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1-Isopropenyl-3a,5a,5b,8,8,11a-hexamethylicosahydro-1*H*-cyclopenta[*a*]chrysen-9-yl 4-hydroxy-3-methoxycinnamate

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Key indicators

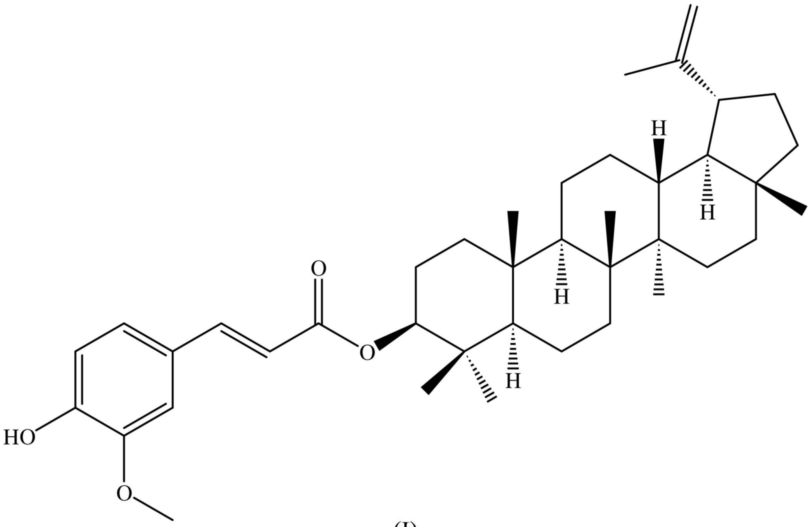
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
R factor = 0.089
wR factor = 0.264
Data-to-parameter ratio = 7.6

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

The title compound, $C_{40}H_{58}O_4$, a lupane triterpene, was isolated from the hypocotyls of *Ceriops tagal* (Perr.) C. B. Robinson. There are two crystallographically independent molecules in the asymmetric unit. In both molecules, the cyclopentane ring adopts an envelope conformation. The molecular structure is stabilized by O—H···O and C—H···O hydrogen bonds. C—H···O intermolecular hydrogen bonds link the molecules into chains along the *a* axis.

Comment

The genus *Ceriops* (Rhizophoraceae) comprises two species, namely *Ceriops tagal* (Perr.) C. B. Robinson and *Ceriops decandra* (Griff.) Ding Hou. These are mangrove plants widely distributed from East Africa and Madagascar throughout tropical Asia and Queensland to Melanesia and Micronesia (Tomlinson, 1986). The bark of *C. tagal* (Perr.) has been used for the treatment of infected wounds in Thailand and as a treatment for obstetric and haemorrhagic conditions in the Philippines, and its decoction used as a substitute for quinine in the treatment of malaria (Bamroongrugsa, 1999). Investigation of the crude hexane and dichloromethane extract of the hypocotyls of *C. tagal* (Perr.) has exhibited antituberculous and cytotoxic activity. The results prompted us to make a further study of the extracts.



(I)

The title compound, (I), also known as 3β-*E*-feruloyllupeol, has been isolated for the first time from *C. tagal* (Perr.), which was collected from Nakhon-Si-Thammarat province in

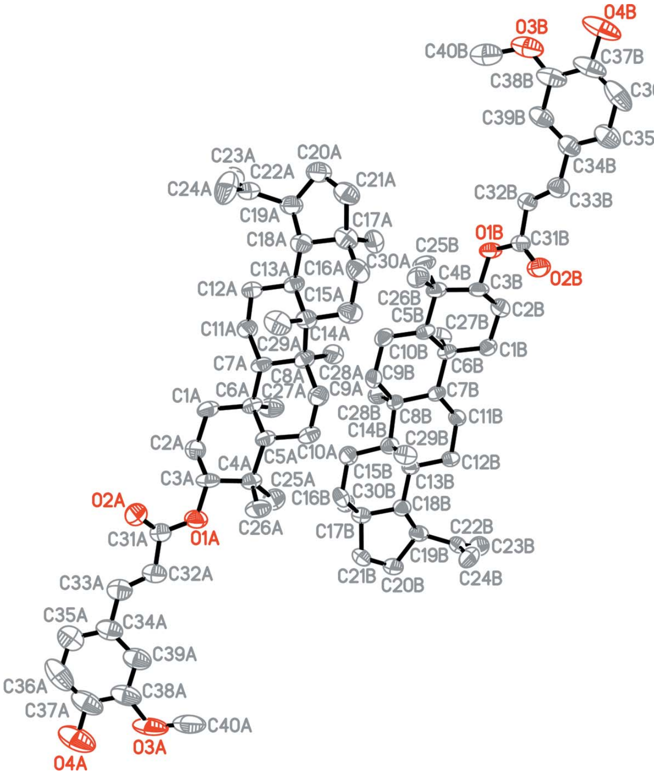


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atomic numbering scheme. For clarity, H atoms have been omitted.

southern Thailand. As part of our research on bioactive compounds from Thai medicinal plants (Chantrapromma *et al.*, 2003, 2004, 2005; Boonnak *et al.*, 2005; Thongdeeying *et al.*, 2005), we have undertaken the X-ray crystal structure analysis of (I) in order to establish its molecular structure and relative stereochemistry. The title compound exhibits significant levels of strong activity (1.75 μg ml^{-1}) against the NIC-H187 cell line (human small-cell lung cancer).

The asymmetric unit of (I) contains two crystallographically independent molecules, *A* and *B*, which have similar chiralities, bond lengths and angles (Fig. 1). The molecules are approximately related by a local twofold rotation axis. The bond lengths in (I) show normal values (Allen *et al.*, 1987). All the ring junctions in the lupane nucleus are *trans*-fused. In both molecules, the cyclohexane rings adopt chair conformations and the cyclopentane ring has an envelope conformation, with atom C17 displaced from the C18/C19/C20/C21 plane by 0.676 (10) Å in molecule *A* and 0.700 (10) Å in molecule *B*. The feruloyloxy group (O1–O4/C31–C40) is equatorially attached at atom C3 [C1—C2—C3—O1 = −178.8 (5)° in molecule *A* and −179.9 (5)° in molecule *B*], and the C31—O1—C3—C2 torsion angle of −88.8 (7)° in molecule *A* [−85.7 (7)° in molecule *B*] indicates a (−)-synclinal conformation. The methoxy group is slightly twisted away from the benzene ring [C40—O3—C38—C39 = 8.9 (13)° in molecule *A* and 15.5 (12)° in molecule *B*]. The C20—C19—C22—C23 torsion angle of 104.6 (9)° [102.5 (8)° in molecule *B*] describes the orientation of the isopropenyl group with respect to the lupane nucleus. The C18—C19—C22—C24 torsion angle is 47.3 (11)° [46.4 (8)° in molecule *B*]. The bond lengths and angles in the lupane skeleton are comparable with the corresponding values in 3*β*-hydroxylupan-29-oic acid (Thongdeeying *et al.*, 2005) and those in the feruloyloxy substituent are comparable with the closely related substituent in 3*α*-feruloyltaraxerol dichloromethane solvate (Chantrapromma *et al.*, 2003).

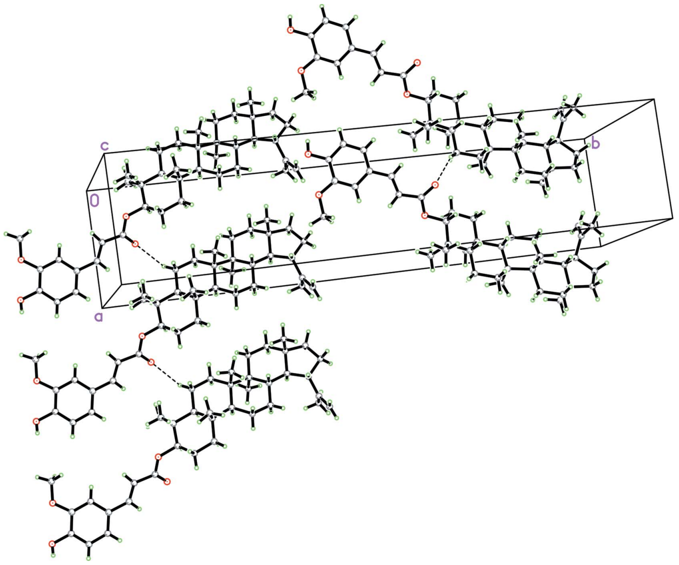


Figure 2
The crystal packing of (I), viewed down the *c* axis. O—H···O hydrogen bonds are shown as dashed lines.

The molecular structure of (I) is stabilized by O—H···O and C—H···O hydrogen bonds (Table 2). C—H···O intermolecular hydrogen bonds link the molecules into chains along the *a* axis (Fig. 2).

Experimental

Dried milled hypocotyls of *Ceriops tagal* (Perr.) C. O. Robinson (5.3 kg) were successively extracted with hexane and CH_2Cl_2. Evaporation resulted in crude extracts of hexane (32.9 g) and CH_2Cl_2 (128.6 g), respectively. A portion of the hexane extract (17.1 g) was subjected to column chromatography using gradient elution of hexane and ethyl acetate (10:0 to 7:3), to afford 12 fractions (*A*1–*A*12). Fraction *A*2 (1.43 g) was subjected to quick column chromatography (QCC) using hexane and ethyl acetate mixtures with increasing polarity as eluting solvent (10:0 to 9:1), to afford compound (I) (160 mg). Single crystals of (I) were obtained after recrystallization from acetone {m.p. 502–503 K, $[\alpha]^{27}_{D}$ +23.26° (*c* = 0.043, MeOH)}.

Crystal data

$C_{40}H_{58}O_4$
$M_r = 602.86$
Monoclinic, $P2_1$
$a = 7.9738\ (17)$ Å
$b = 36.351\ (8)$ Å
$c = 11.875\ (3)$ Å
$\beta = 92.012\ (3)°$
$V = 3439.9\ (14)$ Å^3
$Z = 4$

$D_x = 1.164$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 17061 reflections
$\theta = 1.7–25.0°$
$\mu = 0.07$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.56 × 0.29 × 0.20 mm

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Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.960$, $T_{\max} = 0.985$
17061 measured reflections
6145 independent reflections
5155 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\max} = 25.0°$
$h = -9 \rightarrow 9$
$k = -40 \rightarrow 43$
$l = -12 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.089$
$wR(F^2) = 0.264$
$S = 1.05$
6145 reflections
811 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1917P)^2 + 1.227P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.60$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*B*—C31*B*	1.334 (8)	O1*A*—C31*A*	1.322 (9)
O1*B*—C3*B*	1.465 (7)	O1*A*—C3*A*	1.462 (7)
O2*B*—C31*B*	1.191 (8)	O2*A*—C31*A*	1.221 (9)
O3*B*—C38*B*	1.334 (12)	O3*A*—C38*A*	1.375 (12)
O3*B*—C40*B*	1.424 (13)	O3*A*—C40*A*	1.405 (15)
O4*B*—C37*B*	1.371 (10)	O4*A*—C37*A*	1.374 (12)
C32*B*—C33*B*	1.306 (10)	C32*A*—C33*A*	1.304 (11)
C31*B*—O1*B*—C3*B*	117.8 (5)	C31*A*—O1*A*—C3*A*	118.6 (5)
O1*B*—C31*B*—C32*B*	111.0 (5)	O1*A*—C31*A*—C32*A*	112.4 (6)
C31*B*—O1*B*—C3*B*—C2*B*	−85.7 (7)	C31*A*—O1*A*—C3*A*—C2*A*	−88.8 (7)
C1*B*—C2*B*—C3*B*—O1*B*	−179.9 (5)	C1*A*—C2*A*—C3*A*—O1*A*	−178.8 (5)
C20*B*—C19*B*—C22*B*—C23*B*	102.5 (8)	C20*A*—C19*A*—C22*A*—C23*A*	104.6 (9)
C18*B*—C19*B*—C22*B*—C24*B*	46.4 (8)	C18*A*—C19*A*—C22*A*—C24*A*	47.3 (11)
C40*B*—O3*B*—C38*B*—C39*B*	15.5 (12)	C40*A*—O3*A*—C38*A*—C39*A*	8.9 (13)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4*B*—H4*BA*···O3*B*	0.82	2.22	2.639 (12)	112
C10*A*—H10*B*···O2*A*$^{\rm i}$	0.97	2.50	3.378 (9)	150
C3*A*—H3*AA*···O2*A*	0.98	2.37	2.719 (9)	100
C26*B*—H26*A*···O1*B*	0.96	2.48	2.897 (9)	106
C26*A*—H26*D*···O1*A*	0.96	2.52	2.899 (10)	103
C33*B*—H33*A*···O2*B*	0.93	2.53	2.852 (9)	101
C33*A*—H33*B*···O2*A*	0.93	2.54	2.858 (9)	100

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

H atoms were placed in calculated positions, with O—H distances of 0.82 Å and C—H distances in the range 0.93–0.98 Å. The $U_{\rm iso}$(H) values were constrained to be $1.5U_{\rm eq}$ of the carrier atom for hydroxyl and methyl H atoms and $1.2U_{\rm eq}$ for the remaining H atoms. A rotating group model was used for the methyl and hydroxy groups. In the absence of significant anomalous dispersion effects, Friedel pairs were merged before the final refinement. The high *R* values may be a result of the poor diffraction quality of the crystal or of unresolved twinning [F^2(observed) is greater than F^2(calculated) for the most disagreeable/anomalous reflections]. It is very difficult to obtain good crystals of the title compound, and that which was used for the present experiment was the best available after many crystallization attempts.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); 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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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.

Bamroongrugsa, N. (1999). *Songklanakarin J. Sci. Technol.* **21**, 377–386.

Boonnak, N., Chantrapromma, S., Fun, H.-K., Anjum, S., Atta-ur-Rahman & Karalai, C. (2005). *Acta Cryst.* E**61**, o410–o412.

Bruker (2002). *SMART* (Version 5.62) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.

Chantrapromma, K., Saewan, N., Fun, H.-K., Chantrapromma, S. & Rahman, A. A. (2004). *Acta Cryst.* E**60**, o312–o314.

Chantrapromma, S., Boonnak, N., Fun, H.-K., Anjum, S. & Atta-ur-Rahman (2005). *Acta Cryst.* E**61**, o2136–o2138.

Chantrapromma, S., Fun, H.-K., Razak, I. A., Laphookhieo, S. & Karalai, C. (2003). *Acta Cryst.* E**59**, o1864–o1866.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Thongdeeying, P., Chantrapromma, S., Fun, H.-K., Anjum, S., Ali, S. & Ponglimanont, C. (2005). *Acta Cryst.* E**61**, o1861–o1863.

Tomlinson, P. B. (1986). *The Botany of Mangroves*, pp. 352–357. Cambridge University Press.

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