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(24*R*)-24,25-Dihydroxycycloartan-3-one

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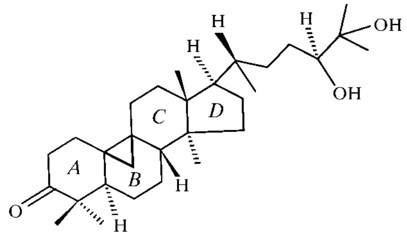
In the title compound, $C_{30}H_{50}O_3$, the three six-membered rings adopt chair, twist and twist-boat conformations. The five-membered ring is in a slightly distorted envelope conformation. The substituent on the five-membered ring is in an extended conformation, with its two hydroxyl O atoms forming an intramolecular hydrogen bond. One of these O atoms also forms an intermolecular hydrogen bond with the oxygen of the carbonyl group in a neighbouring molecule.

Comment

The title compound has been isolated from leaves of *Aglaia harmsiana* Perkins (Meliaceae) collected in Java, Indonesia. Extracts from this plant are used as a Chinese crude drug to treat arthritis, pharyngitis, tonsillitis and other ailments (Inada *et al.*, 1994). NMR spectroscopic investigations of this compound have also been reported (Inada *et al.*, 1995), but in order to establish the structure unequivocally, an X-ray structure analysis has been carried out.

The molecule (Fig. 1) contains a methine proton geminal to an hydroxy group at C24, a cyclopropyl methylene group, a secondary methyl group at C20 and the six tertiary methyl groups are present at C4, C13, C14 and C25. Two hydroxyl groups are present in the side chain, at C24 and C25. The differentiation of the 24*R* and 24*S* stereomers of cycloartane-type triterpenes using ^{13}C NMR techniques has been reported by Greca *et al.* (1994). It has been found that the chemical shifts of the side chain C atoms and C17 of the title compound are the same as those of (24*R*)-cycloartane-3β-24,25-triol and are different from those of the 24*S* isomer (Inada *et al.*, 1995). Based on this evidence the compound is (24*R*)-24,25-dihydroxycycloartan-3-one, (I). The structure determination also establishes this fact.



(I)

In the steroid skeleton, ring *A* (see Scheme) adopts a chair conformation while ring *B* adopts a twist conformation (Honda *et al.*, 1996) with C6 and C7 deviating by 0.391 (1) and −0.418 (1) Å, respectively, from the least-squares mean plane through C5, C8, C9 and C10. Ring *C* is in a twist-boat conformation while in ring *D* C13, C15, C16 and C17 are almost coplanar with C14 deviating by −0.620 (1) Å from this plane to give a 14α envelope conformation (Anthony *et al.*, 1999). The carbonyl C3 is twisted from the plane of ring *A*, the associated torsion angles being −138.3 (1) for C1—C2—C3—O1 and 138.7 (1)° for O1—C3—C4—C5. The cyclopropyl group is axial to ring *B*, as demonstrated by the torsion angle C7—C8—C9—C19 of 89.1 (1)°. The side chain at C17 is equatorial to ring *D* and in an extended conformation (Honda *et al.*, 1996). Ring-puckering parameters (Table 3) were calculated using the method of Cremer & Pople (1975).

Atom O3 of the hydroxyl group attached to the quaternary C25 atom forms an intramolecular hydrogen bond with O2 of the hydroxyl group on C24; O3 also forms an intermolecular hydrogen bond with the carbonyl-O atom O1 (Table 2). The former interaction generates a five-membered OCCOH ring while the latter links molecules into infinite chains running in the $[10\overline{1}]$ direction.

Although we have determined the relative configuration of the title compound, the value of the Flack parameter [0.1 (3)] together with the total absence of any Friedel reflections in the refinement do not allow the absolute configuration to be established unequivocally. However, Greca *et al.* (1994) and Boar & Damps (1977) have isolated and examined by chemical methods a few cycloartane-type triterpenes. Both have determined the absolute configuration at C24 by a modified Horeau's method (Brooks & Gilbert, 1973) and using this method the authors have differentiated between 24*R* and 24*S* configurations. Inada *et al.* (1995) found that the

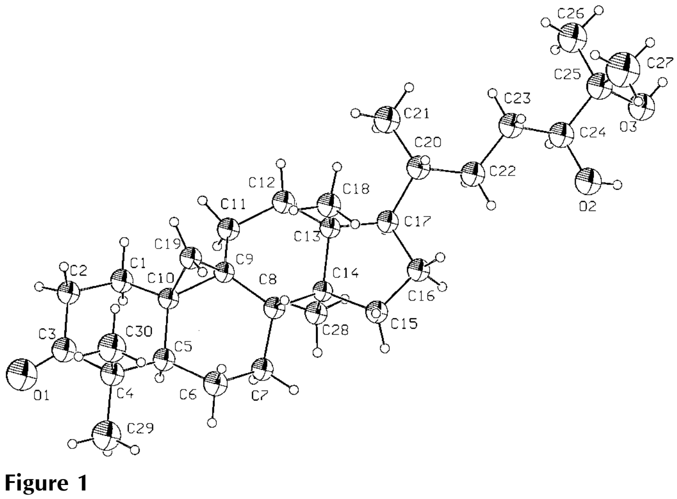


Figure 1
The structure of (I) showing the atom-numbering scheme and 30% probability displacement ellipsoids.

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chemical shifts of the side chain C atoms and C17 of the present compound are the same as those of 24*R* isomers of the above mentioned cycloartane-type triterpenes. The configuration adopted for the analysis and shown in the scheme and Fig. 1 is in accord with the known configuration.

Experimental

The dried and crushed leaves (700 g) were extracted with EtOH (3 × 10 l) and the solvent was removed *in vacuo*. The EtOH extract (30.2 g) was suspended in H_2O (600 ml) and the aqueous suspension was extracted successively with EtOAc (3 × 300 ml) and *n*-BuOH (3 × 300 ml). The EtOAc extract (25 g) was chromatographed on Si gel and fractions were further purified by high-pressure liquid chromatography to afford the title compound (140 mg) (Inada *et al.*, 1995). Crystals were obtained from a solution of the compound in EtOH–hexane by slow evaporation at room temperature.

Crystal data

$C_{30}H_{50}O_3$
$M_r = 458.70$
Monoclinic, $P2_1$
$a = 9.9534$ (10) Å
$b = 10.530$ (3) Å
$c = 13.837$ (2) Å
$\beta = 110.942$ (10)°
$V = 1354.4$ (5) Å^3
$Z = 2$

$D_x = 1.125$ Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 25 reflections
$\theta = 38$–70°
$\mu = 0.538$ mm^{-1}
$T = 273$ (2) K
Plate, colourless
0.20 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/*θ* scans
Absorption correction: *ψ* scan (North *et al.*, 1968)
$T_{\min} = 0.92$, $T_{\max} = 0.95$
6647 measured reflections
2825 independent reflections
2722 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.028$
$\theta_{\max} = 74.22°$
$h = -12 \rightarrow 9$
$k = -13 \rightarrow 0$
$l = -17 \rightarrow 17$
2 standard reflections every 200 reflections intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.114$
$S = 1.032$
2825 reflections
308 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0796P)^2 + 0.0939P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.022$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0102 (6)

Table 1
Selected geometric parameters (Å, °).

O1—C3	1.2192 (17)	C17—C20	1.5399 (15)
O2—C24	1.4096 (16)	C20—C21	1.525 (2)
O3—C25	1.4420 (16)	C20—C22	1.5338 (17)
C9—C19	1.5120 (16)	C24—C25	1.5301 (17)
C10—C19	1.5107 (17)		
O1—C3—C2	119.37 (12)	C10—C19—C9	61.03 (8)
O1—C3—C4	122.27 (11)	O2—C24—C23	108.37 (11)
C19—C9—C10	59.44 (7)	O2—C24—C25	111.15 (11)
C19—C10—C9	59.53 (7)	O3—C25—C26	109.21 (12)
C20—C17—C16	112.22 (10)	O3—C25—C27	109.70 (13)
C20—C17—C13	120.70 (8)		
C1—C2—C3—O1	−138.3 (1)	C15—C16—C17—C20	151.1 (1)
O1—C3—C4—C5	138.7 (1)	C14—C13—C17—C20	−165.5 (1)
C7—C8—C9—C19	89.1 (1)	C5—C10—C19—C9	109.1 (1)
C6—C5—C10—C19	−49.1 (1)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3	0.82	2.28	2.693 (2)	112
O3—H3···O1$^{\rm i}$	0.82	2.13	2.930 (2)	166

Symmetry code: (i) $1 + x, y, z - 1$.

Table 3
Ring-puckering parameters (Å,°) for four rings.

Ring	q_2	q_3	Q_T	*θ*
A	0.120 (1)	0.520 (1)	0.533 (1)	13.0 (1)
B	0.385 (1)	0.373 (1)	0.536 (2)	45.9 (1)
C	0.619 (1)	0.198 (1)	0.649 (1)	72.3 (1)
D	0.447 (1)			

The methyl H atoms on C18, C21, C26, C27, C28, C29 and C30 and the hydroxyl H atoms attached to O2 and O3 were found from circular difference Fourier synthesis. They were then refined as part of a rigid rotating group with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}$(parent). Other H atoms were included at geometrically calculated positions and allowed to ride on their parent atoms with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *CADRAL* (CCP4, 1993); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Huttner, 1994); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997) and *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1401). Services for accessing these data are described at the back of the journal.

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