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Leonotinin

J. Sivaraman,[a] K. Subramanian[a] and S. Vasanth[b]

[a]*Department of Physics, Anna University, Madras-25, India, and* [b]*Captain Srinivasa Murti Drug Research Institute, Madras-106, India*

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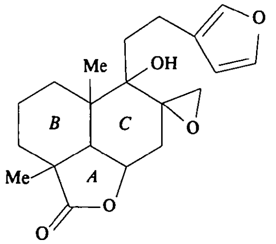
Abstract

Leonotinin has been elucidated as 8β,17:9,13-diepoxy-labdane-16,15:19,6β-diolactone, [2a*S*-(2aα,5aβ,6α,7β,8aα,8*b*α)]-6-[2-(3-furanyl)ethyl]octahydro-6-hydroxy-2a,5a-dimethylspiro[2*H*-naphtho[1,8-*bc*]furan-7(3*H*),2'-oxiran]-2-one, $C_{20}H_{26}O_5$. The furan ring is exocyclic to the fused ring system. The three-membered oxirane ring is inclined at 67.4 (5)° to the furan ring. The packing of the molecules in the unit cell is purely the result of van der Waals interactions.

Comment

Leonotinin (I) is a furanoditerpenoid obtained from a hexane extraction of the plant *Leonotis nepetaefolia* (R. Br) belonging to the family Labiateae. The plant is reported to be used to treat skin infections and also as a laxative and narcotic. Ash from the flowers is also applied to treat burns (Wealth of India, 1962). Leonotinin is the second major compound in the hexane extraction (Purushothaman, Vasanth & Connolly, 1974).



(I)

An interesting structural aspect of the molecule is the presence of one three-membered ring comprising atoms C(16), O(15) and C(6). This oxirane ring is almost perpendicular [101.1 (4)°] to ring *A*. The average C*sp*^{3}—C*sp*^{3} bond length in (I) is found to be 1.524 (1) Å which is in agreement with related structures (Sivaraman, Subramanian, Velmurugan, Subramanian & Balakrishna, 1993; Subramanian, Selladurai, Sivakumar, Ponnuswamy & Sukumar, 1989).

Ring *A* is in a chair conformation, ΔC_s[C(1)–C(4)] = 5.7°, whereas ring *B* and the α-substituted tetrahydrofuran are in sofa conformations, ΔC_2[C(3)–C(4)] = 21.1 and ΔC_s[C(8)–C(7)] = 2.9°. The fusion of α-substituted tetrahydrofuran with rings *A* and *B* is *cis* and the *A*/*B* ring junction is *trans* fused. The methyl group C(18) [bonded to C(4)] lies 1.798 (3) Å from the *A*/*B* plane. The methyl atom C(13) lies 1.662 (1) Å below the *B*/*C* plane. The ketone O atom, O(14), of the tetrahydrofuran lies 0.379 (9) Å above the ring plane.

The standard tetrahedral and bend angles at C and O atoms are 109.5 and 104.5°, respectively; in the oxirane ring of the title structure these angles are close to 60° and the sum of the angles within the ring system is 180°. This indicates that the ring is under great strain. If any reaction were to take place with this structure, the oxirane ring would be the first to be broken. The O(15)—C(16) bond length [1.509 (9) Å] is significantly elongated from the normal value of 1.43 Å, reflecting the strain in the system.

The furan ring, which is essentially planar [$(\Delta/\sigma)^2$ = 5.99], makes a dihedral angle with the *A*/*B*/*C* fused ring system of 101.2 (2)°, showing it to be almost perpendicular in orientation. The molecular conformation with atomic numbering is shown in Fig. 1. A stereoview of molecular packing viewed down the *a* axis is shown in Fig. 2.

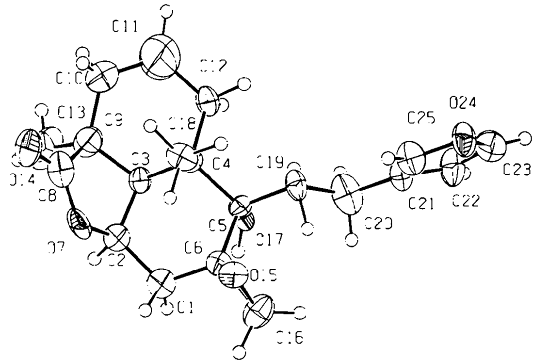


Fig. 1. Perspective view and numbering scheme of leonotinin. Displacement ellipsoids are drawn at the 50% probability level.

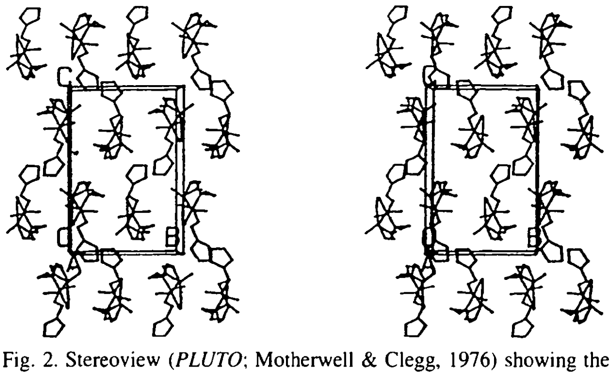


Fig. 2. Stereoview (*PLUTO*; Motherwell & Clegg, 1976) showing the molecular packing viewed down the *a* axis.

Experimental

Leonotinin is obtained from a hexane extraction of the plant *Leonotis nepetaefolia* (R. Br). The compound was crystallized from methanol.

Crystal data

$C_{20}H_{26}O_5$
$M_r = 346$
Orthorhombic
$P2_12_12_1$
$a = 10.144\,(4)$ Å
$b = 10.962\,(3)$ Å
$c = 15.683\,(3)$ Å
$V = 1744.0\,(9)$ Å^3
$Z = 4$
$D_x = 1.3168$ Mg m^{-3}
$D_m = 1.362$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 15\text{–}25°$
$\mu = 0.094$ mm^{-1}
$T = 293$ K
Rectangular block
0.46 × 0.41 × 0.36 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (ψ scan; Frenz, 1978)
$T_{\min} = 0.92$, $T_{\max} = 1.00$
1731 measured reflections
1621 independent reflections
1242 observed reflections [$I > 3\sigma(I)$]

$R_{\text{int}} = 0.091$
$\theta_{\max} = 65°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 18$
2 standard reflections monitored every 100 reflections
intensity decay: <2%

Refinement

Refinement on F
$R = 0.057$
$wR = 0.058$
$S = 1.08$
1242 reflections
306 parameters
$w = 2.8727/[\sigma^2(F) + 0.000529F^2]$

$(\Delta/\sigma)_{\max} = 0.076$
$\Delta\rho_{\max} = 0.308$ e Å^{-3}
$\Delta\rho_{\min} = -0.226$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	−0.0971 (4)	0.1222 (4)	0.4327 (4)	0.055 (6)
C(2)	−0.2403 (5)	0.0786 (4)	0.4212 (4)	0.047 (5)
C(3)	−0.2711 (3)	0.0204 (5)	0.3348 (5)	0.037 (4)
C(4)	−0.2105 (5)	0.0897 (4)	0.2591 (5)	0.037 (5)
C(5)	−0.0523 (6)	0.0847 (7)	0.2715 (5)	0.030 (4)
C(6)	−0.0198 (4)	0.1557 (7)	0.3541 (5)	0.036 (4)
O(7)	−0.3406 (5)	0.1732 (7)	0.4297 (4)	0.048 (3)
C(8)	−0.4492 (7)	0.1473 (11)	0.3814 (7)	0.071 (7)
C(9)	−0.4225 (5)	0.0259 (9)	0.3340 (6)	0.052 (6)
C(10)	−0.4852 (2)	0.0206 (7)	0.2438 (4)	0.090 (8)
C(11)	−0.4030 (5)	0.0202 (5)	0.1689 (5)	0.165 (4)
C(12)	−0.2534 (9)	0.0269 (9)	0.1776 (5)	0.050 (5)
C(13)	−0.4819 (3)	−0.0765 (11)	0.3887 (7)	0.090 (8)
O(14)	−0.5473 (5)	0.2077 (9)	0.3791 (5)	0.072 (6)
O(15)	0.0085 (6)	0.2839 (5)	0.3438 (4)	0.036 (4)
C(16)	0.1166 (5)	0.1991 (9)	0.3730 (6)	0.059 (6)
O(17)	−0.0145 (6)	−0.0374 (5)	0.2946 (3)	0.026 (3)
C(18)	−0.2470 (4)	0.2283 (3)	0.2503 (5)	0.042 (5)
C(19)	0.0184 (8)	0.1334 (7)	0.1908 (5)	0.039 (5)
C(20)	0.1364 (5)	0.0580 (6)	0.1626 (7)	0.078 (8)
C(21)	0.2061 (6)	0.1091 (8)	0.0861 (5)	0.044 (5)
C(22)	0.2993 (4)	0.0467 (4)	0.0359 (6)	0.058 (6)
C(23)	0.3340 (5)	0.1156 (4)	−0.0307 (6)	0.065 (7)
O(24)	0.2621 (7)	0.2279 (3)	−0.0245 (4)	0.050 (5)
C(25)	0.1884 (10)	0.2190 (9)	0.0469 (5)	0.054 (6)

Table 2. *Selected geometric parameters (Å, °)*

C(1)—C(2)	1.540 (6)	O(24)—C(23)	1.434 (6)
C(2)—C(3)	1.530 (9)	C(23)—C(22)	1.336 (11)
C(3)—C(4)	1.538 (9)	C(22)—C(21)	1.408 (10)
C(4)—C(5)	1.617 (8)	C(4)—C(18)	1.570 (6)
C(5)—C(6)	1.547 (11)	C(4)—C(12)	1.516 (11)
C(6)—C(16)	1.493 (8)	C(12)—C(11)	1.525 (10)
C(6)—O(15)	1.443 (9)	C(11)—C(10)	1.440 (9)
C(16)—O(15)	1.509 (9)	C(10)—C(9)	1.552 (11)
C(5)—O(17)	1.439 (9)	C(9)—C(3)	1.537 (6)
C(5)—C(19)	1.550 (11)	C(9)—C(13)	1.536 (11)
C(19)—C(20)	1.520 (16)	C(9)—C(8)	1.548 (15)
C(20)—C(21)	1.501 (12)	C(8)—O(14)	1.196 (11)
C(21)—C(25)	1.364 (13)	C(8)—O(7)	1.367 (10)
C(25)—O(24)	1.350 (11)	O(7)—C(2)	1.459 (8)
C(2)—C(1)—C(6)	118.1 (4)	C(12)—C(11)—C(10)	120.2 (6)
C(1)—C(6)—C(5)	116.8 (5)	C(11)—C(10)—C(9)	120.4 (3)
C(6)—C(5)—C(4)	107.2 (5)	C(10)—C(9)—C(3)	114.5 (5)
C(5)—C(4)—C(3)	106.7 (5)	C(16)—O(15)—C(6)	60.7 (4)
C(4)—C(3)—C(2)	113.3 (4)	O(15)—C(16)—C(6)	57.5 (4)
C(3)—C(2)—C(1)	115.2 (4)	C(16)—C(6)—O(15)	61.8 (4)
C(9)—C(3)—C(2)	101.2 (5)	C(5)—C(19)—C(20)	114.5 (6)
C(3)—C(9)—C(8)	101.8 (5)	C(19)—C(20)—C(21)	113.6 (6)
C(9)—C(8)—O(7)	107.1 (6)	C(22)—C(23)—O(24)	107.3 (6)
C(8)—O(7)—C(2)	111.3 (7)	C(23)—O(24)—C(25)	106.0 (5)
O(7)—C(2)—C(3)	103.6 (5)	O(24)—C(25)—C(21)	111.4 (8)
C(9)—C(3)—C(4)	111.9 (5)	C(25)—C(21)—C(22)	105.4 (6)
C(3)—C(4)—C(12)	108.2 (5)	C(21)—C(22)—C(23)	109.8 (5)
C(4)—C(12)—C(11)	112.5 (6)		
C(1)—C(2)—C(3)—C(4)	−42.9 (6)		
C(2)—C(3)—C(4)—C(5)	62.3 (6)		
C(3)—C(4)—C(5)—C(6)	−64.3 (6)		
C(4)—C(5)—C(6)—C(1)	50.4 (7)		
C(5)—C(6)—C(1)—C(2)	−31.9 (8)		
C(6)—C(1)—C(2)—C(3)	26.0 (7)		
C(4)—C(3)—C(9)—C(10)	36.7 (8)		
C(3)—C(9)—C(10)—C(11)	−4.5 (9)		
C(9)—C(10)—C(11)—C(12)	−0.9 (9)		
C(10)—C(11)—C(12)—C(4)	−26.4 (9)		
C(11)—C(12)—C(4)—C(3)	57.5 (8)		
C(12)—C(4)—C(3)—C(9)	−63.5 (7)		
C(9)—C(3)—C(2)—O(7)	−36.2 (6)		
C(3)—C(2)—O(7)—C(8)	23.9 (8)		
C(2)—O(7)—C(8)—C(9)	−0.9 (9)		
O(7)—C(8)—C(9)—C(3)	−22.1 (9)		
C(8)—C(9)—C(3)—C(2)	34.3 (7)		

The structure was solved by direct methods. The H atoms located from a difference Fourier map were refined for one cycle whereas the geometrically fixed H atoms were not refined. Full-matrix least-squares refinement of anisotropic displacement parameters for all non-H atoms; H atoms were refined isotropically.

Data collection: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Acetylphenyl 1-Naphthoate

ANDRÉS E. GOETA,[a] GRACIELA PUNTE,[a] JORGE L. JIOS[b] AND JUAN C. AUTINO[b]

[a]*Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CC67-(1900)-La Plata, Argentina, and* [b]*LADECOM-CONICET, Laboratorio de Estudio de Compuestos Orgánicos, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Argentina. E-mail: goeta@ayelen.fisica.unlp.edu.ar*

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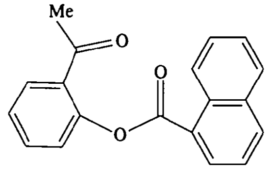
Abstract

The crystal structure of the title compound, $C_{19}H_{14}O_3$, an intermediate in the synthesis of 2-naphthylchromones, has been determined by X-ray diffraction. The title molecule, which can be viewed as the fusion of 1-naphthoic acid and acetophenone, is not planar. The dihedral angle between the benzene and naphthalene planes is 77.39 (7)°. Two intramolecular C—H···O bonds and a short intramolecular O···O distance of 2.719 (2) Å have been observed.

Comment

2-Acetylphenyl 1-naphthoate (2A1N) belongs to the family of 2-acetylphenyl naphthoates which are potentially important intermediates in the synthesis of several compounds with different kinds of activities, *e.g.* antimicrobial (Vibhute, 1976) and antitumor (Atassi, Briet, Berthelon & Collonges, 1985). 2A1N was synthesized by means of a known reaction (Virkar & Shah, 1942).



2A1N

An exhaustive search of the Cambridge Structural Database (Allen & Kennard, 1993) showed that the only related compounds already solved are 1-naphthoic acid (1NA) (Trotter, 1960) and acetophenone (AP) (Tanimoto, Kobayashi, Nagakura & Saito, 1973). The phenyl and naphthalene rings are essentially planar. The dihedral angle between the benzene mean plane (BMP) and the naphthalene mean plane (NMP) is 77.39 (7)°. The angle formed between the carboxyl mean plane and NMP is 14.3 (2)° in 2A1N (11° in 1NA), and the angle between the carboxyl group and BMP is 88.3 (2)°.

Comparison of the geometry of the bridging carboxyl group in 2A1N with that of the carboxyl group in 1NA displays a noticeable variation in bond lengths and angles. The C(9)—C(8)—O(1) and O(1)—C(8)—O(2) angles alter from 122 to 111.0 (1)° and from 110 to 121.7 (1)° in 2A1N and 1NA, respectively, and the bond length O(1)—C(8) stretches from 1.28 to 1.360 (2) Å. Although the structure of 1NA was determined from film data, we think that the differences are large enough to permit the assumption of a variation in the character of the C—O bond. There is also a significant change in the dihedral angle between the mean planes formed by O(3)—C(10)—C(21) and BMP from a value of 4.0 (2) in AP to 24.9 (2)° in 2A1N. These large modifications in the carboxyl and acetophenone group geometry may be a result of the short intramolecular contact between O(1) and O(3) [2.719 (2) Å] in 2A1N. There is some evidence of short intramolecular contacts between O atoms in the literature (Punte, Rivero, Cerdeira & Nudelman, 1990; Faerman *et al.*, 1985), but this has not been discussed thoroughly.

In addition to the short distance mentioned above, we have found two intramolecular *D*—H···*A* interactions. These are C(13)—H(131)···O(1) and C(15)—H(151)···O(2), where the C···O distances are 2.652 (2) and 2.886 (2) Å, the H···O distances are 2.28 (2) and

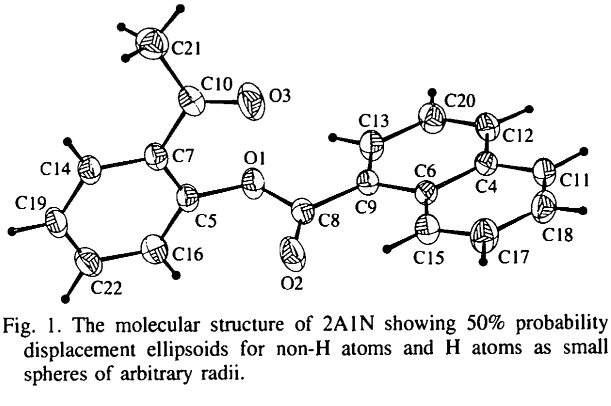


Fig. 1. The molecular structure of 2A1N showing 50% probability displacement ellipsoids for non-H atoms and H atoms as small spheres of arbitrary radii.