

8-Hydroxy-13-methoxy-17,17-dimethyl-15-(3-methyl-2-butenyl)-3,16-dioxapentacyclo[11.4.1.0^{2,11}.0^{2,15}.0^{4,9}]octadeca-4,6,8,11-tetraene-10,14-dione**Suchada Chantrapromma,^{a*}
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Hoong-Kun Fun^{b*}**^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, Malaysia

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Key indicatorsSingle-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.063
 wR factor = 0.183
Data-to-parameter ratio = 15.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{24}\text{H}_{26}\text{O}_6$, is a caged-polyprenylated xanthone which has been isolated for the first time from the roots of *C. cochinchinense*. The cyclohexane ring adopts a standard boat conformation, the cyclohexene rings are in twisted boat and twist-boat conformations, and the tetrahydrofuran ring has an envelope conformation. The structure is stabilized by intramolecular $\text{C}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. $\text{C}-\text{H}\cdots\text{O}$ intermolecular hydrogen bonds and $\text{C}-\text{H}\cdots\pi$ stacking interactions link the molecules into molecular sheets parallel to the bc plane.

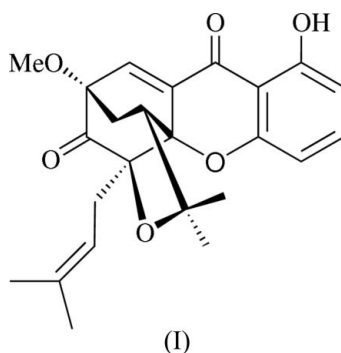
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Comment

The title compound, (I), is a caged-polyprenylated xanthone which has been isolated for the first time from *Cratoxylum cochinchinense* which was collected from Nhonkhai province in the northeastern part of Thailand. More importantly, (I) has never before been isolated from any natural product resources.



This plant is a medicinal plant belonging to the genus *Cratoxylum* (Bennett & Lee, 1989) and widely distributed, mainly in Southeast Asia. Some species of this genus have been used as traditional medicines (Usher, 1984). The bark, root and leaves of *C. cochinchinense* are used in folk medicines to treat fevers, coughs, diarrhea, itches, ulcers and abdominal complaints (Vo, 1997). As part of our research on bioactive compounds from medicinal plants (Chantrapromma *et al.*, 2003, 2004; Chantrapromma, Boonnak *et al.*, 2005; Chantrapromma, Fun *et al.*, 2005; Boonnak *et al.*, 2005; Fun *et al.*, 2005), we have undertaken the X-ray crystal structure analysis of (I) in order to establish its molecular structure and relative stereochemistry.

Compound (I) is a chiral molecule, which crystallized in the centrosymmetric space group $P2_1/c$. This indicates that (I) was produced by non-enzymatic reactions during the chromatographic process (Chantrapromma, Boonnak *et al.*, 2005; Chantrapromma, Fun *et al.*, 2005).

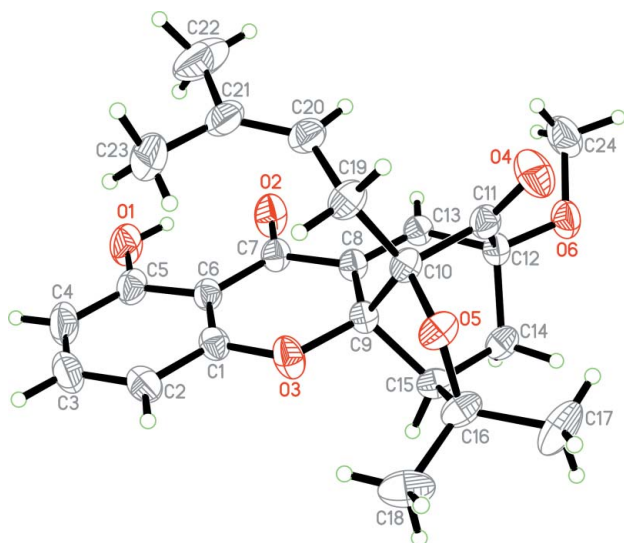


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atomic numbering.

The molecular structure of (I) is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1. The bond lengths in (I) show normal values (Allen *et al.*, 1987). In the xanthone skeleton (C1–C13/O2/O3), there are two cyclohexene rings, *viz.* C8–C13 and C8–C9/C12–C15. The former adopts a slightly twisted boat conformation and the latter has a twist-boat conformation, with puckering parameters $Q = 0.778$ (3), $\theta = 88.092^\circ$, $\varphi = 240.00$ (18) $^\circ$ and $Q = 0.765$ (3), $\theta = 96.7$ (2) $^\circ$, $\varphi = 49.62$ (19) $^\circ$, respectively (Cremer & Pople, 1975). The cyclohexane ring (C9–C12/C14–C15) is in a boat conformation; the tetrahydrofuran ring (O5/C10/C9/C15/C16) has an envelope conformation, with C9 as the most flap atom [displacement 0.291 (2) Å] and $Q = 0.463$ (3) (Cremer & Pople, 1975). The hydroxyl group is coplanar with the attached benzene ring. The methoxy group is in a (+)-anti-periplanar conformation (Fig. 1), as evidenced by the torsion angle O6–C12–C13–C8 of 175.0 (2) $^\circ$. The orientation of C11=O4 is defined by the C9–C10–C11–O4 torsion angle of 179.3 (2) $^\circ$. The 3-methyl-2-butenyl (C19–C23) substituent group involves the C9–C10–C19–C20 torsion angle of -58.5 (3) $^\circ$, indicating a (–)-synclinal conformation. The two methyl groups are axially and bisectionally attached to the tetrahydrofuran ring at atom C16.

The molecular structure is stabilized by intramolecular C–H \cdots O interactions and O–H \cdots O hydrogen bonds (Table 2). C–H \cdots O intermolecular interactions link the molecules into molecular sheets parallel to the *bc* plane (Fig. 2). In addition, the molecular packing is stabilized by C–H \cdots π interactions involving Cg1 where Cg1 is the centroid of the cyclohexene ring (C8–C13) (Table 2).

Experimental

Air-dried roots of *C. cochinchinense* (2 kg) were extracted successively with hexane. The hexane extract (17 g) was subjected to QCC over silica gel and eluted with a gradient of hexane–EtOAc to afford nine fractions (A1–A9). Fraction A2 was subjected to column chroma-

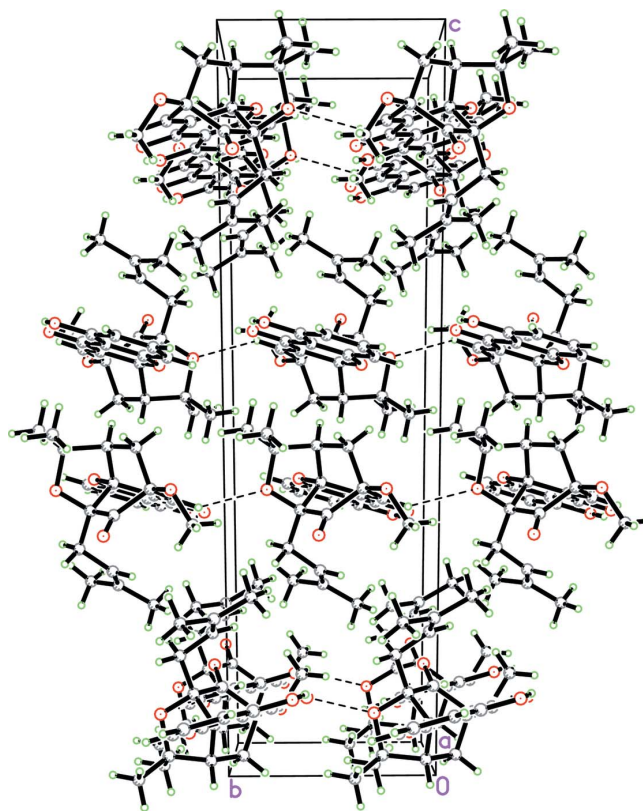


Figure 2
The crystal packing of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

tography using 20% EtOAc–hexane as eluent to give seven sub-fractions. Subfractions A2-2 (1.2 g) was crystallized from 20% EtOAc–hexane to yield compound (I) (0.5 g). Compound (I) was recrystallized from CHCl₃/CH₃OH (8:2 v/v) to give pale-yellow single crystals after several days (m.p. 431–432 K).

Crystal data

C₂₄H₂₆O₆
M_r = 410.45
 Monoclinic, *P*2₁/*c*
a = 11.4622 (4) Å
b = 7.3284 (2) Å
c = 26.7829 (9) Å
 β = 109.709 (2) $^\circ$
V = 2117.96 (12) Å³
Z = 4

D_x = 1.287 Mg m⁻³
 Mo K α radiation
 Cell parameters from 4636 reflections
 θ = 1.6–27.0 $^\circ$
 μ = 0.09 mm⁻¹
T = 273 (2) K
 Block, pale yellow
 0.55 × 0.44 × 0.34 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.953$, $T_{\max} = 0.969$
 35056 measured reflections

4636 independent reflections
 4048 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 27.0^\circ$
 $h = -14 \rightarrow 14$
 $k = -9 \rightarrow 9$
 $l = -34 \rightarrow 34$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.063$
 $wR(F^2) = 0.183$
 $S = 1.09$
 4636 reflections
 303 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.063P)^2 + 2.6144P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.19 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.28 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O1—C5	1.347 (3)	O5—C16	1.466 (3)
O2—C7	1.241 (3)	O6—C12	1.401 (3)
O3—C1	1.356 (3)	O6—C24	1.431 (4)
O3—C9	1.425 (3)	C8—C13	1.334 (3)
O4—C11	1.195 (3)	C20—C21	1.325 (4)
O5—C10	1.426 (3)		
C1—O3—C9	122.71 (18)	C12—C11—C10	113.51 (18)
C10—O5—C16	109.93 (17)	O6—C12—C14	107.96 (19)
C12—O6—C24	115.9 (2)	C16—C15—C9	102.37 (18)
C19—C10—C11	112.8 (2)	C20—C19—C10	113.2 (2)
C7—C8—C9—C15	128.1 (2)	O6—C12—C13—C8	175.0 (2)
O3—C9—C10—O5	68.3 (2)	C9—C15—C16—C17	-143.0 (3)
C9—C10—C11—O4	179.3 (2)	C9—C15—C16—C18	90.4 (2)
C24—O6—C12—C13	50.8 (3)	C9—C10—C19—C20	-58.5 (3)
C24—O6—C12—C14	169.2 (2)	C11—C10—C19—C20	65.8 (3)

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—H1A...O2 ⁱ	0.82	1.86	2.591 (3)	147
C13—H13A...O5 ⁱⁱ	0.93	2.53	3.335 (3)	145
C18—H18C...O3 ⁱ	0.96	2.30	2.978 (4)	127
C24—H24B...O4 ⁱ	0.96	2.58	3.106 (4)	115
C15—H15A...Cg1 ⁱⁱⁱ	0.98	2.82	3.66	144
C23—H23B...Cg1 ⁱ	0.96	2.92	3.56	125

Symmetry codes: (i) *x*, *y*, *z*; (ii) *x*, *y* + 1, *z*; (iii) -*x* + 1, -*y* - 2, -*z*. Cg1 is the centroid of the cyclohexene ring (C8—C13).

H atoms were placed in calculated positions, with an O—H distance of 0.82 Å and C—H distances in the range 0.93–0.97 Å. The $U_{\text{iso}}(\text{H})$ values were constrained to be $1.5U_{\text{eq}}$ of the carrier atom for hydroxyl and methyl H atoms and $1.2U_{\text{eq}}$ for the remaining H atoms.

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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