

Swietenine

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.047

w R factor = 0.132

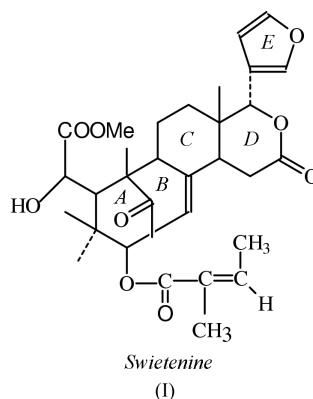
Data-to-parameter ratio = 8.7

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

The crystal structure of swietenine, $\text{C}_{32}\text{H}_{40}\text{O}_9$, from *Swietenia macrophylla*, a plant belonging to the meliaceae family, is reported. The crystal structure is stabilized by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds. A comparison of structural features with a de-tigloylated iodobenzene derivative shows that the overall conformation is not affected by substitution of the (1-methylpropyl)carboxyloxy side chain.

Comment

The title compound, (I), a B,D-seco limonoid, has been isolated from a methanol extract of the seeds of *Swietenia macrophylla* belonging to the meliaceae family. The plant is used in the treatment of hypertension, diabetes and malaria (Chadha, 1976). The compound exhibits minimum antifeedant activity against *spodoptera litura* (Govindachari, Banumathy *et al.*, 1999). The present study was undertaken as a part of our work on ecofriendly bioinsecticides and their chemical modifications.



The geometric features of (I) (Fig. 1) are similar to its de-tigloylated iodobenzene derivative (McPhail & Sim, 1966). However, there is a lengthening of bonds $\text{C5}-\text{C10}$ [$1.577(3)\text{ \AA}$] and $\text{C9}-\text{C10}$ [$1.574(3)\text{ \AA}$] accompanied by a decrease in the value of the $\text{C1}-\text{C10}-\text{C9}$ bond angle from the normal tetrahedral angle. There is a corresponding increase in the values of the $\text{C2}-\text{C30}-\text{C8}$, $\text{C2}-\text{C1}-\text{O9}$ and $\text{C10}-\text{C1}-\text{O9}$ bond angles [$124.0(1)$, $123.5(2)$ and $124.5(1)^\circ$ respectively]. These variations in the bond lengths and bond angles may be attributed to the fusion of A and B rings. The ORTEPIII (Burnett & Johnson, 1996) diagram of this molecule shows that there is a rotational flexibility about the $\text{C3}-\text{O2}$ bonds, as seen from a gradual increase of displacement parameters from O2 to C32 and C27. Similarly, this kind of flexibility is also seen about the $\text{C5}-\text{C6}$ and $\text{C17}-\text{C20}$ bonds. Similar kinds of rotational flexibility, possibly with some

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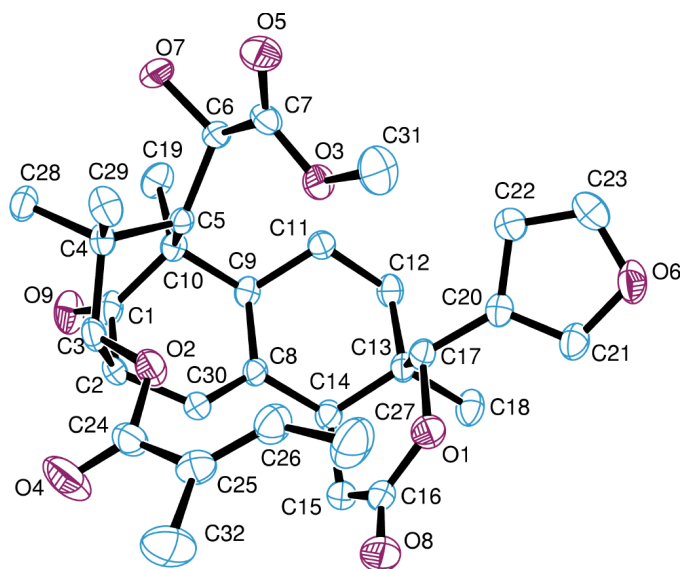


Figure 1
The molecular structure of the title compound, with 30% probability displacement ellipsoids and the atomic numbering scheme.

disorder are observed in a large number of compounds extracted from *Azadirachta indica* (neem) (Kabaleeswaran *et al.*, 1997). The methyl groups at C13 and C10 are in an α configuration. The puckering amplitudes (Cremer & Pople, 1975) [$Q_T = 0.804$ (2) Å, $\theta = 91.5$ (1)° and $\varphi_2 = 78.6$ (1)°; $Q_T = 0.599$ (2) Å, $\theta = 127.3$ (3)° and $\varphi_2 = -145.9$ (3)°; $Q_T = 0.523$ (2) Å, $\theta = 7.1$ (2)° and $\varphi_2 = -160.1$ (2)°; and $Q_T = 0.508$ (2) Å, $\theta = 37.2$ (3)° and $\varphi_2 = 16.31$ (5)°] show that rings A, B, C and D are in sofa, half-chair, chair and sofa conformations, respectively. The furan ring E adopts a planar conformation (Nardelli, 1995). The tigloyl group at C3 is (+)ac with respect to ring A [$C4-C3-O2-C24 = -137.70$ (2)°; Klyne & Prelog, 1960]. The C13-C17-C20-C21 torsion angle [-95.07 (2)°] shows that ring E is equatorial to ring D. The crystal structure is stabilized by C-H...O hydrogen bonds. There is an intramolecular hydrogen bond between hydroxy atom O7 and the O atom (O5) of the carbonyl group attached to C6, forming a graph-set motif of $S(5)$ (Bernstein *et al.*, 1995). The molecule forms an infinite chain along the [100] direction via a C-H...O hydrogen bond, viz. C22-H22...O8($1-x, y-\frac{1}{2}, \frac{1}{2}-z$). Superposition of swietenine and its de-tigloylated iodo-substituted derivative at O2 shows that the conformation is not affected by the substitution at O2.

Experimental

Powdered seed kernels of *Swietenia macrophylla* (7.5 kg) were defatted with hexane (30 l), and the defatted seeds were extracted with methanol (25 l). The extract (~75 g) was mixed with 500 g of silica gel (70–325 mesh) and packed in an MPLC column containing 4 kg of silica gel (70–325 mesh) and eluted with a solvent system ranging from 10:90 ethyl acetate–hexane to 90:10, followed by 100% ethyl acetate and 100% methanol. One of the fractions yielded a pure compound, which was identified as swietenine on the basis of one- and two-dimensional NMR data. Swietenine was crystallized by slow evaporation from a mixture of ethyl acetate–hexane (60:40).

Crystal data

$C_{32}H_{40}O_9$
 $M_r = 568.64$
Orthorhombic, $P2_12_12_1$
 $a = 9.866$ (3) Å
 $b = 16.092$ (5) Å
 $c = 18.392$ (5) Å
 $V = 2920.1$ (14) Å³
 $Z = 4$
 $D_x = 1.293$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 5750 reflections
 $\theta = 1.7$ – 26.0°
 $\mu = 0.09$ mm⁻¹
 $T = 293$ (2) K
Prism, colourless
0.20 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
22 610 measured reflections
3243 independent reflections
2916 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$
 $\theta_{max} = 26.0^\circ$
 $h = -12 \rightarrow 11$
 $k = -19 \rightarrow 19$
 $l = -22 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.132$
 $S = 1.09$
3243 reflections
371 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0894P)^2 + 0.282P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.002$
 $\Delta\rho_{max} = 0.25$ e Å⁻³
 $\Delta\rho_{min} = -0.17$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

C1–O9	1.201 (3)	C5–C10	1.577 (3)
C2–C30	1.514 (4)	C8–C30	1.326 (4)
C2–C3	1.550 (5)	C9–C10	1.574 (4)
O9–C1–C2	123.3 (3)	C1–C10–O9	101.9 (2)
O9–C1–C10	124.7 (3)	C8–C30–C2	124.3 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
O7–H7...O5	0.82	2.15	2.640 (3)	119
C18–H18B...O9 ⁱ	0.96	2.59	3.435 (4)	147
C21–H21...O7 ⁱⁱ	0.93	2.58	3.510 (4)	174
C22–H22...O8 ⁱⁱⁱ	0.93	2.38	3.276 (4)	162

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

In the absence of significant anomalous scattering, Friedel pairs could not be used to determine the absolute configuration. Refinement of the Flack (1983) parameter led to an inconclusive value (Flack & Bernadinelli, 2000) for this parameter [0.13 (1)]. Therefore, the 2507 Friedel equivalents were merged before the final refinement. The enantiomer employed in the refined model was chosen to agree with the accepted configuration of limonoids (Govindachari, Suresh *et al.*, 1999). The methyl and hydroxy H atoms were constrained to an ideal geometry (C–H = 0.96 Å and O–H = 0.82 Å), with $U_{iso}(H) = 1.5U_{eq}(\text{parent atom})$, but were allowed to rotate freely about the C–C and C–O bonds, respectively. All remaining H atoms were placed in geometrically idealized positions (C–H = 0.97–0.98 Å) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: SMART (Bruker, 1999); cell refinement: SMART; data reduction: SAINT (Bruker, 1999); program(s) used to solve structure: SHELXS97-2 (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97-2* (Sheldrick, 1997); molecular graphics: *ORTEP* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97-2* and *PARST97* (Nardelli, 1995).

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