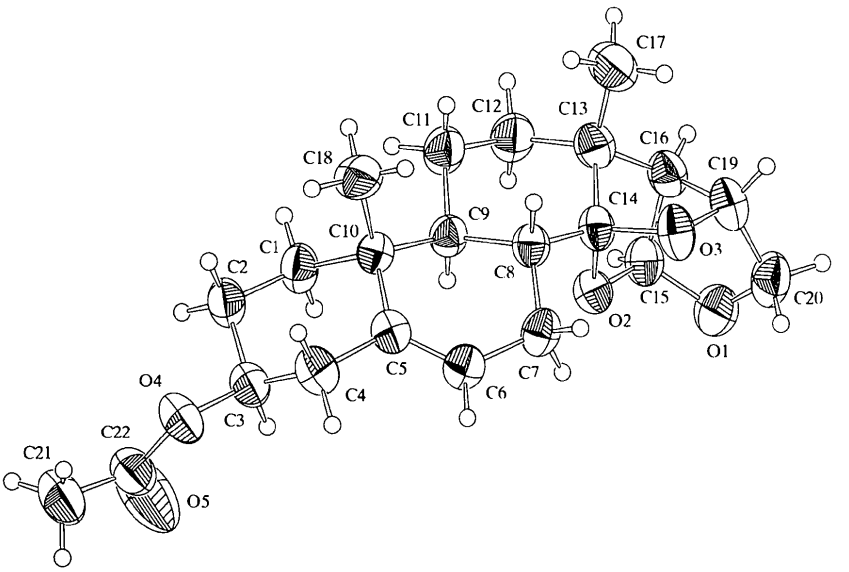
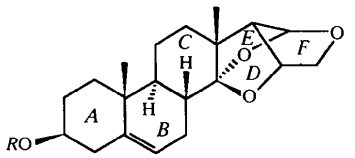
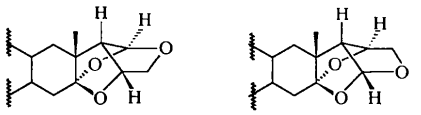


Fig. 1. A *ZORTEP* (Zsolnai *et al.*, 1996) drawing of the molecular structure of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

the isomer, (III) or (IV), to which this compound corresponds, and to determine the molecular structure of the unusual 1-methyl-2,5,9-trioxatricyclo[4.2.1.$0^{3,7}$]-nonane moiety assigned from one- and two-dimensional NMR spectroscopy (Yunes, Brum *et al.*, 1993). We have found no examples of this tricyclic system in the Cambridge Structural Database (1997).



(I) R = H
(II) R = CH_3CO



(III) (IV)

A *ZORTEP* (Zsolnai *et al.*, 1996) illustration of the molecular structure of (II) is shown in Fig. 1 and selected bond distances and angles are given in Table 1. Based on the known absolute stereochemistry at six of the chiral centres shown in (II) (Yunes, Brum *et al.*, 1993), the present crystal structure defines the absolute stereochemistry at the other three chiral centres, and it is clear that the molecular structure corresponds to isomer (III). The C5—C6 distance of 1.327 (6) Å is consistent with a C=C double bond. The C5—C6—C7 bond angle of 125.2 (4)° confirms the sp^2 character of C6. The tricyclo rings show several distortions in bond distances and angles. Within the cage, the C—C lengths vary from 1.503 (7) to 1.539 (7) Å and the C—C—C angles lie in the range 91.1 (3)–104.6 (4)°. As a consequence, the bond angles involving atoms C13 and C14 also show distortions. These distortions would presumably contribute to the potential instability of the molecule.

Cremer & Pople (1975) puckering parameters show that ring *A* (C1–C5, C10) is in a chair conformation [Q = 0.556 (5) Å, θ = 9.5 (5) and φ = 213 (3)°], ring *B* (C5–C9) is in a half-chair, distorted towards a half-boat conformation [Q = 0.455 (4) Å, θ = 53.2 (5) and φ = 78.6 (7)°] and ring *C* (C8, C9, C11–C14) is in a chair conformation [Q = 0.558 (5) Å, θ = 4.3 (5) and φ = 184 (7)°]. Ring *D* (C13, C14, O3, C19, C16) adopts an envelope conformation with C13 *endo* [q_2 = 0.561 (5) Å and φ_2 = 65.9 (5)°], ring *E* (C13, C14, O2, C15, C16) is in an envelope conformation with C13 in the flap position [q_2 = 0.562 (5) and φ_2 = 66.7 (5)°] and ring *F* (C15, O1, C20, C19, C16) is in an envelope conformation with C16 *exo* [q_2 = 0.416 (5) and φ_2 = 66.8 (7)°].

The intermolecular packing is stabilized by a C—H···O interaction (Desiraju, 1996) [C19···O5^{i} 3.230 (7), H19···O5^{i} 2.33 (6) Å and C19—H19··· O5^{i} 155 (5)°; symmetry code: (i) $x-1$, $1+y$, z]. Examination of the structure with *PLATON* (Spek, 1990) showed that there were no solvent-accessible voids in the crystal lattice.

Experimental

The ethyl acetate extract was prepared as described previously by Yunes, Brum *et al.* (1993). This extract (40 g) was filtered

over silica gel using hexane and dichloromethane as solvents. Removal of these solvents gave 0.9 and 14 g of the respective fractions. The latter fraction (14 g) was then submitted to repeated column chromatography on silica gel (120 g) with a hexane/acetone gradient, giving compound (II) (80 mg). Crystals of (II) were obtained by recrystallization from a hexane/acetone (4:1) solution.

Crystal data

$C_{22}H_{30}O_5$
$M_r = 374.46$
Orthorhombic
$P2_12_12_1$
$a = 8.144\ (2)$ Å
$b = 10.004\ (2)$ Å
$c = 24.101\ (5)$ Å
$V = 1963.6\ (7)$ Å^3
$Z = 4$
$D_x = 1.267$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 17.54$–$20.86°$
$\mu = 0.088$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.52 × 0.42 × 0.33 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2023 measured reflections
2000 independent reflections
1644 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 25°$
$h = 0 \rightarrow 9$
$k = -11 \rightarrow 0$
$l = -28 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.143$
$S = 1.069$
2000 reflections
248 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.057P)^2 + 1.534P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.076$
$\Delta\rho_{max} = 0.236$ e Å^{-3}
$\Delta\rho_{min} = -0.198$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.031 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C15	1.406 (5)	C5—C6	1.327 (6)
O1—C20	1.440 (6)	C13—C16	1.521 (6)
O2—C15	1.437 (5)	C13—C14	1.524 (6)
O2—C14	1.450 (5)	C15—C16	1.518 (6)
O3—C14	1.419 (5)	C16—C19	1.539 (7)
O3—C19	1.469 (5)	C19—C20	1.503 (7)
O5—C22	1.191 (7)		
C15—O1—C20	106.6 (3)	O3—C14—C13	104.3 (4)
C15—O2—C14	106.0 (3)	O2—C14—C13	102.5 (3)
C14—O3—C19	104.6 (3)	C8—C14—C13	119.0 (4)
C22—O4—C3	116.6 (4)	O1—C15—O2	111.6 (4)
C16—C13—C14	91.1 (3)	O1—C15—C16	107.9 (4)
C16—C13—C12	118.3 (4)	O2—C15—C16	102.6 (3)
C14—C13—C12	108.5 (4)	C15—C16—C13	104.0 (4)
C16—C13—C17	112.5 (4)	C15—C16—C19	95.9 (4)
C14—C13—C17	113.5 (4)	C13—C16—C19	103.4 (4)
C12—C13—C17	111.3 (4)	O3—C19—C20	109.8 (4)
O3—C14—O2	106.7 (3)	O3—C19—C16	102.6 (3)
O3—C14—C8	114.4 (3)	C20—C19—C16	104.6 (4)
O2—C14—C8	108.7 (3)	O1—C20—C19	106.4 (4)
C10—C5—C6—C7	4.0 (7)	C14—O3—C19—C16	7.9 (4)
C14—O2—C15—C16	−6.5 (4)	C15—O1—C20—C19	−5.1 (5)

All H atoms, except H19, for which only the coordinates were refined, were included in the calculations in idealized positions, with $U_{iso} = 1.5U_{eq}$ that of the parent atom. Atom O5 has an unusually large U_{eq} value, reflecting highly anisotropic displacement parameters. As this could be related to disorder, the anisotropic atom was replaced with two isotropic half atoms. Refinement with this model was worse than with the anisotropic model. The absolute structure could not be determined by X-ray methods but is known from the chemical studies of Yunes, Brum *et al.* (1993).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *SET*4 in *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai *et al.*, 1996). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1075). Services for accessing these data are described at the back of the journal.

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