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Oleana-12(13),15(16)-diene-3*α*,28-diyl diacetate

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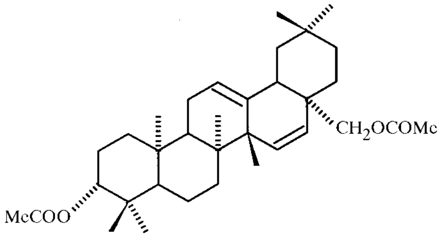
The title compound, $C_{34}H_{52}O_4$, consists of five six-membered rings. Barring the two rings, with double bonds, all other rings are in chair conformations. Mean-plane and ring-puckering calculations indicate these two rings to be in distorted-chair conformations, with distortion towards the boat conformation. There are no strong hydrogen bonds and the structure is stabilized by van der Waals interactions only. The structure is compared with those reported for other triterpenes.

Comment

The title compound, (I), has been isolated from the leaves of the plant *Jacquinia Ruscifolia* which is found in Mexico. Air-dried crushed leaves of the plant was extracted with petroleum ether (333–353 K), chloroform and methanol successively. The methanol extract in turn was refluxed with 6% methanolic hydrochloric acid (250 ml) for 6 h. The solvent was removed under reduced pressure, water being added during distillation to keep the acid concentration constant. The resulting mixture was extracted with a large volume of ether. The ethereal solution in turn was extracted with a saturated solution of sodium bicarbonate. The neutral fraction was washed thoroughly with water, dried and chromatographed over silica gel repeatedly. Benzene–ether (1:1) eluate afforded a white solid, crystallized from methanol. The diol was then acetylated by heating it with pyridine and acetic anhydride over water bath for 2 h. Usual work up, followed by crystallization from methanol resulted in oleana-12(13),15(16)-diene-3*α*,28-diyl diacetate (Dutta, 1972; Rao & Bose, 1962).



(I)

Several studies have been made on this class of triterpenes. The structure elucidation by X-ray method of several triterpenes such as Acide acetoxy-3*β* e oleanane-12(13)oique-28*α* (Roques *et al.*, 1978), triterpene gymnemagenin (Hoge & Nordman, 1974), 18-*α*(H)-oleanane (Fowell *et al.*, 1978) and (+)oleanolic acid (van Schalkwyk & Kruger, 1974) has also been performed. By convention the stereochemistry of this class of compounds is 3*β*-OAc,8*β*-Me,10*β*-Me,14*α*-Me,17*β*-COOMe. In the case of the present compound, we have obtained opposite chirality. However the crystallographic study does not provide an unambiguous determination of the absolute configuration. In our previous work on Oleana-13(18),15(16)-diene-3beta,28-diyl diacetate, we reported the conventional structure.

In the case of the present compound, except for the two rings with double bonds, all other rings are in chair conformation. The acetate group at C3 is almost planar with a tortion angle C32—C31—O1—C3 = 175°. The atom O1, attached to the atom C3 is lying below the least-squares plane defined by the atoms C2, C3, C5 and C10 of the ring A. The torsion angle is C2—C3—O1—C31 = −113.9 (3)°. The acetate group at C17, is almost planar, with mean deviation from the least-squares plane defined by the constituent atoms is 0.0274 Å, and C34 atom has the maximum out of plane deviation of 0.0337 Å This acetate group is equatorial to ring *E* (torsion angle, O3—C28—C17—C16 = −180°) and twisted from the plane of the ring *D* [torsion angle O3—C28—C17—C22 = −60.4 (3)°]. The mean Csp^3—Csp^3 bond length is 1.533 (3) Å with C8—C14 different with a value of 1.600 Å. As in the previous compound, this is attributed to the steric effects as these two bonded Csp^3 atoms have no attached H atoms.

Mean-plane calculations show similar behavior for the rings *C* and *D* containing double bonds. C9, C11, C13, C14 atoms of ring *C* define a least-squares plane, whose mean deviation from planarity is only 0.006 Å. The atom C8 is 0.7604 Å below this plane and C12 is 0.0262 Å above the plane. However the puckering parameter, φ = 178.2 (3)° which indicates distortion is towards boat. Similarly for the ring *D*, atoms C13, C14, C16, C17 define a least squares plane with mean deviation of 0.0006°. The atom C15 is 0.0205 Å below this plane, where as atom C18 is 0.6199° above the plane. Hence this ring is also a distorted chair and the distortion is towards boat as its puckering parameter φ is 59.6 (4)°. The puckering parameters of all the six-membered rings *A*, *B*, *C*, *D* and *E* have been calculated using the method of Cremer & Pople (1975), using

e60 Kinkini Bhattacharyya *et al.* • $C_{34}H_{52}O_4$ *Acta Cryst.* (2000). C**56**, e60–e61

the program *PARST* (Nardelli, 1983). There are no hydrogen bonds and the structure is stabilized by van der Waals interaction.

Experimental

The crystals of the title compound were obtained from a solution of the compound in methanol by slow evaporation at room temperature.

Crystal data

$C_{34}H_{52}O_4$
$M_r = 524.76$
Orthorhombic, $P2_12_12_1$
$a = 16.645$ (2) Å
$b = 25.768$ (2) Å
$c = 7.066$ (3) Å
$V = 3030.7$ (14) Å^3
$Z = 4$
$D_x = 1.150$ Mg m^{-3}

Cu $K\alpha$ radiation
Cell parameters from 49 reflections
$\theta = 12.3$–$40.8°$
$\mu = 0.568$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
0.4 × 0.3 × 0.1 mm

Data collection

Siemens AED diffractometer
ω–θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.94$, $T_{\max} = 0.97$
3292 measured reflections
3292 independent reflections
2929 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 70.01°$
$h = -19 \rightarrow 20$
$k = -30 \rightarrow 31$
$l = -8 \rightarrow 1$
2 standard reflections every 100 reflections intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0463$
$wR(F^2) = 0.1367$
$S = 1.162$
3292 reflections
347 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1016P)^2 + 0.1981P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.014$
$\Delta\rho_{\max} = 0.191$ e Å^{-3}
$\Delta\rho_{\min} = -0.207$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0057 (6)
Absolute structure: Flack (1983)
Flack parameter = −0.39 (36)

Table 1
Selected geometric parameters (Å, °).

C3—O1	1.463 (3)	C14—C27	1.564 (3)
C4—C24	1.528 (4)	C15—C16	1.324 (4)
C4—C23	1.547 (3)	C20—C30	1.532 (4)
C8—C26	1.539 (3)	C20—C29	1.532 (4)
C8—C14	1.600 (3)	C31—O2	1.189 (4)
C10—C25	1.543 (3)	C33—O4	1.195 (5)
C12—C13	1.330 (3)		
C2—C3—C4	114.4 (2)	C27—C14—C8	111.2 (2)
C26—C8—C14	108.7 (2)	C16—C15—C14	125.5 (2)
C13—C12—C11	125.4 (2)	C15—C16—C17	124.9 (2)
C12—C13—C14	120.6 (2)		
C1—C2—C3—O1	178.0 (2)	C12—C13—C18—C19	107.8 (3)
O1—C3—C4—C5	176.4 (2)	C16—C17—C28—O3	−180.0 (2)
C26—C8—C14—C27	−177.4 (2)	C22—C17—C28—O3	−60.4 (3)
C14—C15—C16—C17	−2.3 (4)	C32—C31—O1—C3	175.0 (3)

Table 2
Ring-puckering parameters (Å,°) for four rings.

Ring	q_2	q_3	Q_T	θ
A	0.047 (2)	−0.560 (3)	0.562 (3)	175.2 (3)
B	0.128 (2)	−0.563 (3)	0.577 (3)	167.2 (2)
C	0.427 (3)	−0.342 (2)	0.547 (3)	128.7 (3)
D	0.344 (3)	0.273 (3)	0.439 (3)	51.6 (4)
E	0.083 (2)	0.539 (2)	0.546 (2)	8.7 (2)

All the H atoms were included at geometrically calculated positions. For the methyl groups attached to sp^3 centres (*i.e.* for C23, C24, C25, C26, C27, C29 and C30), H atoms are placed in a unique staggered conformation For methyl groups on sp^2 centres, *i.e.* for C32 and C34 atoms, H atoms were located from a circular Fourier synthesis. They were then allowed to ride on their parent atom with $U_{\rm iso} = xU_{\rm eq}$ (parent), where x = 1.5 for methyl H atoms and x = 1.2 for all other atoms.

Data collection: Local Program (Belletti *et al.*, 1993); cell refinement: Local Program (Belletti *et al.*, 1993); data reduction: Local Program (Belletti *et al.*, 1993); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1993).

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References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, C. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Belletti, D., Cantoni, A., Pasquinelli, G. (1993). *Gestone om-line di Diffractometro Siemens AED con Personal Computer*. Internal Report 1–93. Centro di Studio per la Strutturistica Diffractometrica del CNR.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Dutta, P. K. (1972). PhD thesis, Calcutta University, India.
Fowell, D. T., Melsom, B. G. & Smith, G. W. (1978). *Acta Cryst.* B**34**, 2244–2250.
Flack, H. D. (1983). *Acta Cryst.* A39, 876–881
Hoge, R. & Nordman, C. E. (1974). *Acta Cryst.* B**30**, 1435–1440.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–353.
Rao, K. V. & Bose, P. K. (1962). *Tetrahedron*, **18**, 461–464.
Roques, P. R., Declercq, J. P. & Germain, G. (1978). *Acta Cryst.* C**34**, 2367–2370
Schalkwyk, T. G. D. van & Kruger, G. J. (1974). *Acta Cryst.* B**30**, 2261–2264.
Sheldrick, G. M. (1993). *SHELXL*93. University of Göttingen, Germany.