Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

7a-*O*-Methyldeguelol

Suchada Chantrapromma,[a] Hoong-Kun Fun,[b]* Yupparase Pullaput,[c] Hathaichanok Wongtap,[c] Saravut Dejmanee[c] and Kan Chantrapromma[c]*

[a]Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand, [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [c]Research Unit of Natural Products Utilization, School of Science, Walailak University, Thasala, Nakhon Si Thammarat 80160, Thailand

Correspondence e-mail: hkfun@usm.my, ckan@wu.ac.th

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.084
wR factor = 0.199
Data-to-parameter ratio = 11.4

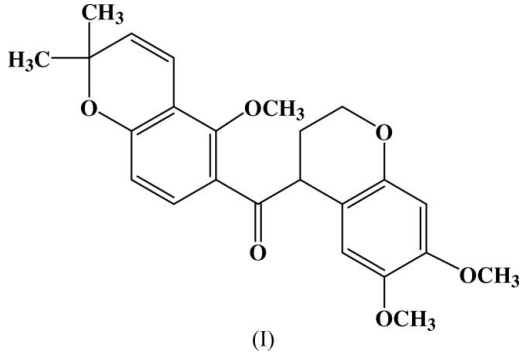
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 13 June 2005
Accepted 27 June 2005
Online 6 July 2005

The title compound, (6,7-dimethoxy-3,4-dihydro-2*H*-chromen-4-yl)(5-methoxy-2,2-dimethyl-2*H*-chromen-6-yl)-methanone, $C_{24}H_{25}O_6$, is a modified rotenoid. In the crystal structure, the chromene ring is disordered, together with its attached methyl and methoxy groups. The molecules are packed as layers parallel to the *ac* plane. These layers are interconnected through C—H···O interactions to form a three-dimensional network.

Comment

The title compound, (I), is a new modified rotenoid which was isolated from the seeds of *Derris trifoliata* Lour, a mangrove plant belonging to the Leguminosae family and distributed widely in the coastal areas of south east Asia and the Indian Ocean. The plant is a creeping or climbing vinelike shrub with long trailing branches and compound leaves, mostly of 3–5 dark-green leaflets. The seed pods are flat, containing 1–3 seeds. The whole plant is used as a stimulant, antispasmodic and counterirritant (Nair & Seetharaman, 1986). The bark is used as an alternative treatment for rheumatism and was originally used to paralyze fish, before being used as an insecticide (Ito *et al.*, 2004). Previous phytochemical studies on the leaves of *D. trifoliata* Lour have resulted in the isolation of flavonoid glycosides (Nair & Seetharaman, 1986) and pentacyclic triterpenoids (Ghosh *et al.*, 1985). The title compound has been isolated from the roots of the same plant (Yenesew *et al.*, 2005). It exhibits cytotoxic activity against oral human epidermoid carcinoma (KB), human breast cancer cell (BC) and human small cells lung cancer (NCI-H187), with ED50 values of 1.51, 1.36 and 1.1 μg ml^{-1}, respectively. In view of its biological activities, we have undertaken the X-ray crystal structure analysis of (I), to establish its molecular structure and relative stereochemistry.



(I)

The title compound is a chiral molecule but crystallizes in the centrosymmetric space group $P\overline{1}$. This indicates that the

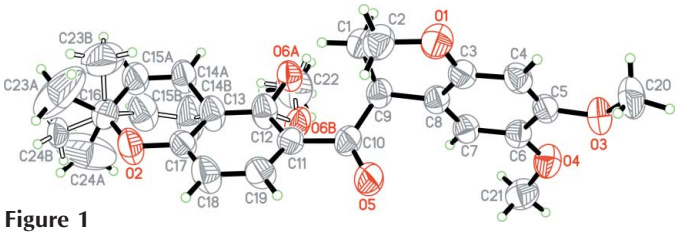


Figure 1
The structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

crude extract from which the compound was obtained is a racemic mixture and that (I) had been produced by non-enzymatic cyclization of a side chain (Chantrapromma *et al.*, 2005).

The molecular structure of (I) is illustrated in Fig. 1. The chromene ring is disordered over two sites, conformations *A* and *B*; these adopt a boat form and twist-boat form, respectively (Cremer & Pople, 1975), with puckering parameters Q = 0.124 (5) Å, θ = 98.1 (23)° and φ = 64 (3)° (conformation *A*) and Q = 0.578 (1) Å, θ = 83.8 (12)° and φ = 228.0 (12)° (for conformation *B*). The two methyl groups attached to the chromene ring are disordered over two sites, conformations *A* and *B*. They are bisectionally and axially attached, with torsion angles C23*A*—C16—C15*A*—C14*A* = 127.0 (11)° and C24*A*—C16—C15*A*—C14*A* = −108.6 (11)° for conformation A, and C24*B*—C16—C15*B*—C14*B* = −147.8 (19)° and C23*B*—C16—C15*B*—C14*B* = 89 (2)° for conformation B.

The dihydropyran ring is in a half-chair form, with puckering parameters Q = 0.483 (3) Å, θ = 52.2 (4)° and φ = 102.8 (5)°; atoms C1 and C2 deviate from the plane of the other four atoms by −0.332 (3) and 0.289 (4) Å, respectively. The methoxy group attached to C12 (Fig. 1) is disordered; the O atom and the methyl H atoms are disordered over two sites, *A* and *B*. The dihedral angle between the two benzene rings is 76.64 (1)°. The bond lengths and angles in (I) show normal values (Allen *et al.*, 1987). Selected bond lengths and angles are given in Table 1.

Weak intramolecular and intermolecular C—H···O interactions are observed (Table 2). The molecules are linked together by these interactions to form a sheet parallel to the *ac* plane (Fig. 2). These layers are interconnected through C—H···O interactions to form a three-dimensional network.

Experimental

Air-dried and powdered seeds of *D. trifoliata* Lour (3.50 kg) were extracted with CH_2Cl_2 at room temperature. The CH_2Cl_2 extract was dried under reduced pressure to a crude extract (35.50 g). The latter was separated by column chromatography on silica gel and eluted initially with hexane enriched with CH_2Cl_2 and EtOAc, then with an increasing amount of CH_3OH in EtOAc, and finally with CH_3OH. Each fraction was monitored by thin layer chromatography (TLC); fractions that appeared similar on TLC were combined to give 12 fractions. Fraction 7 (14.53 g) was repeatedly rechromatographed on a silica gel flash column chromatography, subsequently by preparative TLC with 20% EtOAc in CH_2Cl_2 to afford compound (I) (0.011 g). This was recrystallized from CH_2Cl_2 in CH_3OH to give colorless single crystals after several days (m.p. 391–392 K).

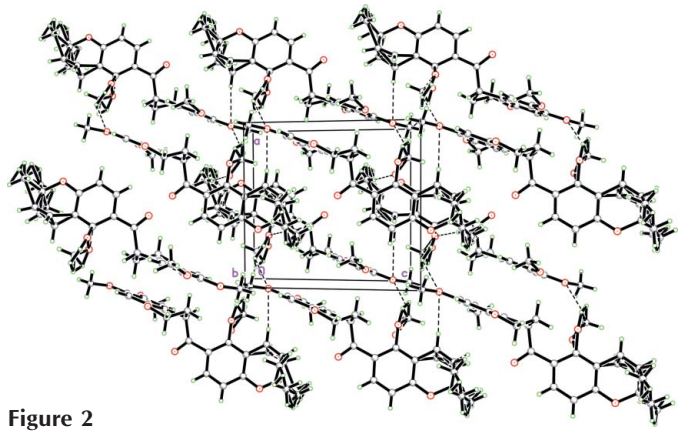


Figure 2
A view of the molecular packing down the *b* axis. Dashed lines indicate hydrogen bonds.

Crystal data

$C_{24}H_{25}O_6$	Z = 2
M_r = 410.45	D_x = 1.302 Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
a = 9.7861 (14) Å	Cell parameters from 10872 reflections
b = 10.4999 (15) Å	θ = 2.0–25.0°
c = 10.7337 (15) Å	μ = 0.09 mm^{-1}
α = 72.329 (3)°	T = 293 (2) K
β = 88.734 (3)°	Block, colorless
γ = 84.930 (3)°	0.45 × 0.38 × 0.32 mm
V = 1046.8 (3) Å^3	

Data collection

Siemens SMART CCD area detector diffractometer	3700 independent reflections
	3292 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.018
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	θ_{max} = 25.0°
	$h = -11 \rightarrow 11$
T_{min} = 0.959, T_{max} = 0.971	$k = -12 \rightarrow 12$
10872 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2 + 0.6285P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.084	
$wR(F^2)$ = 0.199	
S = 1.23	$(\Delta/\sigma)_{max} < 0.001$
3700 reflections	$\Delta\rho_{max}$ = 0.42 e Å^{-3}
324 parameters	$\Delta\rho_{min}$ = −0.20 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C3	1.370 (4)	O5—C10	1.207 (4)
O1—C2	1.422 (4)	C14*A*—C15*A*	1.292 (7)
O2—C17	1.345 (3)	C14*B*—C15*B*	1.29 (2)
O2—C16	1.439 (4)		
C15*A*—C16—C23*A*	114.9 (6)	C24*B*—C16—C15*B*	111.3 (9)
C15*A*—C16—C24*A*	110.5 (6)	C23*B*—C16—C15*B*	105.4 (13)
C3—C4—C5—O3	−178.8 (3)	C17—O2—C16—C24*A*	113.8 (8)
O4—C6—C7—C8	179.4 (3)	C17—O2—C16—C23*B*	−74.9 (12)
C19—C11—C12—O6*A*	172.2 (3)	C23*A*—C16—C15*A*—C14*A*	127.0 (11)
C19—C11—C12—O6*B*	−132.7 (5)	C24*A*—C16—C15*A*—C14*A*	−108.6 (11)
C17—O2—C16—C24*B*	158.6 (8)	C24*B*—C16—C15*B*—C14*B*	−147.8 (19)
C17—O2—C16—C23*A*	−132.7 (8)	C23*B*—C16—C15*B*—C14*B*	89 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···O6A^{i}	0.97	2.51	3.018 (4)	113
C9—H9A···O6A^{i}	0.98	2.37	2.863 (4)	110
C14A—H14A···O3^{ii}	0.93	2.56	3.456 (5)	161

Symmetry codes: (i) x, y, z; (ii) $x, y, z-1$.

H atoms were placed in calculated positions with C—H distances in the range 0.93–0.98 Å. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atoms for methyl H atoms and $1.2U_{eq}$ for the remaining H atoms. The following atoms are disordered over two sites, A and B: C14 and C15 with attached H atoms, C23 and C24 with attached H atoms, O6 and the methyl H atoms attached to C22. For A and B the site occupancy factors refined to 0.776 (7) and 0.224 (7), respectively.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); 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).

We thank the Biodiversity Research and Training Program (BRT), the Taiyo Group of Japan, the Shell Centennial Education Fund and the Graduate Research Fund, Walailak University, for financial support. The Bioassay Research Facility of BIOTEC is also gratefully acknowledged for bioactivity tests. HKF and SC also thank the Malaysian Government and Universiti Sains Malaysia for the Scientific Advancement Grant Allocation (SAGA) grant No. 304/PFIZIK/635003/A118.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Chantrapromma, S., Boonnak, N., Fun, H. K., Anjum, S. & Rahman, A. (2005). *Acta Cryst.* E**61**, o2136–o2138.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Ghosh, A., Misra, S., Dutta, A. K. & Choudhury, A. (1985). *Phytochemistry*, **24**, 1725–1727.
Nair, A. G. R. & Seetharaman, T. R. (1986). *J. Nat. Prod.* **49**, 710–711.
Ito, C., Itoigawa, M., Kojima, N., Tan, H. T. W., Takayasu, J., Tokuda, H., Nishino, H. & Furukawa, H. (2004). *Planta Med.* **70**, 8–11.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Yenesew, A., Mushibe, E. K., Induli, M., Derese, S., Midiwo, J. O., Kabaru, J. M., Heydenreich, M., Koch, A. & Peter, M. G. (2005). *Phytochemistry*, **66**, 653–657.