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Samaderin B and C from *Samadera indica*

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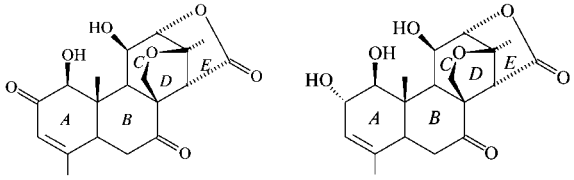
Samaderin B, or (1*R*,2*S*,5*R*,5a*R*,7a*S*,11*S*,11a*S*,11b*R*,14*S*)-1,7,-7a,11,11a,11b-hexahydro-1,11-dihydroxy-8,11a,14-trimethyl-2*H*-5a,2,5-(methanoxymetheno)naphth[1,2-*d*]oxepine-4,6,10-(5*H*)-trione, $C_{19}H_{22}O_7$, and samaderin C, or (1*R*,2*S*,5*R*,5a*R*,-7a*S*,10*S*,11*S*,11a*S*,11b*R*,14*S*)-7,7a,10,11,11a,11b-hexahydro-1,10,11-trihydroxy-8,11a,14-trimethyl-2*H*-5a,2,5-(methanoxymetheno)naphth[1,2-*d*]oxepine-4,6(1*H*,5*H*)-dione, $C_{19}H_{24}O_7$, were isolated from the seed kernels of *Samadera indica* and were shown to exhibit antifeedant activity against *Spodoptera litura* third-instar larvae. The replacement of the carbonyl group in samaderin B by a hydroxy group in samaderin C causes conformational changes at the substitution site, but the overall conformation is not affected; however, the compounds pack differently in the crystal lattice.

Comment

Samaderin B and C, (I) and (II), respectively, were extracted from the seed kernels of *Samadera indica*. Compounds (I) and (II) belong to the quassinoid class (Polonsky, 1973, 1985), a diverse group of structurally complex and highly oxygenated lactones (δ-lactones in C_{20} and γ-lactones in C_{19} compounds) that generally exhibit antifeedant and insecticidal (Leskinen *et al.*, 1984) activities similar to those of limonoids from neem.



Compounds (I) and (II) exhibit antifeedant activity against *Spodoptera litura* third-instar larvae (Govindachari *et al.*, 2001). We have carried out a crystallographic study of these compounds as part of our work on the structures of ecofriendly bioinsecticides. Chemically, (I) and (II) differ in the substitution at the C2-atom position, *viz*. a carbonyl group on atom C2 in (I) and a hydroxy group in (II) (Fig. 1). The compounds both crystallize in space group $P2_12_12_1$, but they have different unit-cell parameters.

The present study shows that the bond lengths and angles in both structures are close to those observed for other quassinoids (Onan & McPhail, 1978; Suong *et al.*, 1982; Chan *et al.*, 1992; Zukerman-Schpector *et al.*, 1994; Kabaleeswaran *et al.*, 2000). In (II), the hydroxy groups on atoms C1 and C2 are staggered with respect to one another, as described by the O1—C1—C2—O2 torsion angle of 77.3 (2)°. The hydroxy group on atom C1 is in a (−)-antiperiplanar conformation (Klyne & Prelog, 1960) with respect to the C2—C3 bond [C3—C2—C1—O1 = −156.5 (2)°], while the hydroxy group on atom C2 is (+)-anticlinal with respect to the C3—C4 bond [C4—C3—C2—O2 = 131.9 (3)°]. In (I), the hydroxy and carbonyl groups attached to atoms C1 and C2, respectively, are nearly in an eclipsed conformation [O1—C1—C2—O2 = 12.0 (9)°]. The hydroxy group on atom C1 assumes a (−)-antiperiplanar conformation with respect to the C2—C3 bond [C3—C2—C1—O1 = −166.4 (6)°]. The hydroxy groups on atoms C1 and C11 of both molecules are in a β orientation, and the hydroxy group on atom C2 of (II) is in an α orientation. In both compounds, the C19 methyl group is in a β orientation, while atom C17 is in an α orientation. The

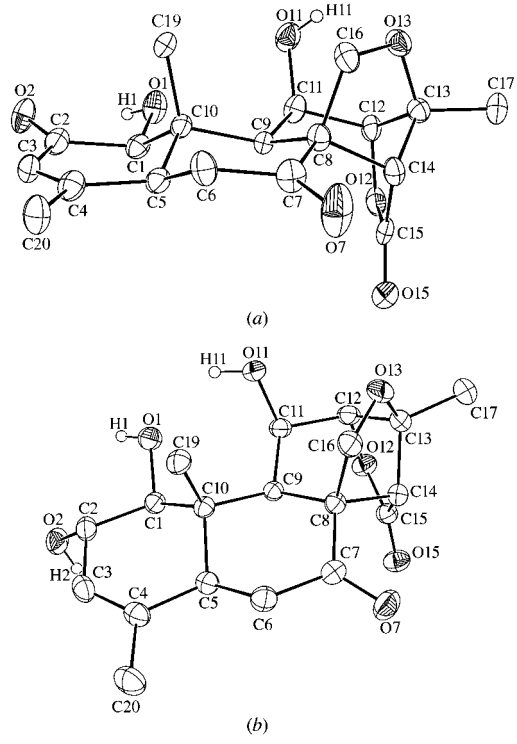


Figure 1
*ORTEP*III (Burnett & Johnson, 1996) views of (*a*) (I) and (*b*) (II), showing displacement ellipsoids at the 30% probability level and the atomic numbering schemes.

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γ-lactone ring, *E*, and the oxymethylene bridge attached to ring *C* are in α and β orientations, respectively. When the two molecules are superimposed, the other parts of the molecules show negligible conformational differences.

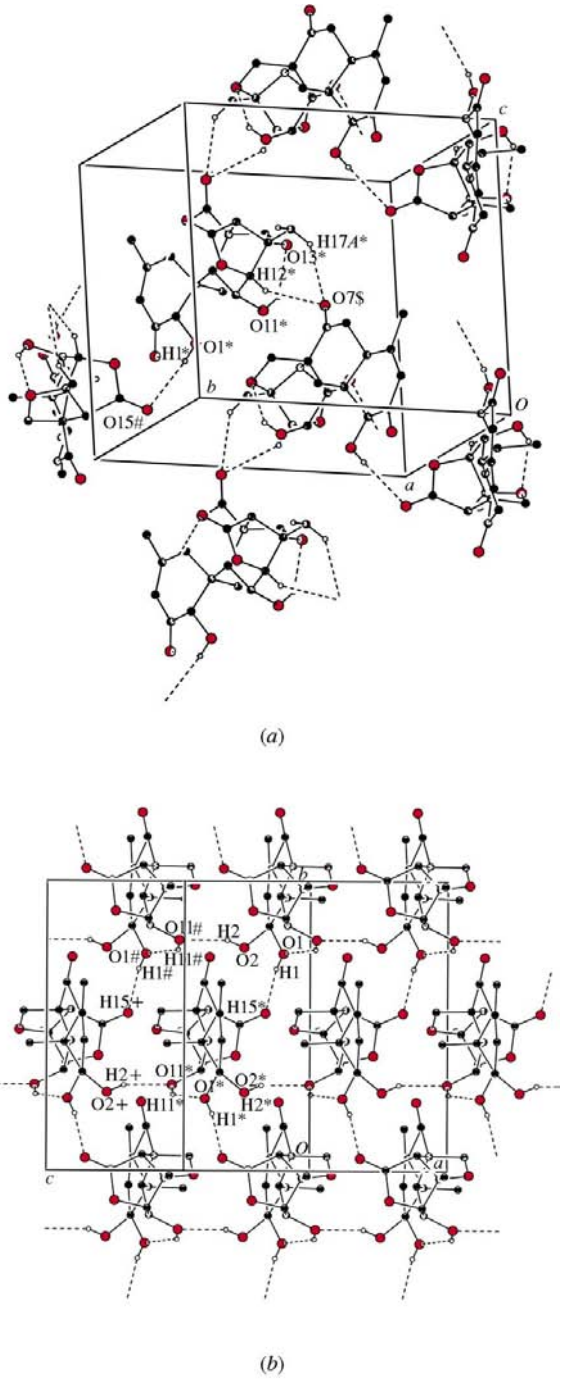

Figure 2
(*a*) The packing of (I) in the crystal lattice. Atoms marked with an asterisk (*), dollar sign ($) or hash (#) are at the symmetry positions $(1+x, y, z)$, $(\frac{1}{2}-x, 1-y, z-\frac{1}{2})$ and $(\frac{3}{2}+x, \frac{3}{2}-y, 1-z)$, respectively. (*b*) The packing of (II) in the crystal lattice. Atoms marked with an asterisk (*), hash (#) or plus sign (+) are at the symmetry positions $(-x, y-\frac{1}{2}, \frac{1}{2}-z)$, $(x-1, y, z)$ and $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$, respectively. For clarity, H atoms bonded to C atoms have been omitted from both figures.

In both molecules, ring *A* is in a sofa conformation [Q_T = 0.495 (7) Å, θ = 46.5 (9)° and φ_2 = −43 (1)° in (I), and Q_T = 0.491 (2) Å, θ = 46.6 (3)° and φ_2 = −54.5 (4)° in (II); Cremer & Pople, 1975], ring *B* is in a highly distorted chair conformation [Q_T = 0.541 (7) Å, θ = 18.9 (8)° and φ_2 = −32 (2)° in (I), and Q_T = 0.536 (2) Å, θ = 20.4 (2)° and φ_2 = −47.2 (7)° in (II)] and ring *C* assumes a distorted chair conformation [Q_T = 0.733 (7) Å, θ = 22.5 (5)° and φ_2 = −84 (1)° in (I), and Q_T = 0.718 (2) Å, θ = 28.1 (2)° and φ_2 = −80.8 (4)° in (II)]. The five-membered ring *D* adopts a half-chair conformation [q_2 = 0.452 (7) Å and φ_2 = −51.9 (8)° in (I), and q_2 = 0.439 (2) Å and φ_2 = 164.0 (3)° in (II)], with atoms C8 and C14 deviating from the least-squares plane of atoms C13, O13 and C16. The γ-lactone ring, *E*, adopts a conformation intermediate between half-chair and envelope in both compounds [q_2 = 0.434 (6) Å and φ_2 = 149.7 (7)° in (I), and q_2 = 0.443 (2) Å and φ_2 = 153.7 (3)° in (II)]. In both molecules, the *A*/*B*, *B*/*C* and *C*/*D* rings are *trans*-fused.

The crystal packing is stabilized by both inter- and intramolecular hydrogen bonds (Tables 1 and 2). An intramolecular O11—H11···O13 hydrogen bond in (I) forms a ring graph-set motif (Bernstein *et al.*, 1995) of *S*(6), while an intramolecular O11—H11···O1 interaction in (II) forms an *S*(7) ring. In (I), an intermolecular O1—H1···O15($\frac{1}{2}+x$, $\frac{3}{2}-y$, $1-z$) hydrogen bond links the molecules into *C*(9) chains, which run along [100] and are generated by the 2_1 screw axis along (x, $\frac{3}{4}$, $\frac{1}{2}$). In addition, there are C—H···O hydrogen bonds involving methine atom H12 and methylene atom H17*A*, which interact with a common acceptor, namely atom O7 at ($-\frac{1}{2}-x$, $1-y$, $z-\frac{1}{2}$). This three-centered hydrogen bond generates a graph-set motif of $R_2^1(6)$. Compound (II) is similar to (I) in that an intermolecular O1—H1···O15($-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$) hydrogen bond links the molecules into chains, but these run along [010] and are generated by a 2_1 screw axis along ($-\frac{1}{2}$, y, $\frac{1}{4}$). Another O2—H2···O11($x-1$, y, z) hydrogen bond links the molecules into *C*(8) chains that run along the [100] direction. These two intermolecular O—H···O hydrogen bonds in combination generate a two-dimensional network in (II), in which a ring graph-set motif of $R_5^5(27)$ can be detected (Fig. 2).]

Experimental

Compounds (I) and (II) were isolated from the seed kernels of *Samadera indica* according to the procedure described by Govindachari *et al.* (2001).

Samaderin B, (I)

Crystal data

$C_{19}H_{22}O_7$
M_r = 362.37
Orthorhombic, $P2_12_12_1$
a = 10.342 (4) Å
b = 13.328 (7) Å
c = 11.956 (9) Å
V = 1648.0 (16) Å^3
Z = 4
D_x = 1.460 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 15–30°
μ = 0.94 mm^{-1}
T = 293 (2) K
Rod, colorless
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 72.0°$
Non-profiled $\omega/2\theta$ scans	$h = -12 \rightarrow 12$
1807 measured reflections	$k = 0 \rightarrow 16$
1741 independent reflections	$l = 0 \rightarrow 14$
1203 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{int} = 0.060$	every 200 reflections
	intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1269P)^2 + 0.1667P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.074$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.208$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{min} = -0.42$ e Å^{-3}
1741 reflections	
238 parameters	
H-atom parameters constrained	

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

D—H···A	D—H	H···A	D···A	D—H···A
O11—H11···O13	0.82	2.11	2.766 (8)	136
O1—H1···O15^{i}	0.82	2.45	3.252 (8)	168
C12—H12···O7^{ii}	0.98	2.58	3.468 (10)	151
C17—H17A···O7^{ii}	0.96	2.55	3.364 (11)	143

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

Samaderin C, (II)

Crystal data

$C_{19}H_{24}O_7$	Cu $K\alpha$ radiation
$M_r = 364.38$	Cell parameters from 25 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 15$–$30°$
$a = 7.5278$ (16) Å	$\mu = 0.91$ mm^{-1}
$b = 12.418$ (3) Å	$T = 293$ (2) K
$c = 18.037$ (4) Å	Rod, colorless
$V = 1686.2$ (7) Å^3	0.25 × 0.15 × 0.15 mm
$Z = 4$	
$D_x = 1.435$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	$h = 0 \rightarrow 9$
Non-profiled $\omega/2\theta$ scans	$k = 0 \rightarrow 14$
1846 measured reflections	$l = 0 \rightarrow 22$
1846 independent reflections	3 standard reflections
1660 reflections with $I > 2\sigma(I)$	every 200 reflections
$\theta_{max} = 71.8°$	intensity decay: 2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0713P)^2 + 0.2417P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.103$	$\Delta\rho_{max} = 0.18$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -0.15$ e Å^{-3}
1846 reflections	Extinction correction: *SHELXL*97
240 parameters	Extinction coefficient: 0.0031 (5)
H-atom parameters constrained	

In the absence of suitable anomalous scatters, Friedel equivalents could not be used to determine the absolute structures. Refinement of the Flack (1983) parameters led to inconclusive values (Flack & Bernadinelli, 2000) [0.9 (8) in (I) and −0.2 (3) in (II)]. The enantiomers employed in the refined models were chosen to agree with the accepted configuration of quassinoids (Polonsky, 1985). 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}(parent atom)] but were allowed to rotate freely about the C—C and C—O bonds, respectively. All remaining H atoms were placed in idealized positions (C—H = 0.97–0.98 Å) and constrained to ride on their parent atoms, with U_{iso}(H) values equal to 1.2U_{eq}(C).

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

D—H···A	D—H	H···A	D···A	D—H···A
O11—H11···O1	0.82	2.04	2.692 (3)	136
O1—H1···O15^{iii}	0.82	1.99	2.762 (3)	158
O2—H2···O11^{iv}	0.82	2.08	2.802 (3)	147

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

For both compounds, data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1170). Services for accessing these data are described at the back of the journal.

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