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Nimonol and 6-oxonimonol

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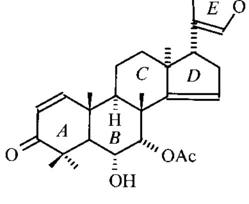
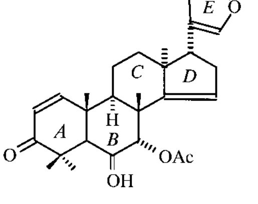
The crystal structures of two intact limonoids, nimonol, 7α-acetyl-17α-(3-furyl)-6α-hydroxy-4α,4β,8β-trimethyl-5α,18α-androsta-1,14-dien-3-one ($C_{28}H_{36}O_5$), and 6-oxonimonol, 7α-acetyl-17α-(3-furyl)-4α,4β,8β-trimethyl-5α,18α-androsta-1,14-diene-3,6-dione ($C_{28}H_{34}O_5$), are reported. The molecular features are mostly the same in the two structures; however the orientations of the acetoxy group are different in the two structures. The packing in nimonol is due to O—H···O hydrogen bonds while in 6-oxonimonol it is due to C—H···O hydrogen bonds.

Comment

Neem leaves and neem oil have been used as ecofriendly insecticides in India for a long time and the constituents of neem like azadirachtins and a few other bioactive constituents have been studied for their biological activity (Govindachari, Narashiman *et al.*, 1996). Recently the X-ray structures of a few azadirachtins and a few other compounds have been reported (Bilton *et al.*, 1987; Kabaleeswaran *et al.*, 1994; Govindachari, Geetha Gopalakrishnan *et al.*, 1996). Nimonol, one of the limonoids, isolated from the leaves of neem (Suresh *et al.*, 1997) exhibits antifeedant and ecdysis activity similar but to a lesser extent than the azadirachtins. The stereochemistry was clearly established by NMR techniques (Suresh *et al.*, 1997). 6-Oxonimonol is a derivative of nimonol and was prepared to study the change of activity with the native compound. This paper reports the crystal structures of both nimonol, (I), and 6-oxonimonol, (II). However the absolute structure was not established by X-ray techniques.



(I)



(II)

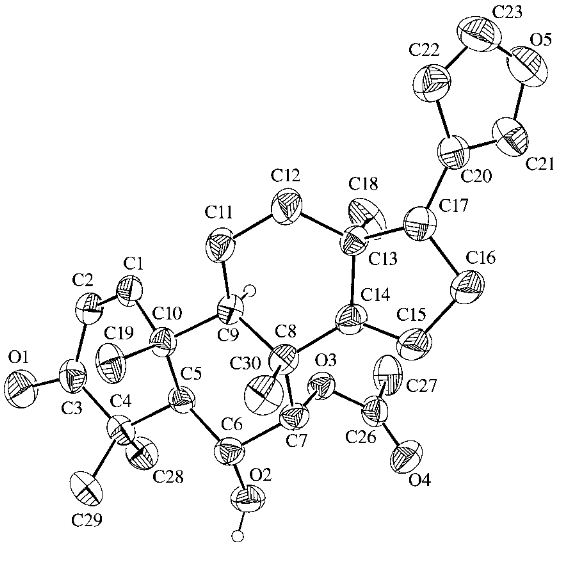


Figure 1
*ORTEP*II (Johnson, 1976) diagram of nimonol (I) at the 30% probability level.

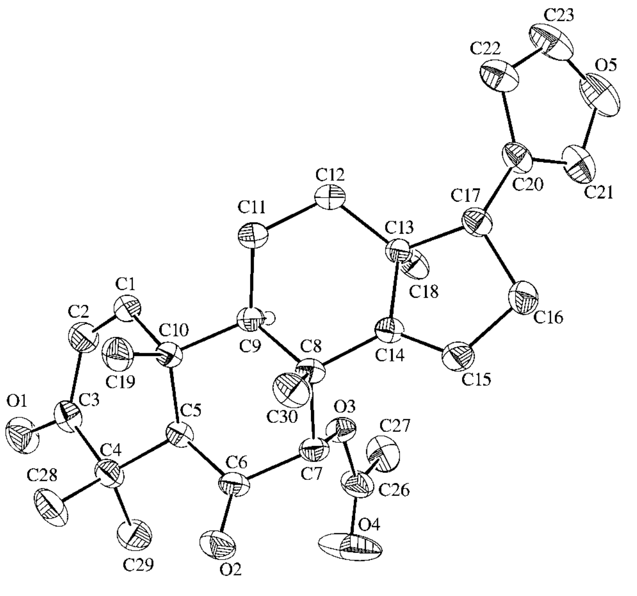


Figure 2
*ORTEP*II (Johnson, 1976) diagram of 6-oxonimonol (II) at the 30% probability level.

The conformations of the *B*, *C* and *D* rings are chair, sofa and envelope, respectively, in both structures (Duax *et al.*, 1975). However the ring *A* exists as a half-chair in nimonol and as a sofa in 6-oxonimonol. Consequently the torsion angles C1—C2—C3—O1, C2—C3—C4—C28 and C2—C3—C4—C29 are different in two structures. The furan ring *E* is pseudoaxially subsituted in both the structures with respect to the ring *D*. The orientation of the acetoxy group at C7, defined by the torsion angle C6—C7—O3—C26 is 109.1 (3)° (anticlinal) in nimonol and 70.4 (3)° (synclinal) in 6-oxonimonol.

However, the orientations of the methyl C atoms are close to one another. The ring pairs *A*/*B* and *B*/*C* are *trans* fused and *C*/*D* is quasi-*trans* fused in the two structures. The structures of (I) and (II) are shown in Figs. 1 and 2, respectively.

The geometric data pertinent to defining the hydrogen bonding scheme in nimonol, (I) are given in Table 2. However in 6-oxonimonol the molecular packing is due to C—H···O hydrogen bonds.

Experimental

Crystals of nimonol (I) and 6-oxonimonol (II) were prepared from the methanol by slow evaporation.

Compound (I)

Crystal data

$C_{28}H_{36}O_5$
$M_r = 452.57$
Monoclinic, $P2_1$
$a = 10.087$ (3) Å
$b = 11.044$ (3) Å
$c = 12.342$ (3) Å
$\beta = 113.86$ (2)°
$V = 1257.3$ (6) Å^3
$Z = 2$
$D_x = 1.195$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 14$–35°
$\mu = 0.646$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3002 measured reflections
2612 independent reflections
2443 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\rm max} = 71.97°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = -15 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.194$
$S = 1.153$
2612 reflections
298 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1295P)^2 + 0.1402P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0022 (14)

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C3	1.223 (5)	O4—C26	1.195 (6)
O2—C6	1.428 (4)	O5—C23	1.325 (10)
O3—C26	1.344 (5)	O5—C21	1.350 (6)
O3—C7	1.445 (4)		
C26—O3—C7	119.4 (3)	O3—C7—C6	106.5 (3)
C23—O5—C21	105.5 (5)	C8—C7—C6	113.6 (3)
O1—C3—C2	118.9 (4)	O4—C26—O3	124.7 (4)
O1—C3—C4	121.2 (4)	O4—C26—C27	126.1 (4)
O2—C6—C5	110.9 (3)	O3—C26—C27	109.2 (4)
O2—C6—C7	106.7 (3)	C20—C21—O5	112.9 (5)
O3—C7—C8	107.6 (3)	O5—C23—C22	111.9 (5)
O1—C3—C4—C29	46.3 (6)	C26—O3—C7—C6	109.1 (3)
O1—C3—C4—C28	−68.7 (5)	O2—C6—C7—O3	−60.4 (4)
C4—C5—C6—O2	−53.1 (4)		

Compound (II)

Crystal data

$C_{28}H_{34}O_5$
$M_r = 450.55$
Orthorhombic, $P2_12_12_1$
$a = 10.805$ (1) Å
$b = 12.710$ (2) Å
$c = 17.538$ (2) Å
$V = 2408.5$ (5) Å^3
$Z = 4$
$D_x = 1.243$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12$–36°
$\mu = 0.674$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
0.30 × 0.25 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2481 measured reflections
2481 independent reflections
2222 reflections with $I > 2\sigma(I)$
$\theta_{\rm max} = 67.92°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 21$
3 standard reflections every 100 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.129$
$S = 0.800$
2481 reflections
298 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1007P)^2 + 1.2632P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0053 (5)

The H atoms were placed at calculated positions and refined as riding using *SHELXL*97 (Sheldrick, 1997).

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SDP*

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O1$^{\rm i}$	0.82	1.950 (6)	2.768 (6)	175 (4)
C1—H1···O5$^{\rm ii}$	0.93	2.56 (6)	3.325 (7)	130 (4)
C23—H23···O4$^{\rm iii}$	0.93	2.48 (8)	3.472 (9)	153 (5)

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

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C3	1.220 (4)	O4—C26	1.170 (4)
O2—C6	1.208 (3)	O5—C23	1.345 (6)
O3—C26	1.336 (3)	O5—C21	1.371 (5)
O3—C7	1.446 (3)		
C26—O3—C7	119.1 (2)	O3—C7—C8	105.9 (2)
C23—O5—C21	105.8 (3)	C20—C21—O5	111.5 (4)
O1—C3—C2	119.5 (3)	O4—C26—O3	121.9 (4)
O1—C3—C4	121.3 (3)	O4—C26—C27	126.5 (3)
O3—C7—C6	111.6 (2)	O3—C26—C27	111.6 (3)
O1—C3—C4—C29	47.3 (4)	C26—O3—C7—C6	−70.4 (3)
O1—C3—C4—C28	−69.6 (4)	O2—C6—C7—O3	132.3 (3)
C4—C5—C6—O2	−23.8 (4)		

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(Frenz, 1984); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); 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: BK1476). Services for accessing these data are described at the back of the journal.

References

Bilton, J. N., Broughton, H. B., Jones, P. S., Ley, S. V., Lidert, Z., Morgan, E. D., Rzepa, H. S., Sheppard, R. N., Slawin, A. M. Z. & Williams, D. J. (1987). *Tetrahedron*, **43**, 2805–2816.

Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1975). In *Topics in Stereochemistry*, edited by E. L. Eliel & N. L. Allinger, Vol. 9. New York: Interscience.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Frenz, B. A. (1984). Enraf–Nonius *SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Govindachari, T. R., Geetha Gopalakrishnan, Rajan, S. S., Kabaleeswaran, V. & Lessinger, L. (1996). *Acta Cryst.* B**52**, 145–150.

Govindachari, T. R., Narashiman, N. S., Suresh, G., Partho, P. D. & Geetha Gopalakrishnan (1996). *J. Chem. Ecol.* **22**, 1453–1460.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kabaleeswaran, V., Rajan, S. S., Geetha Gopalakrishnan & Govindachari, T. R. (1994). *Curr. Sci.* **66**, 362–364.

Sheldrick, G. M. (1986). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Suresh, G., Narashiman, N. S. & Palani, R. (1997). *Phytochemistry*, **45**, 807–810.