$S = 1.102$
2256 reflections
207 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 0.2332P]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0085 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—O10	1.216 (2)	C3—O11	1.233 (2)
C1—N2	1.369 (2)	C4—C4a	1.359 (2)
N2—C3	1.379 (2)		
N2—C1—N9	115.44 (11)	C2′—C1′—C6′	118.72 (13)
N2—C3—C4	115.14 (11)		
N9—C4a—C5—C6*B*	30.7 (3)	C6*A*—C7*A*—C8—N9	56.9 (6)
N9—C4a—C5—C6*A*	−0.9 (5)	C6*B*—C7*B*—C8—N9	−39.0 (7)
C4a—C5—C6*A*—C7*A*	34.5 (8)	C5—C4a—N9—C8	−5.0 (2)
C5—C6*A*—C7*A*—C8	−62.3 (8)	C7*A*—C8—N9—C4a	−25.6 (4)
C4a—C5—C6*B*—C7*B*	−58.0 (6)	C7*B*—C8—N9—C4a	10.1 (4)
C5—C6*B*—C7*B*—C8	62.8 (8)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O11^{i}	0.90 (2)	1.92 (2)	2.821 (2)	175 (2)
C2′—H2′···O10^{ii}	0.97 (2)	2.55 (2)	3.472 (2)	159 (1)
C8—H8*B*···O11^{iii}	0.97	2.52	3.450 (2)	159
C8—H8*C*···O11^{iii}	0.97	2.55	3.450 (2)	154
C7*A*—H7*C*···O10^{iv}	0.97	2.81	3.430 (4)	122
C7*B*—H7*C*···O10^{iv}	0.97	2.72	3.241 (4)	114

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, -y, 1 - z$; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

The H atoms in the piperidine ring were refined with a riding model and their $U_{\rm iso}$ values were set at $1.2U_{\rm eq}$ of their carrier atoms. The other H atoms were refined isotropically [C—H distances in the range 0.96 (2)–1.00 (2) Å].

Data collection: *Kuma KM*-4 *Software* (Kuma, 1992). Cell refinement: *Kuma KM*-4 *Software*. Data reduction: *Kuma KM*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1351). Services for accessing these data are described at the back of the journal.

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Salannin and 3-deacetylsalannin

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Abstract

The crystal structures of two tetranortriterpenoids, salannin [$C_{34}H_{44}O_9$, (I)] and 3-deacetylsalannin [$C_{32}H_{42}O_8$, (II)], are described. The orientation and conformation of the tigloyl (2-methyl-2-butenoyl) group, the carbomethoxy group and ring *E* are different in the two structures. The molecular packing depends on C—H···O hydrogen bonds in (I) and on O—H···O hydrogen bonds in (II). A comparison of the structural features indicates that the conformations of large parts of the molecules are similar to those in azadirachtins.

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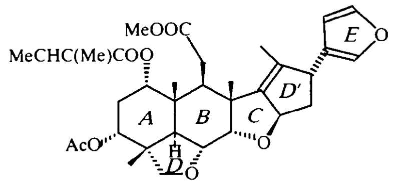
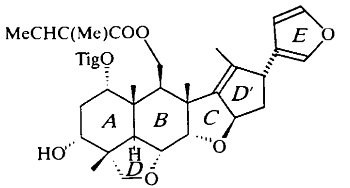
Comment

The title compounds, which belong to a family of *C-seco* limonoids, were isolated from the kernels of neem, *Azadirachta indica*, by HPLC techniques. They show antifeedant and growth-regulating activities (Govindachari, Narasimhan *et al.*, 1996) similar to, but less strong than, those of azadirachtins isolated from the same source. The stereochemistry for these coumpounds was established through NMR and other spectroscopic techniques (Henderson *et al.*, 1968; Narayanan *et al.*, 1964; Harris *et al.*, 1968). They are characterized by two oxygen bridges between C6 and C28, and C7 and C15. The present studies were undertaken to obtain the three-dimensional structures of (I) and (II), and to explore structure–activity relationships.



(I)



(II)

Most of the bond lengths are as expected (Allen *et al.*, 1987), except for the bonds C7—C8, C8—C9 and C9—C10, which are longer than normal. This is also observed in azadirachtins (Kabaleeswaran *et al.*, 1994; Govindachari, Geetha Gopalakrishnan *et al.*, 1996; Broughton *et al.*, 1986) and in a few related structures (Nakai *et al.*, 1980; Bilton *et al.*, 1987; Romers *et al.*, 1974; Smith, 1975). This bond lengthening is accompanied by a decrease in the C7—C8—C4 bond angle and may be attributed to the bulky substitutions at C9 and C1.

The ring junctions *A*/*B*, *A*/*D* and *B*/*D* are *trans*- and *B*/*C* is *cis*-fused in both (I) and (II). The *C*/*D* junction in both (I) and (II) is quasi-*trans*-fused due to the sp^2 hybridization of C13. The cyclohexane rings *A* and *B* in both (I) and (II) approximate to chair conformations, as observed in azadirachtins (Kabaleeswaran *et al.* 1994; Govindachari, Geetha Gopalakrishnan *et al.*, 1996; Broughton *et al.*, 1986). The *C* ring in (I) is in the envelope conformation and in (II) it exists as a distorted chair, with asymmetry parameter (Duax *et al.*, 1976) ΔC_2 = 6.3 (3)°. Ring *D* is in a half-chair conformation and *D'* is close to the envelope conformation in both structures, as seen from their asymmetry parameters (ΔC_2 = 2.2 and 3.5°, and ΔC_s = 0.1 and 3.5°, respectively).

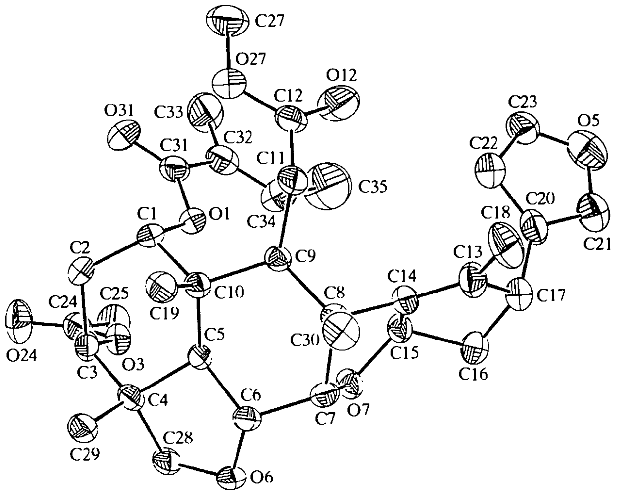


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of (I) showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

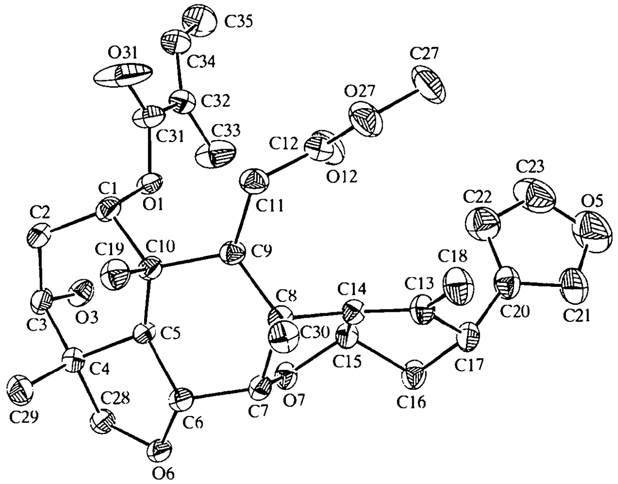


Fig. 2. *ORTEP*II (Johnson, 1976) diagram of (II) showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

The orientation of the tigloyl group in (I), defined by C2—C1—O1—C31, is 75.0 (6)° and this is close to that observed in azadirachtin A (Kabaleeswaran *et al.*, 1994) and azadirachtin H (Govindachari, Geetha Gopalakrishnan *et al.*, 1996). However, in (II), it is somewhat different, having a value of 98.3 (3)°. The acetyl group at C3 in (I) is axially oriented and in (II) it is replaced by the hydroxyl group. The carbomethoxy substituent at C11 in (I) is anticlinal and in (II) it is close to antiperiplanar (Klyne & Prelog, 1960). The C16—C17—C20—C22 torsion angle, which defines the orientation of ring *E* with respect to ring *D*, is 76.9 (10)° in (I) and 63.9 (5)° in (II). All the methyl groups in the two structures are β-oriented, in agreement with the results obtained from spectral studies (Narayanan *et al.*, 1964; Ziffer *et al.*, 1966; Henderson *et al.*, 1968; Harris *et al.*, 1968).

In (I), there is an intramolecular C—H···O hydrogen bond between C22 of the furan ring and O12 of the carbomethoxy group. Molecular packing is achieved by a C—H···O hydrogen bond between C11 and O6 of the molecule translated along **c**. However, in (II), the hydroxyl oxygen O3, which replaces the acetoxy group in (I), participates in an intermolecular hydrogen bond with O6$(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$.

A comparison of the structural features of (I) with those of the azadirachtins (Kabaleeswaran *et al.*, 1994; Govindachari, Geetha Gopalakrishnan *et al.*, 1996; Broughton *et al.*, 1986) shows that rings *A* and *B* and the tigloyl groups agree closely in conformation in all these structures, indicating the necessity of these groups for the antifeedant activity of the compounds. The conformation of the tiglolyl group is different in (II).

Experimental

Compounds (I) and (II) were crystallized from methanol by slow evaporation.

Compound (I)

Crystal data

$C_{34}H_{44}O_9$
$M_r = 596.71$
Monoclinic
$P2_1$
$a = 11.963\,(2)$ Å
$b = 7.824\,(2)$ Å
$c = 17.573\,(2)$ Å
$\beta = 106.90\,(2)°$
$V = 1573.8\,(5)$ Å^3
$Z = 2$
$D_x = 1.259$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å
Cell parameters from 23 reflections
$\theta = 15–35°$
$\mu = 0.740$ mm^{-1}
$T = 293\,(2)$ K
Needle
$0.34 \times 0.20 \times 0.16$ mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: none
3183 measured reflections
3039 independent reflections
2322 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.016$
$\theta_{\rm max} = 67.90°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 8$
$l = -21 \rightarrow 20$
2 standard reflections every 100 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.212$
$S = 0.833$
3039 reflections
389 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1784P)^2 + 1.0214P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.507$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.226$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0018 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C22—H22···O12	0.93	2.52	3.398 (12)	158
C11—H11*A*···O6$^{\rm i}$	0.97	2.62	3.553 (7)	163
C19—H19*A*···O6$^{\rm i}$	0.96	2.52	3.478 (7)	174

Symmetry code: (i) $x, 1+y, z$.

Compound (II)

Crystal data

$C_{32}H_{42}O_8$
$M_r = 554.66$
Orthorhombic
$P2_12_12_1$
$a = 7.236\,(3)$ Å
$b = 12.764\,(4)$ Å
$c = 31.892\,(4)$ Å
$V = 2945.6\,(16)$ Å^3
$Z = 4$
$D_x = 1.251$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å
Cell parameters from 25 reflections
$\theta = 13–37°$
$\mu = 0.725$ mm^{-1}
$T = 293\,(2)$ K
Needle
$0.36 \times 0.24 \times 0.12$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3205 measured reflections
3205 independent reflections
2870 reflections with $I > 2\sigma(I)$

$\theta_{\rm max} = 69.94°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 38$
3 standard reflections every 100 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.134$
$S = 1.079$
3205 reflections
364 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0831P)^2 + 0.4682P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.246$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.220$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0027 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O6$^{\rm i}$	0.82	1.97	2.777 (3)	168

Symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

H atoms were included at geometrically calculated positions and refined using a riding model. The hydroxyl H in (II) was placed using the *HFIX*147 facility in *SHELXL*97 (Sheldrick, 1997).

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SDP* (Frenz, 1978); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*97; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1256). Services for accessing these data are described at the back of the journal.

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