

Suchada Chantrapromma,^{a*}
Charoen Pakathirathien,^a
Hoong-Kun Fun,^{b*}
Ibrahim Abdul Razak^b and
Chatchanok Karalai^a^aDepartment of Chemistry, Faculty of Science,
Prince of Songkla University, Hat-Yai, Songkhla
90112, Thailand, and ^bX-ray Crystallography
Unit, School of Physics, Universiti Sains
Malaysia, 11800 USM, Penang, MalaysiaCorrespondence e-mail: suchada.c@psu.ac.th,
hkfun@usm.my

Key indicators

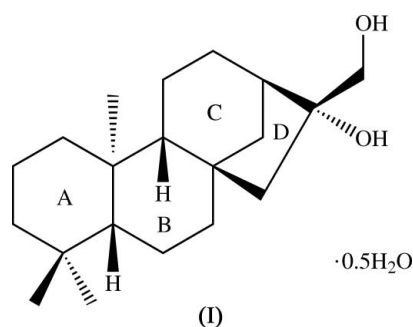
Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.009$ Å
 R factor = 0.086
 wR factor = 0.251
Data-to-parameter ratio = 9.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.14-Hydroxy-14-hydroxymethyl-5,5,9-trimethyltetra-
cyclo[11.2.1.0^{1,10}.0^{4,9}]hexadecane hemihydrate

The title compound, $\text{C}_{20}\text{H}_{34}\text{O}_2 \cdot 0.5\text{H}_2\text{O}$, is a diterpene known as *ent*-16 β -17 α -dihydroxykaurane. The cyclohexane rings adopt chair conformations and the cyclopentane ring adopts a half-chair form. The hydroxyl and hydroxymethyl substituents are attached pseudo-axially to the cyclopentane ring. The uncoordinated water molecule participates in intermolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, which link the molecules into ribbons extending along the a axis.

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Comment

We have previously reported the crystal structure of a lupane triterpene, namely 3 β -*E*-feruloyllupeol, which was isolated from *Ceriops tagal* (Perr.) (Pakhathirathien *et al.*, 2005). The bark of this plant has been used for the treatment of infected wounds in Thailand and as a treatment for obstetric and haemorrhagic conditions in the Philippines. Its decoction is used as a substitute for quinine in the treatment of malaria (Bamroongruga, 1999). The title compound, (I), has been isolated for the first time from *C. tagal* (Perr.). It has previously been isolated from other plants such as *Fritillariae bulbis* (Kitajima *et al.*, 1982), *Isodon flavidus* (Zhao *et al.*, 1998), *Aristolochia elegans* (Shi *et al.*, 2004) and *Croton malambo* (Morales *et al.*, 2005). Compound (I) has been reported to exhibit cytotoxicity against a human mammary carcinoma cell line, MCF-7 (Morales *et al.*, 2005). We report here the crystal structure of (I).



The crystal structure of (I) was previously reported by Lu *et al.* (1997) in the monoclinic space group $C2$, with $a = 12.940$ (12), $b = 6.253$ (8), $c = 24.01$ (2) Å, $\beta = 113.24$ (9)°, $Z = 4$, incorrectly as a monohydrate, without atomic coordinates for all the atoms. In the present study, the O atom of the water molecule lies on a twofold rotation axis, identifying (I) as a hemihydrate.

The molecule contains a fused four-ring system $A/B/C/D$. The A/B ring junction is *trans*-fused, whereas B/C and C/D are *cis*-fused. The cyclohexane rings adopt chair conformations,

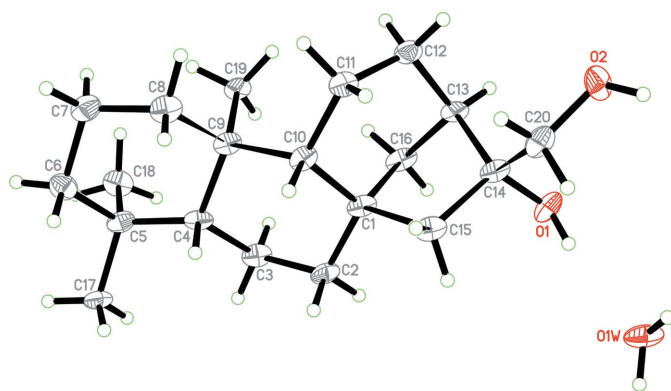


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atomic numbering scheme.

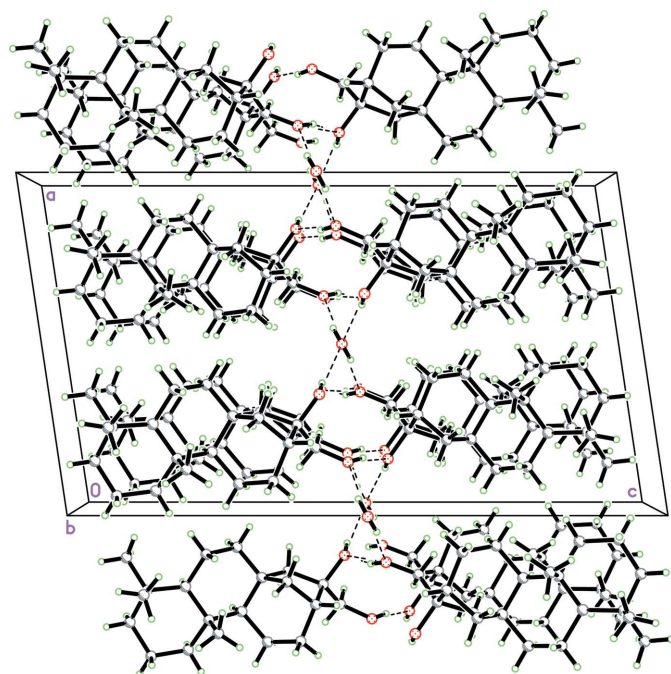


Figure 2
The packing of (I), viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

whereas the cyclopentane ring is in a half-chair form (Cremer & Pople, 1975), with puckering parameters $Q = 0.484$ (7) Å and $\varphi = 132.8$ (8)°. The hydroxyl and hydroxymethyl substituents are attached pseudo-axially to cyclopentane ring *D* at atom C14. The torsion angles (Table 1) C9–C4–C5–C18 = 70.9 (6)° and C7–C8–C9–C19 = 70.9 (6)° describe the orientation of the two methyl groups attached to ring *A* at atom C5. The C9–C4–C5–C17 torsion angle of -168.5 (5)° indicates a (–)-antiperiplanar conformation of the methyl group at C9. The bond distances and angles in (I) show normal values (Allen *et al.*, 1987). The water molecule participates in intermolecular O–H...O hydrogen bonds (Table 2), which link the molecules into ribbons extending along the *a* axis (Fig. 2).

Experimental

The air-dried and crushed stem bark of *Ceriops tagal* (4.8 kg) was extracted twice with dichloromethane. The extracts were combined and concentrated using a rotary evaporator, giving a residue (17.4 g) which was subjected to quick column chromatography over silica gel using solvents of increasing polarity starting from hexane through to 50% acetone–hexane. The elutions were collected, recombined and then separated, based on thin-layer chromatography, to give 20 fractions. Fraction 14 was further purified by repeated quick column chromatography with 5% acetone in dichloromethane, yielding the title compound (4.6 mg). Single crystals of (I) were obtained after recrystallization from acetone after several days (m.p. 447–448 K). The water comes from the solvent (acetone) which was used.

Crystal data

C₂₀H₃₄O₂·0.5H₂O
M_r = 315.48
 Monoclinic, C2
a = 12.8348 (13) Å
b = 6.2254 (5) Å
c = 22.202 (2) Å
 β = 98.493 (5)°
V = 1754.5 (3) Å³
Z = 4

D_x = 1.194 Mg m^{−3}
 Mo K α radiation
 Cell parameters from 6362 reflections
 θ = 0.9–26.0°
 μ = 0.08 mm^{−1}
T = 100.0 (1) K
 Slab, colourless
 0.28 × 0.19 × 0.07 mm

Data collection

Bruker SMART APEX-2 CCD
 area-detector diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
T_{min} = 0.983, *T_{max}* = 0.995
 6362 measured reflections

1894 independent reflections
 1506 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
 θ_{\max} = 26.0°
h = −13 → 15
k = −6 → 7
l = −27 → 23

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.086$
 $wR(F^2) = 0.251$
S = 1.19
 1894 reflections
 210 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1537P)^2 + 0.3783P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.56 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.38 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O1–C14	1.446 (7)	O2–C20	1.412 (8)
C9–C4–C5–C17	−168.5 (5)	C20–C14–C15–C1	136.5 (5)
C9–C4–C5–C18	70.9 (6)	C15–C14–C20–O2	−176.2 (5)
C7–C8–C9–C19	70.9 (6)	C13–C14–C20–O2	−56.9 (7)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1–H1O1...O1W	0.82	2.08	2.842 (6)	156
O1W–H1W1...O2 ⁱ	0.84 (4)	1.98 (3)	2.802 (6)	164 (5)
O2–H1O2...O1 ⁱⁱ	0.82	2.01	2.799 (6)	161

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

The H atom of the water molecule was located in a difference map. Constraints were applied to yield an ideal water molecule configuration [$O1W-H1W1 = 0.84$ (1) Å and $H1W1 \cdot \cdot H1W1(1-x, y, -z) = 1.37$ (2) Å]. H atoms of hydroxyl groups were placed in calculated positions, with an O–H distance of 0.82 Å. The C-bound H atoms were positioned geometrically, with C–H distances in the range 0.93–0.98 Å. $U_{iso}(H)$ values were constrained to be $1.5U_{eq}$ of the carrier atom for hydroxyl and methyl H atoms and $1.2U_{eq}$ for the remaining H atoms. Due to the absence of any significant anomalous scatterers in the molecule, Friedel pairs were merged before the final refinement and the absolute configuration, shown in Fig. 1, was assigned arbitrarily. The low-temperature data were collected with an Oxford Cryosystem Cobra low-temperature attachment.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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