Absorption correction: empirical (Ugozzoli, 1987)

$h = -22 \rightarrow 22$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 11$

$T_{min} = 0.930$, $T_{max} = 1.052$

2 standard reflections monitored every 200 reflections intensity variation: insignificant

2420 measured reflections
1347 independent reflections
981 observed reflections
$[F>4\sigma(F)]$

Refinement

Refinement on F
Final $R = 0.0317$
$wR = 0.0438$
$S = 1.44$
981 reflections
109 parameters
$w = 1.0/[\sigma^2(F)+0.0005F^2]$

$(\Delta/\sigma)_{max} = 0.000$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}

Atomic scattering factors from *SHELXTL/PC* (Sheldrick, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

The coordinates for the second half of the molecule are generated by the symmetry operation $\frac{1}{2}-x, -\frac{1}{2}-y, 2-z$; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
N	0.2666 (1)	−0.3122 (2)	0.9721 (1)	0.044 (1)
C(1)	0.3388 (1)	−0.1013 (2)	0.8145 (2)	0.038 (1)
C(2)	0.3898 (1)	−0.0788 (2)	0.7032 (2)	0.042 (1)
C(3)	0.4205 (1)	−0.2228 (2)	0.6358 (2)	0.045 (1)
C(4)	0.4020 (1)	−0.3894 (2)	0.6803 (2)	0.042 (1)
C(5)	0.3512 (1)	−0.4109 (2)	0.7920 (2)	0.040 (1)
C(6)	0.3180 (1)	−0.2683 (2)	0.8611 (2)	0.037 (1)
F(1)	0.3112 (1)	0.0439 (1)	0.8749 (1)	0.051 (1)
F(2)	0.4089 (1)	0.0818 (1)	0.6607 (1)	0.061 (1)
F(3)	0.4690 (1)	−0.2009 (2)	0.5276 (1)	0.065 (1)
F(4)	0.4327 (1)	−0.5287 (1)	0.6166 (1)	0.061 (1)
F(5)	0.3337 (1)	−0.5734 (1)	0.8324 (1)	0.054 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)—F(1)	1.333 (2)	C(3)—C(4)	1.375 (2)
C(2)—F(2)	1.330 (2)	C(4)—C(5)	1.381 (2)
C(3)—F(3)	1.330 (2)	C(5)—C(6)	1.393 (2)
C(4)—F(4)	1.332 (2)	C(1)—C(6)	1.393 (2)
C(5)—F(5)	1.330 (2)	N—C(6)	1.414 (2)
C(1)—C(2)	1.382 (2)	N—N^i	1.231 (3)
C(2)—C(3)	1.375 (2)		
C(6)—N—N^i	115.6 (1)	C(3)—C(4)—C(5)	119.3 (1)
C(2)—C(1)—C(6)	121.2 (1)	C(3)—C(4)—F(4)	120.4 (1)
C(2)—C(1)—F(1)	116.8 (1)	C(5)—C(4)—F(4)	120.3 (1)
C(6)—C(1)—F(1)	122.1 (1)	C(4)—C(5)—C(6)	121.9 (1)
C(1)—C(2)—C(3)	119.9 (1)	C(4)—C(5)—F(5)	118.3 (1)
C(1)—C(2)—F(2)	120.1 (1)	C(6)—C(5)—F(5)	119.9 (1)
C(3)—C(2)—F(2)	120.0 (1)	N—C(6)—C(1)	127.7 (1)
C(2)—C(3)—C(4)	120.5 (1)	N—C(6)—C(5)	115.0 (1)
C(2)—C(3)—F(3)	119.8 (1)	C(1)—C(6)—C(5)	117.3 (1)
C(4)—C(3)—F(3)	119.7 (1)		

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

The density was measured by flotation in a mixture of CCl_4 and bromoform. The data were collected using a variable scan speed of 5.33–29.3° min $^{-1}$ in ω. The structure was solved by direct methods and refined by full-matrix least squares. *SHELXTL/PC* (Sheldrick, 1990) was used for all calculations.

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Structure of Zizyberannalic Acid

K. Sekar and S. Parthasarathy

*Department of Crystallography and Biophysics,†
University of Madras, Guindy Campus,
Madras-600 025, India*

A. B. Kundu and B. R. Barik

*Chemical Research Unit, CCRAS, Department of
Chemistry, University College of Science,
92 APC Road, Calcutta-700 009, India*

Abstract

In the pentacyclic triterpenoid zizyberannalic acid several C—C bonds and C—C—C angles deviate by more than 3σ from their expected values. The five-membered rings A and E are in a distorted envelope conformation. The six-membered rings B, C and D are in a slightly distorted chair conformation with mean torsion angles of 55.7 (6), 58.1 (6) and 55.7 (6)°, respectively. The structure is stabilized by O—H···O hydrogen bonds in addition to van der Waals forces.

Comment

The pentacyclic triterpenoid zizyberannalic acid was isolated by Kundu and co-workers from both the bark and the roots of *Zizyphus jujuba* (Kundu,

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Barik, Mondal, Dey & Banerji, 1989). Crystals were grown at room temperature from an ethanol/acetone mixture.

Several C—C bonds and C—C—C angles deviate by more than 3σ from their expected values. Similar features are also observed in fused-ring systems having bulky groups as axial substituents (Hall & Maslen, 1965; Gzella, Zaprutko, Wrzeciono & Jaskolski, 1987; Sekar, Parthasarathy, Kundu & Barik, 1992). The five-membered A and E rings are in half-chair and envelope conformations, respectively. The six-membered B, C and D rings are in a slightly distorted chair conformation. Puckering is enchanced in the region of C5 and decreased in the region of C8 in ring B. For rings C and D puckering is similarly altered near C14 and C11, and C17 and C14, respectively. The structure is stabilized by hydrogen bonds O31—H1031···O34[i] [2.832 (7) Å, 148 (5)°; (i) $-x+\frac{1}{2}$, $y-\frac{1}{2}$, $-z+2$] and O33—H1033···O31[ii] [2.719 (7) Å, 168 (5)°; (ii) $x+\frac{1}{2}$, $y+\frac{1}{2}$, z].

Fig. 1. A view of the molecule with atom numbering.

Experimental

Crystal data

$C_{30}H_{46}O_4$
$M_r = 470.69$
Monoclinic
$C2$
$a = 17.002$ (2) Å
$b = 18.399$ (2) Å
$c = 10.056$ (1) Å
$\beta = 119.21$ (2)°
$V = 2745.7$ (8) Å^3
$Z = 4$
$D_x = 1.139$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 25–35°$
$\mu = 0.543$ mm^{-1}
$T = 293$ K
Needle
$0.25 \times 0.20 \times 0.20$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ-scan method
$T_{min} = 0.948$, $T_{max} = 0.989$
2666 measured reflections
2578 independent reflections

2035 observed reflections [$I>3.0\sigma(I)$]
$R_{int} = 0.085$
$\theta_{max} = 70°$
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 22$
$l = -12 \rightarrow 12$
3 standard reflections frequency: 120 min intensity variation: none

Refinement

Refinement on F
Final $R = 0.056$
$wR = 0.061$
$S = 1.918$
2035 reflections
490 parameters
H-atom coordinates refined isotropically

$w = 1/[\sigma^2(F)+0.000943F^2]$
$(\Delta/\sigma)_{max} = 0.070$
$\Delta\rho_{max} = 0.309$ e Å^{-3}
$\Delta\rho_{min} = -0.206$ e Å^{-3}
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

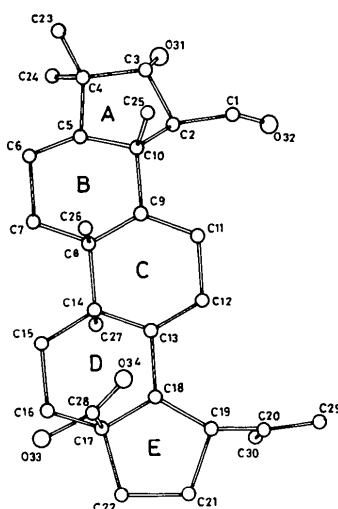Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.0343 (5)	0.0646	0.8605 (9)	0.110 (4)
C2	0.1152 (3)	0.0205 (4)	0.8855 (5)	0.062 (2)
C3	0.1395 (3)	−0.0333 (4)	1.0173 (5)	0.061 (2)
C4	0.2401 (3)	−0.0546 (4)	1.0773 (5)	0.058 (2)
C5	0.2669 (3)	−0.0057 (4)	0.9810 (4)	0.051 (2)
C6	0.3639 (3)	0.0114 (4)	1.0337 (6)	0.070 (2)
C7	0.3689 (3)	0.0466 (4)	0.8982 (5)	0.066 (2)
C8	0.3093 (2)	0.1153 (4)	0.8341 (4)	0.050 (2)
C9	0.2106 (3)	0.0980 (4)	0.7990 (4)	0.048 (2)
C10	0.2048 (3)	0.0610 (4)	0.9334 (4)	0.052 (2)
C11	0.1487 (3)	0.1637 (4)	0.7296 (5)	0.061 (2)
C12	0.1511 (3)	0.1947 (4)	0.5922 (5)	0.060 (2)
C13	0.2484 (3)	0.2102 (4)	0.6270 (4)	0.048 (2)
C14	0.3053 (2)	0.1389 (4)	0.6788 (4)	0.048 (2)
C15	0.4026 (3)	0.1540 (4)	0.7051 (5)	0.062 (2)
C16	0.4063 (3)	0.1929 (4)	0.5725 (5)	0.065 (2)
C17	0.3544 (3)	0.2643 (4)	0.5388 (5)	0.061 (2)
C18	0.2553 (3)	0.2468 (4)	0.4971 (5)	0.055 (2)
C19	0.2044 (3)	0.3189 (4)	0.4296 (5)	0.068 (2)
C20	0.1062 (4)	0.3132 (5)	0.3186 (7)	0.094 (3)
C21	0.2589 (4)	0.3542 (5)	0.3597 (7)	0.093 (3)
C22	0.3397 (4)	0.3054 (4)	0.3951 (6)	0.080 (3)
C23	0.2971 (4)	−0.0412 (5)	1.2494 (5)	0.082 (3)
C24	0.2500 (4)	−0.1342 (4)	1.0479 (7)	0.085 (3)
C25	0.2233 (4)	0.1142 (4)	1.0654 (5)	0.073 (3)
C26	0.3526 (3)	0.1759 (4)	0.9551 (5)	0.068 (2)
C27	0.2655 (3)	0.0796 (4)	0.5562 (5)	0.064 (2)
C28	0.4032 (3)	0.3144 (4)	0.6748 (5)	0.059 (2)
C29	0.0520 (6)	0.3654 (7)	0.3312 (14)	0.173 (6)
C30	0.0743 (5)	0.2558 (8)	0.2092 (8)	0.154 (5)
O31	0.0781 (2)	−0.0927 (4)	0.9663 (4)	0.083 (2)
O32	−0.0399 (4)	0.0569 (5)	0.7624 (9)	0.183 (5)
O33	0.4883 (3)	0.3251 (4)	0.7108 (5)	0.103 (2)
O34	0.3727 (2)	0.3421 (4)	0.7485 (4)	0.080 (2)

Table 2. *Geometric parameters* (Å, °)

C1—C2	1.509 (10)	C11—C12	1.514 (8)
C1—O32	1.171 (8)	C12—C13	1.541 (8)
C2—C3	1.540 (9)	C13—C14	1.561 (9)
C2—C10	1.547 (8)	C13—C18	1.524 (8)
C3—C4	1.561 (7)	C14—C15	1.567 (7)
C3—O31	1.423 (9)	C14—C27	1.534 (8)

C4—C5	1.545 (9)	C15—C16	1.542 (9)
C4—C23	1.536 (6)	C16—C17	1.526 (10)
C4—C24	1.520 (10)	C17—C18	1.559 (7)
C5—C6	1.499 (7)	C17—C22	1.540 (9)
C5—C10	1.535 (9)	C17—C28	1.517 (8)
C6—C7	1.548 (9)	C18—C19	1.548 (9)
C7—C8	1.550 (9)	C19—C20	1.492 (7)
C8—C9	1.570 (7)	C19—C21	1.553 (11)
C8—C14	1.590 (7)	C20—C29	1.379 (16)
C8—C26	1.546 (8)	C20—C30	1.427 (14)
C9—C10	1.559 (8)	C21—C22	1.531 (10)
C9—C11	1.529 (9)	C28—O33	1.324 (7)
C10—C25	1.553 (8)	C28—O34	1.205 (8)

C2—C1—O32	126.5 (5)	C7—C8—C9	109.8 (5)
C1—C2—C10	118.2 (5)	C14—C8—C26	110.6 (4)
C1—C2—C3	109.2 (4)	C9—C8—C26	111.7 (4)
C3—C2—C10	103.4 (4)	C9—C8—C14	107.8 (3)
C2—C3—O31	110.0 (4)	C8—C9—C11	111.4 (5)
C2—C3—C4	106.1 (4)	C8—C9—C10	114.0 (4)
C4—C3—O31	114.8 (5)	C10—C9—C11	114.9 (4)
C3—C4—C24	111.8 (5)	C5—C10—C9	107.1 (4)
C3—C4—C23	111.4 (5)	C2—C10—C9	114.2 (4)
C3—C4—C5	102.4 (4)	C2—C10—C5	97.8 (5)
C23—C4—C24	107.8 (5)	C9—C10—C25	113.2 (5)
C5—C4—C24	110.2 (5)	C5—C10—C25	114.6 (4)
C5—C4—C23	113.3 (5)	C2—C10—C25	109.1 (5)
C9—C11—C12	113.3 (5)	C16—C17—C28	108.7 (4)
C11—C12—C13	111.5 (4)	C16—C17—C22	116.3 (5)
C12—C13—C18	114.2 (4)	C16—C17—C18	108.3 (6)
C12—C13—C14	110.0 (5)	C22—C17—C28	108.3 (5)
C14—C13—C18	111.3 (5)	C18—C17—C28	114.3 (5)
C8—C14—C13	106.3 (3)	C18—C17—C22	101.0 (4)
C13—C14—C27	111.8 (4)	C13—C18—C17	112.7 (4)
C13—C14—C15	109.8 (5)	C17—C18—C19	103.9 (5)
C8—C14—C27	112.7 (4)	C13—C18—C19	119.6 (5)
C8—C14—C15	110.3 (3)	C18—C19—C21	103.2 (5)
C15—C14—C27	106.1 (4)	C18—C19—C20	116.7 (6)
C14—C15—C16	114.9 (4)	C20—C19—C21	112.8 (5)
C15—C16—C17	109.2 (4)	C19—C20—C30	119.6 (7)
C4—C5—C10	107.0 (4)	C19—C20—C29	115.9 (7)
C4—C5—C6	120.7 (4)	C29—C20—C30	124.5 (8)
C6—C5—C10	114.4 (5)	C19—C21—C22	108.4 (6)
C5—C6—C7	107.5 (4)	C17—C22—C21	102.9 (5)
C6—C7—C8	113.7 (4)	C17—C28—O34	127.0 (5)
C7—C8—C26	107.3 (4)	C17—C28—O33	112.4 (5)
C7—C8—C14	109.7 (4)	O33—C28—O34	120.7 (5)

C2—C3—C4—C5	4.3 (6)	C12—C13—C14—C8	−63.9 (5)
C3—C4—C5—C10	25.8 (6)	C13—C14—C8—C9	63.3 (5)
C4—C5—C10—C2	−44.8 (5)	C14—C8—C9—C11	−58.3 (6)
C5—C10—C2—C3	46.1 (5)	C13—C14—C15—C16	−50.6 (6)
C10—C2—C3—C4	−32.6 (6)	C14—C15—C16—C17	56.6 (6)
C5—C6—C7—C8	56.7 (6)	C15—C16—C17—C18	−59.0 (6)
C6—C7—C8—C9	−51.7 (6)	C16—C17—C18—C13	61.8 (6)
C7—C8—C9—C10	50.3 (6)	C17—C18—C13—C14	−57.0 (6)
C8—C9—C10—C5	−53.0 (6)	C18—C13—C14—C15	49.2 (6)
C9—C10—C5—C6	60.3 (6)	C17—C18—C19—C21	29.2 (6)
C10—C5—C6—C7	−62.0 (6)	C18—C19—C21—C22	−3.0 (7)
C8—C9—C11—C12	52.8 (6)	C19—C21—C22—C17	−24.6 (7)
C9—C11—C12—C13	−52.1 (7)	C21—C22—C17—C18	41.8 (6)
C11—C12—C13—C14	58.4 (6)	C22—C17—C18—C19	−44.6 (6)

Data collection: Enraf–Nonius CAD-4 diffractometer. Program used to determine space group: *STATCW* (Sekar, 1991). Program used to solve structure: *SHELX*90 (Sheldrick, 1990). Program used to refine structure: *SHELX*76 (Sheldrick, 1976). Program used to calculate molecular parameters: *PARST* (Nardelli, 1983). Program used to draw stereodiagram: *PLUTO* (Motherwell & Clegg, 1978). Refinement was by full-matrix least-squares methods. All calculations were performed on a MicroVAX II computer.

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Structure and Absolute Configuration of a Monohydrate of Calcipotriol, (1α,3β,5Z,7E,22E,24S)-24-Cyclopropyl-9,10-secochola-5,7,10(19),22-tetraene-1,3,24-triol

SINE LARSEN*

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

ERIK T. HANSEN, LENE HOFFMEYER AND NIELS RASTRUP-ANDERSEN

Leo Pharmaceutical Products Ltd, Industriparken 55, DK-2750 Ballerup, Denmark

(*Received* 23 *June* 1992; *accepted* 2 *October* 1992)

Abstract

The absolute configuration of calcipotriol was established to be 1S,3R,8R,14S,17R,20S,24R. The molecular geometry of calcipotriol is similar to the stereochemistry observed in the structures of the related D vitamins.