

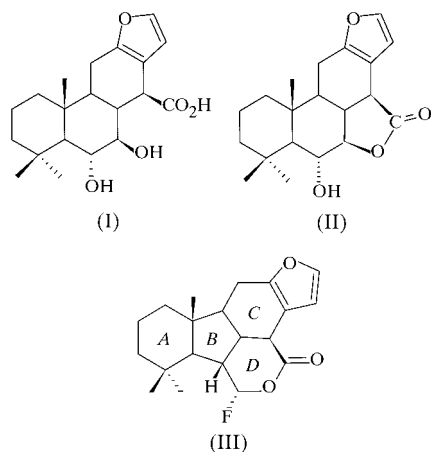
21 α -Fluoro-7-norvouacapane-17 β ,21 α -lactone¹Silvana Guilardi Ruggiero,^a Maria Teresa do Prado Gambardella,^{b*} Marcelo Cardoso Branco,^b Antonio Jacinto Demuner,^c Luis Claudio A. Barbosa^c and Dorila Piló-Veloso^d^aDepartamento de Química, Universidade Federal de Uberlândia, Av. João Naves de Avila, 2160, 38400.089 Uberlândia MG, Brazil, ^bInstituto de Química de São Carlos, USP, Caixa Postal 780, 13560.970 São Carlos SP, Brazil, ^cDepartamento de Química, UFV, Caixa Postal 111, 36571.000 Viçosa MG, Brazil, and ^dDepartamento de Química, ICEX, UFMG, Caixa Postal 702, 31270.901 Belo Horizonte MG, Brazil
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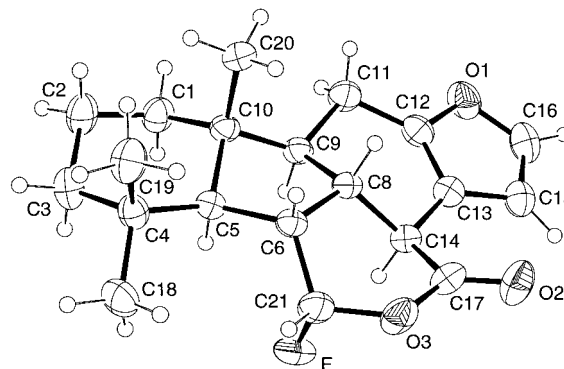
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The crystal structure of 21 α -fluoro-7-norvouacapane-17 β ,21 α -lactone, C₂₀H₂₅FO₃, a new synthetic derivative of the diterpenoid 6 α ,7 β -dihydroxyvouacapane-17 β -oic acid isolated from *Pterodon polygalaeflorus* Benth fruits, is described.

Comment

As part of our investigation of the structural requirements for the biological activities presented by derivatives of the diterpenoid 6 α ,7 β -dihydroxyvouacapane-17 β -oic acid, (I), isolated from *Pterodon polygalaeflorus* Benth (Rubinger *et al.*, 1991), we have described recently an attempt to substitute thehydroxyl groups of compounds (I) and 6 α -hydroxyvouacapane-7 β ,17 β -lactone, (II), with F atoms (Demuner *et al.*, 1998). In both cases, the fluorine derivative 21 α -fluoro-7-norvouacapane-17 β ,21 α -lactone, (III), has been obtained. The¹ Alternative name: 3,3a,7,7a,7b,8,9,10,11,11a,11b,11c-dodecahydro-1-fluoro-7b,11,11-trimethyl-1H-2-oxafuro[2,3-b]fluoranthene-3-one.

introduction of F atoms into new molecules is a common strategy for the development of new drugs (Wilkinson, 1992). Our purpose in this case was to produce more lipophilic analogues of compounds (I) and (II) that would still be able to make hydrogen bonds at position eight and would be less sterically hindered at that position.

The structure of compound (III) was proposed based on spectroscopic data. Electron impact mass spectrometry showed an *M*⁺ ion peak at *m/z* 332.1784, corresponding to the molecular formula C₂₀H₂₅FO₃. In the infrared spectrum, no absorption around 3300 cm⁻¹ was observed, indicating that no hydroxyl group was present in the molecule. Further evidence for the presence of fluorine in this molecule comes from the ¹⁹F-NMR spectrum that showed only one double doublet (*J*_{F,H21} = 54 and *J*_{F,H6} = 33 Hz) at δ -128.1 p.p.m. We now present the X-ray study that confirms the proposed structure of this rearranged diterpenoid. This was important as the product obtained had resulted from an unexpected rearrangement. An ORTEPIII (Burnett & Johnson, 1996) drawing of the title compound is shown in Fig. 1.**Figure 1**
An ORTEPIII view (Burnett & Johnson, 1996) of the title compound showing 40% probability displacement ellipsoids.A conformation analysis (Cremer & Pople, 1975; Iulek & Zukerman-Schpector, 1997) of (III) shows that the *A* [*q*₂ = 0.040 (3), *q*₃ = 0.556 (3), *Q* = 0.557 (3) Å, θ = 4.1 (3), φ = 340 (4)°] and *C* [*q*₂ = 0.418 (3), *q*₃ = 0.365 (3), *Q* = 0.555 (3) Å, θ = 48.8 (3), φ = 15.7 (4)°] rings, respectively, adopt chair and distorted half-chair conformations, like its precursors (I) (Ruggiero *et al.*, 1997) and (II) (Abrahão-Junior *et al.*, 1997). The *B* [*q*₂ = 0.501 (3) Å, φ = 323.6 (3)°] and *D* [*q*₂ = 0.685 (3), *q*₃ = -0.049 (3), *Q* = 0.687 (3) Å, θ = 94.1 (2), φ = 301.2 (2)°] rings have envelope and boat conformations, respectively.The junctions of the rings *AB*, *BC* and *CD* are *trans* and the junction *BD* is *cis*. Some bond distances and angles of the norvouacapane fused rings are shown in Table 1. In the crystal packing there is a short contact: F...C1ⁱ = 3.525 (3), F...H11ⁱ = 2.808 Å, F...H11ⁱ—C1ⁱ = 131° [symmetry code: (i) 2 - *x*, $\frac{1}{2}$ + *y*, 1 - *z*].

Experimental

The title compound has been prepared from both compounds (I) and (II) under the same conditions. Its synthesis and spectroscopic characterization has been reported recently (Demuner *et al.*, 1998).

Suitable single crystals of the title compound were obtained by slow evaporation of a tetrahydrofuran/ethanol (1:10) solution. The absolute structure could not be determined.

Crystal data

$C_{20}H_{25}FO_3$	$D_x = 1.309 \text{ Mg m}^{-3}$
$M_r = 332.40$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25 reflections
$a = 9.440 (1) \text{ \AA}$	$\theta = 10.31\text{--}18.31^\circ$
$b = 9.366 (1) \text{ \AA}$	$\mu = 0.094 \text{ mm}^{-1}$
$c = 9.741 (1) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 101.69 (1)^\circ$	Plate, colourless
$V = 843.4 (2) \text{ \AA}^3$	$0.45 \times 0.40 \times 0.08 \text{ mm}$
$Z = 2$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.031$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 26.29^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 11$
$T_{\text{min}} = 0.961$, $T_{\text{max}} = 0.993$	$k = -11 \rightarrow 0$
1920 measured reflections	$l = -12 \rightarrow 11$
1813 independent reflections	3 standard reflections
1571 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 1%

Table 1

Selected geometric parameters (\AA , $^\circ$).

F—C21	1.390 (3)	C6—C8	1.533 (4)
O2—C17	1.192 (3)	C8—C9	1.528 (3)
O3—C17	1.387 (4)	C8—C14	1.533 (3)
O3—C21	1.421 (3)	C9—C11	1.531 (4)
C5—C6	1.550 (3)	C9—C10	1.539 (3)
C5—C10	1.560 (3)	C13—C14	1.509 (4)
C6—C21	1.518 (3)	C14—C17	1.488 (4)
C17—O3—C21	120.2 (2)	C11—C9—C10	123.4 (2)
C4—C5—C6	121.2 (2)	C1—C10—C9	115.0 (2)
C4—C5—C10	117.0 (2)	C1—C10—C5	108.4 (2)
C6—C5—C10	103.10 (19)	C17—C14—C13	119.0 (2)
C21—C6—C8	109.7 (2)	C17—C14—C8	107.1 (2)
C21—C6—C5	119.4 (2)	C13—C14—C8	106.1 (2)
C8—C6—C5	103.42 (19)	O2—C17—O3	117.9 (3)
C9—C8—C14	110.21 (19)	O2—C17—C14	128.7 (3)
C9—C8—C6	107.32 (19)	O3—C17—C14	113.3 (2)
C14—C8—C6	114.99 (19)	F—C21—O3	107.6 (2)
C8—C9—C11	109.5 (2)	F—C21—C6	111.0 (2)
C8—C9—C10	101.96 (19)	O3—C21—C6	112.1 (2)

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.1231P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.097$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.111$	$\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
1813 reflections	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
218 parameters	H-atom parameters constrained

H atoms were positioned geometrically and a riding model was used during the refinement process with U_{iso} set to 1.5 (for methyl-H atoms) or 1.2 (for the remaining) times the value of U_{eq} of the atom to which they are attached.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *SDP* (Fair, 1990); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1124). Services for accessing these data are described at the back of the journal.

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