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21α-Fluoro-7-nor-12,13,15,16-tetrahydrovouacapane-17β,21α-lactone

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.043
wR factor = 0.107
Data-to-parameter ratio = 9.5

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

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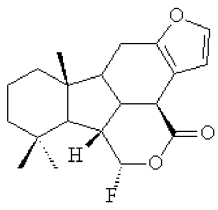
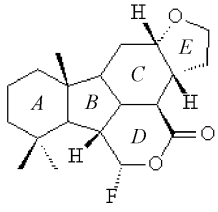
As part of our studies on synthetic derivatives of 6α,7β-dihydroxyvouacapan-17β-oic acid, isolated from the seeds of Pterodon polygalaeflorus Benth, the structure of the title compound, $C_{20}H_{29}FO_3$, was determined. The crystal packing is stabilized by C—H···O and C—H···F intermolecular interactions.

Comment

Natural products have proven commercial impact in the agrochemical arena, both as leads to new modes of action and as products in their own right (Lewer *et al.*, 2003). Several monoterpenes and sesquiterpenes are involved in allelopathic interactions among plant species. Studies have shown that the natural product 6α,7β-dihydroxyvouacapan-17β-oic acid (ADV) and other furan diterpenes affect the growth of *Sorghum bicolor L.* and *Cucumins sativus L.* (Demuner *et al.*, 1996).



(I)



(II)

Like compound (I) (Ruggiero *et al.*, 2000), the title compound, (II), is a derivative of ADV that was obtained in the search for new agrochemicals with herbicidal and/or plant growth regulatory activity. The molecular formula, $C_{20}H_{29}FO_3$, was derived from high-resolution mass spectrometry (M^+ ion peak at *m*/*z* 336.1124). The IR spectrum showed absorptions at 1775 cm^{-1} (C═O) and 1050 cm^{-1} (C—F). In the ^1H NMR spectrum, the signal due to H21, attached to C21, was observed at δ 6.08 as a doublet of doublets with $J_{H(21),F}$ = 54 Hz and $J_{H(21),H(6)}$ = 4 Hz, due to the couplings with both fluorine and H6 (attached to C6) nuclei, respectively. The small vicinal coupling (4 Hz) between H6 and H21 is consistent with fluorine in the α position (Demuner *et al.*, 1998). An *ORTEP*-3 (Farrugia, 1997) drawing of (II) is shown in Fig. 1, and selected geometric parameters are presented in Table 1.

The puckering parameters for the rings (Cremer & Pople, 1975; Iulek & Zukerman-Schpector, 1997) show that the rings *A* [θ = 3.2 (6) and φ = 324 (10)°] and *C* [θ = 19.0 (2) and φ = 13.0 (5)°] are in chair conformations. Rings *D* [θ = 52.2 (2) and φ = 276.4 (2)°] and *E* [θ_2 = 0.550 (1) Å and φ_2 = 128.5 (2)°] adopt half-chair and twist conformations, respectively. The cyclopentane ring (*B*) has an envelope conformation [θ_2 = 0.927 (4) Å and φ_2 = 29.8 (2)°], as in compound (I), and atom

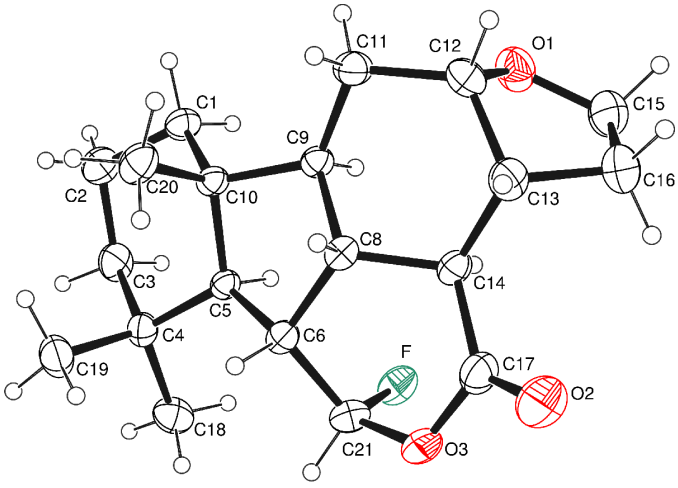


Figure 1
An *ORTEP*-3 (Farrugia, 1997) view of (II), with displacement ellipsoids drawn at the 30% probability level.

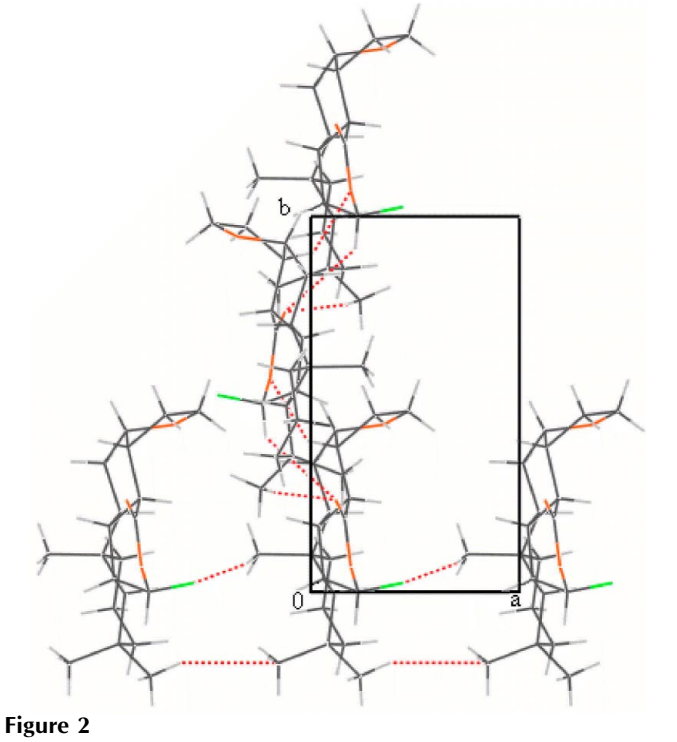


Figure 2
Short contacts in the packing of the title compound, viewed down the *c* axis.

C10 is 0.745 (6) Å out the plane defined by atoms C5, C6, C8 and C9.

The *B*/*D* and *C*/*E* ring junctions are *cis*, while junctions *A*/*B*, *B*/*C* and *C*/*D* are *trans*. A least-squares superposition of the *A*, *B*, *C* and *D* rings of compounds (I) and (II) results in an r.m.s. deviation of 0.104 Å.

Intermolecular short contacts (Table 2 and Fig. 2) link the molecules in chains along the [100] and [010] directions. This packing mode is similar to the hydrogen-bonding packing in ADV (Ruggiero *et al.*, 1997). In the crystal packing of compound (I), there is also a short C—H···F contact.

Experimental

The title compound was prepared from 6α-hydroxyvouacapane-7β,17β-lactone, a derivative of 6α,7β-dihydroxyvouacapan-17β-oic acid, under the same conditions as reported in the literature (Demuner *et al.*, 1998). Suitable single crystals of the compound were obtained by slow evaporation of a dichloromethane–ethanol (1:10) solution.

Crystal data

$C_{20}H_{29}FO_3$
M_r = 336.43
Orthorhombic, $P2_12_12_1$
a = 6.0284 (4) Å
b = 10.850 (2) Å
c = 26.921 (3) Å
V = 1760.8 (4) Å^3
Z = 4
D_x = 1.269 Mg m^{-3}
Mo Kα radiation
Cell parameters from 25 reflections
θ = 10.3–18.3°
μ = 0.09 mm^{-1}
T = 293 (2) K
Prism, colourless
0.02 × 0.01 × 0.01 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: none
2095 measured reflections
2093 independent reflections
1125 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 26.3°
$h = -7 \rightarrow 0$
$k = -13 \rightarrow 0$
$l = 0 \rightarrow 33$
3 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > \sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.107
S = 1.00
2093 reflections
220 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.044P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

F—C21	1.387 (5)	O2—C17	1.186 (4)
O1—C15	1.412 (5)	O3—C17	1.386 (5)
O1—C12	1.439 (5)	O3—C21	1.422 (4)
C15—O1—C12	109.0 (3)	O2—C17—C14	128.4 (4)
C17—O3—C21	119.9 (3)	O3—C17—C14	114.4 (3)
O1—C12—C13	103.2 (3)	F—C21—O3	107.7 (3)
O1—C12—C11	108.7 (3)	F—C21—C6	110.6 (3)
O1—C15—C16	107.8 (4)	O3—C21—C6	112.0 (3)
O2—C17—O3	117.2 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···O3^{i}	0.98	2.65	3.449 (5)	139
C18—H18A···O2^{ii}	0.96	2.76	3.684 (5)	161
C21—H21···O2^{ii}	0.98	2.77	3.560 (6)	138
C20—H20A···F^{iii}	0.96	2.68	3.619 (4)	166

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $x-1, y, z$.

In the absence of significant anomalous scattering effects, the Flack (1983) parameter is essentially meaningless. All H atoms were positioned geometrically, with C—H distances in the range 0.96–0.98 Å, and a riding model was used, with U_{iso} set to 1.5 (for methyl H atoms) or 1.2 (for other H atoms) times the value of U_{eq} of the carrier atom.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 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 Window*s (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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