Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Absolute configuration of diacetylated acrenol as its chloroform solvate

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Received 24 January 2003
Accepted 11 February 2003
Online 21 February 2003

Key indicators

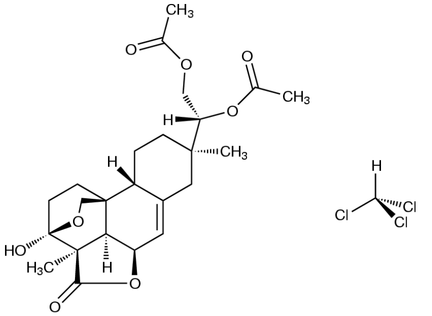
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.013 Å
R factor = 0.063
wR factor = 0.161
Data-to-parameter ratio = 7.3

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

The title compound, (15*S*)-15,16-diacetato-3β,20-epoxy-3α-hydroxy-9-epi-7-pimaren-19,6β-olide chloroform solvate, $C_{24}H_{32}O_8\cdot CHCl_3$, formed from the diacetylation of acrenol, isolated from the tubers of *Humirianthera ampla*, crystallizes as a chloroform solvate. The anomalous dispersion of the Cl atoms allows the absolute configuration to be determined. The structure is based on a pimarane skeleton and shows an identical conformation to the previously determined structures of icancinol and the acetylated derivative of humirianthol.

Comment

The title compound, (I), was derived by an acetylation reaction of acrenol. Acrenol, isolated from the tubers of *Humirianthera ampla* of the Icacinaceae family and obtained from the bush in Rio Branco, Acre, Brazil, was structurally characterized by spectroscopic techniques (Graebner *et al.*, 2000).



(I)

Since the stereochemistry of the numerous chiral centres could not be determined, a single-crystal X-ray structure determination was attempted. The parent compound did not yield crystals and so the acetylated derivative was synthesized. The resulting small crystals diffracted very weakly and reliable data could be obtained only to 20° in θ from the images collected by the CCD system. Solution of the structure revealed that a molecule of chloroform cocrystallized with the title compound. The presence of the Cl atoms generated sufficient anomalous dispersion that the absolute configuration could be determined reliably.

The structure is in agreement with that determined spectroscopically and has a core identical to those of icancinol (On'okoko *et al.*, 1985) and the acetylated derivative of humirianthol (Burrow *et al.*, 2003). Fig. 2 shows a superposition of the latter with the title compound, made with the quaternion transformation method (MacKay, 1984) within *PLATON* (Spek, 2002). Hydrogen-bonding details are given in Table 2.

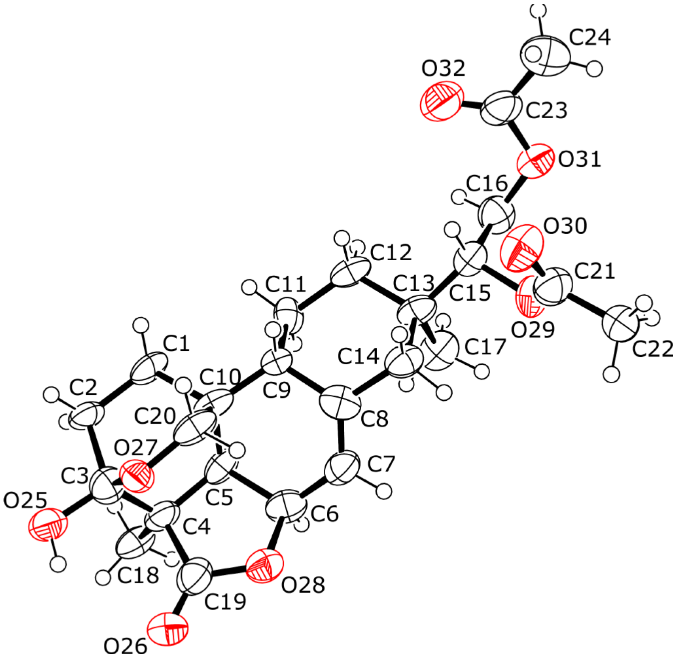


Figure 1
A displacement ellipsoid plot of the title compound drawn at the 50% probability level, with the atomic labelling scheme.

Experimental

The plant source and extraction are detailed in Graebner *et al.* (2000). The purified acrenol was acetylated using a modified version of a procedure by Hennig (1985); 0.5 mmol of acrenol, 3 ml of pyridine and 3 ml of acetic anhydride were stirred for 3 h. The residue was dissolved in chloroform, washed with 2 *M* HCl and precipitated with hexanes. Thin-layer chromatography showed only one product.

Crystal data

$C_{24}H_{32}O_8 \cdot CHCl_3$
$M_r = 567.86$
Orthorhombic, $P2_12_12_1$
$a = 8.0961$ (8) Å
$b = 11.2954$ (18) Å
$c = 28.684$ (4) Å
$V = 2623.1$ (6) Å^3
$Z = 4$
$D_x = 1.438$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8481 reflections
$\theta = 4.2$–$20.1°$
$\mu = 0.40$ mm^{-1}
$T = 100$ (2) K
Block, colourless
0.25 × 0.23 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN* (Otwinowski & Minor, 1997)
$T_{min} = 0.907$, $T_{max} = 0.925$
8481 measured reflections
2410 independent reflections
1863 reflections with $I > 2\sigma(I)$
$R_{int} = 0.132$
$\theta_{max} = 20.1°$
$h = -7 \rightarrow 7$
$k = -10 \rightarrow 10$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.161$
$S = 1.09$
2410 reflections
332 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0743P)^2 + 2.6838P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0068 (19)
Absolute structure: Flack (1983), 985 Friedel pairs
Flack parameter = 0.17 (17)

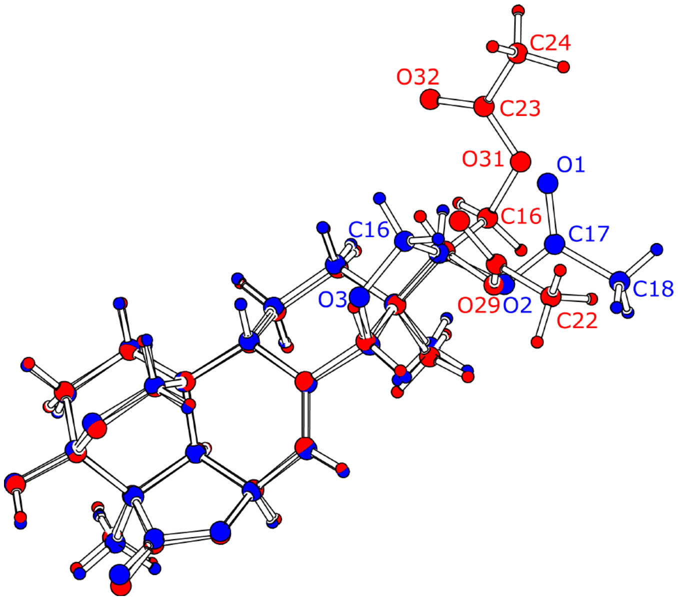


Figure 2
Superposition of the title compound (red) on humirianthol acetal (blue).

Table 1
Selected geometric parameters (Å, °).

C3—O25	1.390 (11)	C16—O31	1.426 (11)
C3—O27	1.469 (10)	C19—O26	1.210 (12)
C4—C18	1.548 (12)	C19—O28	1.388 (12)
C6—C7	1.463 (13)	C20—O27	1.438 (11)
C6—O28	1.484 (11)	C21—O30	1.233 (12)
C7—C8	1.309 (12)	C21—O29	1.333 (13)
C13—C15	1.539 (12)	C21—C22	1.484 (14)
C15—O29	1.473 (10)	C23—O32	1.188 (12)
C15—C16	1.516 (13)	C23—O31	1.333 (13)
C8—C7—C6	125.4 (9)	O32—C23—O31	123.4 (11)
O29—C15—C16	104.2 (7)	O32—C23—C24	123.1 (12)
O29—C15—C13	108.0 (7)	O31—C23—C24	113.5 (12)
C16—C15—C13	115.1 (8)	C20—O27—C3	110.6 (7)
O31—C16—C15	108.5 (8)	C19—O28—C6	109.9 (8)
O30—C21—O29	124.1 (10)	C21—O29—C15	116.7 (8)
O30—C21—C22	123.0 (12)	C23—O31—C16	116.0 (9)
O29—C21—C22	112.9 (11)		
C22—C21—O29—C15	−175.3 (8)	C24—C23—O31—C16	170.4 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O25—H25*A*···O32^i	0.84	2.13	2.840 (11)	142
O25—H25*A*···O26	0.84	2.47	3.075 (9)	130

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

The intensities of the data were, in general, weak, leading to the high R_{int} value. The H atoms of the methyl groups were refined as riding atoms with ideal tetrahedral geometry, allowed to rotate to fit the electron density; the isotropic displacement parameters were fixed to be 50% larger than those of the atoms to which the H atoms were bonded. Atom H25 was assigned an ideal position based on tetrahedral geometry and possible hydrogen bonding; the distance was 0.84 Å and the isotropic displacement parameter 50% larger than

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that of the parent O25. The other H atoms were constrained to ideal geometric positions (tetrahedral for methylene groups or trigonal planar for aromatic groups) with C—H distances fixed to default values. Their isotropic displacement parameters were set to be 20% larger than the those of the atoms to which the H atoms were bonded.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; 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 Windows* (Farrugia, 1997) and *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97.

The authors thank the Conselho Nacional de Pesquisa e Tecnológico (Brazil) and the Fundação de Amparo à Pesquisa (Rio Grande do Sul) for financial support. Fellowships from the Conselho Nacional de Desenvolvimento Científico e Technológico (CNPq, Brasil) for RAB and from CAPES-PICT (Coordenaćão de Aperfeićoamento de Pessoa de Nivel Superior for IBG are gratefully acknowledged. X-ray data were collected at the University of Toronto with funds from NSERC (Canada).

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