

## 2',3'-Dehydrosalannol

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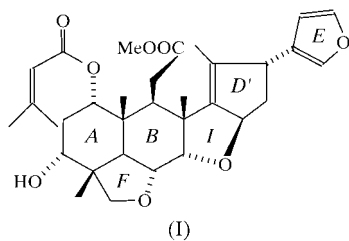
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The title compound, methyl (2*aS*,3*R*,5*R*,5*aS*,6*S*,6*aS*,8*R*,9*aS*,10*aR*,10*bR*,10*cS*)-8-(3-furyl)-2*a*,4,5,5*a*,6,6*a*,8,9,9*a*,10*a*,10*b*,10*c*-dodecahydro-3-hydroxy-2*a*,5*a*,6*a*,7-tetramethyl-5-(3-methylbut-2-enoyloxy)-2*H*,3*H*-cyclopenta[4',5']furo[2',3':6,5]benzo[*cd*]isobenzofuran-6-acetate, C<sub>32</sub>H<sub>42</sub>O<sub>8</sub>, was isolated from uncrushed green leaves of *Azadirachta indica* A. Juss (neem) and has been found to possess antifeedant activity against *Spodoptera litura*. The conformations of the functional groups are similar to those of 3-desacetylsalannin, which was isolated from neem kernels. The molecules are linked into chains by intermolecular O—H...O hydrogen bonds.

## Comment

*Azadirachta indica* A. Juss, an indigenous tree of the Indian subcontinent, has attracted the attention of many chemists and biologists around the world over the past two decades, due to the plethora of biological activities found in the compounds extracted therefrom, in particular insect-antifeedant and growth-inhibition activities (Singh, 1993; Eppler, 1995; Locke, 1995; Schmutterer, 1995). The title compound, (I), was isolated from the hexane extract of uncrushed green neem leaves and purified by preparative high-performance liquid chromatography techniques.



The antifeedant activity of (I) against *Spodoptera litura* (Suresh *et al.*, 2002) is similar to that of 3-desacetylsalannin (DAS; Kabaleeswaran *et al.*, 1999), which was isolated from neem kernels. The difference between the structure of (I) and that of DAS is that in (I), a 3-methylbutenoyl (*O*-senecioxy ester) group has replaced the 2-methylbutenoyl (*O*-tigloyl)

group at C1 in DAS. Due to this difference in the chemical structure, there is a conformational variation in the orientation of this functional group in these structures, and this is evident from the different values for the C1—O1—C31—C32 torsion angle [−177.6 (3)° in (I) and −171.9 (2)° in DAS]. Other functional groups, such as the −CH<sub>2</sub>COOCH<sub>3</sub> group at C9 [C10—C9—C11—C12 is −149.1 (4)° in (I) and −149.6 (2)° in DAS] and the furan ring *E* at C17 [C16—C17—C20—C22 is 64.5 (6)° in (I) and 63.8 (5)° in DAS], show similar conformations.

Rings *A* and *B* in (I) are in chair conformations, as is evident from the ring puckering amplitudes (Cremer & Pople, 1975);  $Q_T = 0.522$  (5) Å,  $\theta = 5.8$  (5)° and  $\varphi_2 = -178$  (5)°, and  $Q_T = 0.552$  (4) Å,  $\theta = 7.0$  (5)° and  $\varphi_2 = -29$  (4)°, respectively. Ring *F* is in a half-chair conformation [ $q_2 = 0.454$  (4) Å and  $\varphi_2 = 93.6$  (5)°], with atoms C4 and C5 deviating from the least-squares plane defined by atoms C6, O6 and C28 by 0.450 (5) and −0.295 (4) Å, respectively. Ring *I* also adopts a half-chair conformation [ $q_2 = 0.405$  (4) Å and  $\varphi_2 = 241.1$  (6)°], with

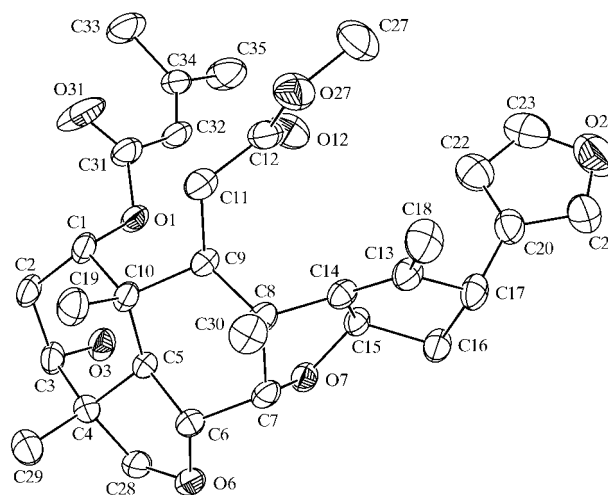


Figure 1

A view of the molecular structure of (I), with 30% probability displacement ellipsoids and the atomic numbering scheme. H atoms have been omitted for clarity.

atoms C7 and C8 deviating from the plane defined by atoms O7, C14 and C15 by −0.214 (4) and 0.459 (4) Å, respectively, while ring *D'* is in an envelope conformation [ $q_2 = 0.319$  (5) Å and  $\varphi_2 = 103.8$  (8)°], with atom C16 at the apex of the envelope. Ring *E* adopts a planar conformation (Nardelli, 1995). The ring junctions *A/B*, *A/F* and *B/F* are *trans*-fused, the *B/I* junction is *cis*-fused and *I/D'* is quasi-*trans*-fused due to the *sp*<sup>2</sup> hybridization of atom C13.

The molecules in the crystal lattice of (I) are stabilized by an O—H...O hydrogen bond between atoms O3 and O6(−*x*, *y* +  $\frac{1}{2}$ ,  $\frac{1}{2}$  − *z*). This hydrogen bond links the molecules into infinite one-dimensional chains, which run parallel to the *y* axis and can be denoted by the graph-set motif *C*(6) (Bernstein *et al.*, 1995). A similar pattern of hydrogen bonds was also observed in DAS (Kabaleeswaran *et al.*, 1999).

Experimental

Fresh uncrushed green leaves of *Azadirachta indica* A. Juss (neem) (5 kg) were soaked in hexane (25 l) for 24 h and the decanted *n*-hexane extract was concentrated to 1 l *in vacuo*. The hexane extract was then partitioned with 95% methanol–water. The methanol layer was concentrated to dryness *in vacuo*, resulting in a residue (16 g) which was subjected to primary preparative high-performance liquid chromatography (HPLC) separation (Shimadzu ODS column, 2 × 25 cm, 215 nm) using MeOH–H<sub>2</sub>O (70:30) as eluent at a flow rate of 4 ml min<sup>-1</sup>, to yield eight peaks with retention times of 6.9, 11.9, 14.1, 18.3, 22.8, 32.2, 47.7 and 61.4 min. The peak with a retention time of 18.3 min (262 mg) was subjected to semi-preparative HPLC on an RP18 column (E-Merck, ODS, 10 μm, 9.96 mm × 25 cm) using acetonitrile–water (55:45) as eluent at a flow rate of 8 ml min<sup>-1</sup>. On evaporation of the solvent, the title compound was obtained as a white solid (80 mg) with a melting point of 457 K. This compound was identified as 2',3'-dehydrosalannol by comparison of its spectroscopic data (one- and two-dimensional NMR) with published data (Garg & Bhakuni, 1985) (positions 2' and 3' are numbered C32 and C34, respectively, in Fig. 1). Diffraction-quality crystals of (I) were obtained from a solution of acetonitrile and water (3:2) at 293 K.

Crystal data

C<sub>32</sub>H<sub>42</sub>O<sub>8</sub>  
*M<sub>r</sub>* = 554.66  
 Orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 7.220 (2) Å  
*b* = 12.728 (2) Å  
*c* = 32.210 (6) Å  
*V* = 2960.0 (11) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.245 Mg m<sup>-3</sup>

Cu *K*α radiation  
 Cell parameters from 25 reflections  
 θ = 15–30°  
 μ = 0.72 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Needle, colourless  
 0.33 × 0.23 × 0.13 mm

Data collection

Enraf–Nonius CAD-4 diffractometer  
 Non-profiled ω/2θ scans  
 3407 measured reflections  
 3280 independent reflections  
 2091 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.028

θ<sub>max</sub> = 75.1°  
*h* = -2 → 8  
*k* = -4 → 15  
*l* = -10 → 40  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 2%

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.045  
*wR*(*F*<sup>2</sup>) = 0.151  
*S* = 1.02  
 3280 reflections  
 367 parameters  
 H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0876*P*)<sup>2</sup> + 0.3127*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.21 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.20 e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97* (Sheldrick, 1997)  
 Extinction coefficient: 0.0025 (4)

Table 1

Hydrogen-bonding 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>
O3–H3...O6 <sup>i</sup>	0.82	2.11	2.900 (4)	161

Symmetry code: (i) -*x*, ½ + *y*, ½ - *z*.

In the absence of suitable anomalous scatters, Friedel equivalents could not be used to determine the absolute structure. Refinement of the Flack parameter (Flack, 1983) led to an inconclusive value (Flack & Bernardinelli, 2000) of -0.3 (4). Therefore, the 133 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 (Narayanan *et al.*, 1964; Harris *et al.*, 1968; Henderson *et al.*, 1968). 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*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(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*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97* and *PARST97* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1144). Services for accessing these data are described at the back of the journal.

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