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[6-(Benzoyloxy)-1,4,5-trihydroxycyclohex-2-en-1-yl]methyl benzoate

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Key indicators

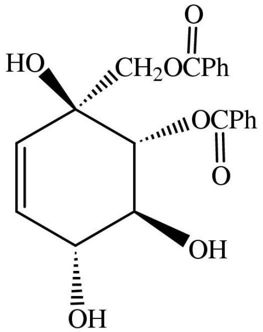
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.055
wR factor = 0.121
Data-to-parameter ratio = 7.7

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

The title compound, $C_{20}H_{21}O_7$, also known as purpuriol, was isolated for the first time from natural product sources. The cyclohexene ring adopts a half-chair conformation with an axially attached methyl benzoate and equatorially attached benzoyloxy substituents. The methyl benzoate and benzoyloxy groups are essentially planar. The dihedral angle between these groups is 9.2 (2)°. O—H···O intermolecular hydrogen bonds link the molecules into chains along the *a* axis and the chains are interlinked by C—H···O hydrogen bonds and C—H···π interactions.

Comment

Purpuriol, (I), is a natural product which was isolated for the first time from *Uvaria purpurea* Blume, and also for the first time from natural product sources by our group. *Uvaria purpurea* Blume is a climbing plant belonging to the family *Annonaceae*. Previous phytochemical studies on the *Uvaria* genus led to the isolation of several polyoxygenated cyclohexenes, some of which have been reported to exhibit antifungal, antibacterial, antitumoural and antimalarial properties (Jolad *et al.*, 1981; Kodpinid *et al.*, 1983, 1984; Nkunya *et al.*, 1987; Ping & Quan, 1995; Schulte *et al.*, 1982; Takeuchi *et al.*, 2001; Thebtaranonth & Thebtaranonth, 1986). The title compound, (I), was isolated from the leaves of *Uvaria purpurea* Blume, which were collected from Phattalung province in the southern part of Thailand. We report here the crystal structure of (I).



(I)

In compound (I) (Fig. 1), the cyclohexene ring adopts a half-chair conformation, with atoms C2 and C3 deviating from the C1—C4—C5—C6 plane by −0.364 (7) and 0.324 (7) Å, respectively. Atoms O5 and C8–14 of the methyl benzoate group are coplanar, and atoms C7 and O4 deviate from that plane by 0.373 (7) and 0.295 (5) Å, respectively. The methyl benzoate group is axially attached to the cyclohexene ring at C1, the C2—C1—C7—O4 torsion angle being −74.9 (4)°,

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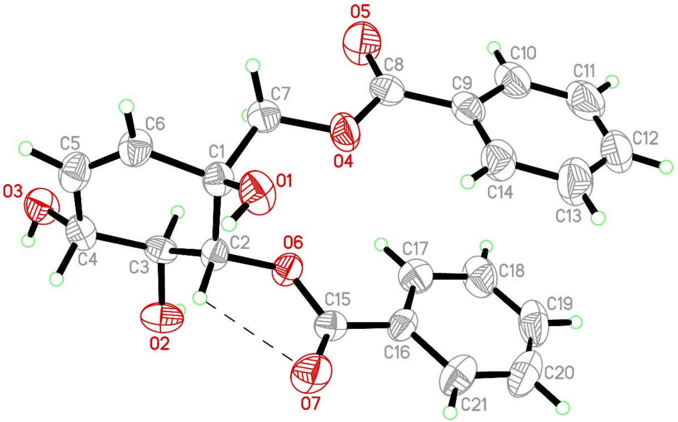

Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering. The intramolecular hydrogen bond is shown as a dashed line.

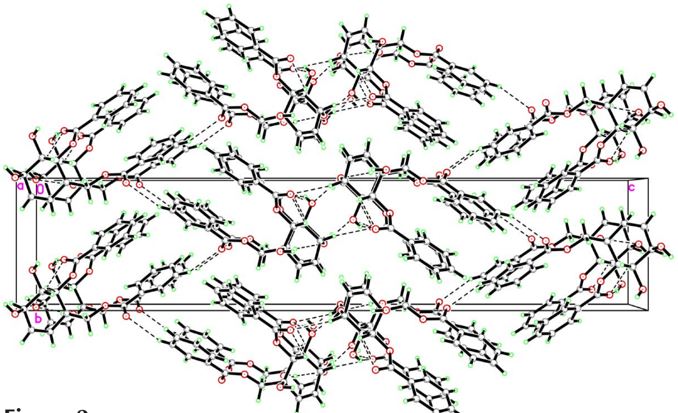

Figure 2
The packing of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

indicating a (−)-synclinal conformation. The benzoyloxy group is planar with a maximum deviation of 0.098 (2) Å for O6; this group is equatorially attached to the cyclohexene ring at C2, with a C2—O6—C15—C16 torsion angle of −172.8 (3)°. The O5/C8–C14 plane through the methyl benzoate group forms a dihedral angle of 9.2 (2)° with the plane of the benzoyloxy group. The two hydroxy substituents at C1 and C4 are bisectionally attached to the ring and the C1—O1 and C4—O3 bonds form angles of 53.1 (2) and 52.6 (2)°, respectively with respect to the Cremer & Pople (1975) plane normal. The other hydroxy group is equatorially attached to the ring at the C3 position with an angle of 70.4 (2)°. All bond lengths and angles in (I) show normal values (Allen *et al.*, 1987).

A weak intramolecular C—H⋯O interaction, *viz*. C2—H2⋯O7 (Table 2), is observed in the molecular structure. This interaction generates a ring of graph-set motif *S*(5) (Bernstein *et al.*, 1995; Etter *et al.*, 1990). A weak π–π interaction is observed between the two aromatic rings, with a centroid–centroid separation of 3.876 (3) Å and perpendicular distance of 3.477 Å. The crystal structure is stabilized by O—H⋯O and C—H⋯O intermolecular hydrogen bonds (Table 2). The O—H⋯O intermolecular hydrogen bonds link the molecules into a chain along the *a* axis (Fig. 2). Adjacent chains are interlinked by C—H⋯O intermolecular hydrogen bonds to form a three-dimensional network. The crystal packing is further stabilized by intermolecular C—H⋯π interactions involving the C16–C21 ring.

Experimental

The air-dried leaves of *Uvaria purpurea* Blume (3.2 kg) were extracted successively with hexane, CH_2Cl_2 and CH_3OH. The dichloromethane extract was evaporated under reduced pressure to yield a crude extract (332.3 g). The crude extract (30 g) was separated by flash column chromatography over silica gel and eluted with a gradient of hexane–ethyl acetate to afford nine fractions (F1–F9). Fraction F7 (9.5 g) was filtered to give the crude yellow solid which was further purified by recrystallization from $CHCl_3$:CH_3OH (3:1 *v*/*v*) for several days to obtain needle-shaped colourless single crystals of compound (I) [m.p. 422–423 K, $[\alpha]_D^{25.9}$−111.11 ° (*c* = 0.018, $CHCl_3$)].

Crystal data

$C_{21}H_{20}O_7$
$M_r = 384.37$
Orthorhombic, $P2_12_12_1$
$a = 5.9532$ (8) Å
$b = 8.1287$ (1) Å
$c = 38.848$ (5) Å
$V = 1879.9$ (4) Å^3
$Z = 4$
$D_x = 1.358$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 1962 reflections
$\theta = 2.1–25.0°$
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
0.41 × 0.12 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.960$, $T_{max} = 0.992$
13378 measured reflections
1961 independent reflections
1788 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 25.0°$
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -46 \rightarrow 45$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.121$
$S = 1.20$
1961 reflections
256 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.6731P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.440 (4)	O6—C15	1.332 (4)
O2—C3	1.432 (4)	O6—C2	1.449 (4)
O3—C4	1.450 (5)	O7—C15	1.208 (4)
O4—C8	1.325 (4)	C4—C5	1.482 (6)
O4—C7	1.445 (4)	C5—C6	1.321 (5)
O5—C8	1.221 (5)		
O5—C8—O4	123.0 (4)	O7—C15—C16	124.9 (4)
O4—C8—C9	113.2 (3)	O6—C15—C16	112.2 (3)
C1—C2—C3—O2	−178.7 (3)	O5—C8—C9—C14	173.0 (4)
O6—C2—C3—C4	−179.0 (3)	C2—O6—C15—C16	−172.8 (3)
C2—C1—C7—O4	−74.9 (4)	O7—C15—C16—C17	175.3 (4)
C7—O4—C8—C9	179.0 (3)	O6—C15—C16—C21	173.3 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3^{i}	0.82	2.03	2.842 (4)	170
O2—H2···O7^{ii}	0.82	2.02	2.768 (4)	151
O3—H3···O2^{iii}	0.82	2.02	2.807 (4)	160
C2—H2A···O7	0.98	2.32	2.733 (5)	105
C4—H4···O7^{iii}	0.98	2.47	3.407 (5)	159
C11—H11···O5^{iv}	0.93	2.55	3.407 (5)	154
C7—H7B···Cg1^{v}	0.97	2.80	3.645 (4)	146

Symmetry codes: (i) $x-1, y, z$; (ii) $1+x, y, z$; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, -z$; (iv) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $x, 1+y, z$. Note: Cg1 is the centroid of the C16–C21 ring.

H atoms were placed in calculated positions, with O—H = 0.82 Å and C—H = 0.93–0.97 Å. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for hydroxy H atoms and $1.2U_{eq}$ for the remaining H atoms. Friedel reflections were merged before the final refinement because of the absence of significant anomalous scattering effects. The absolute configuration assignment is arbitrary.

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).

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