

ORGANIC COMPOUNDS

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Calodendrolide,† a Degraded Limonoid from *Calodendrum capense*

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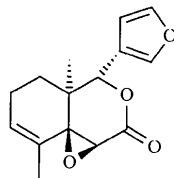
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Abstract

Calodendrolide, C₁₅H₁₆O₄, has its epoxide β oriented and its 3'-furyl group α oriented. There are three independent molecules in the asymmetric unit, differing principally in the conformation of the 3'-furyl group with respect to the remainder of the molecule. One molecule has its 3'-furyl O atom α oriented, with an O—C—C=C torsion angle of 30.7(4)°, while the other two molecules have their 3'-furyl O atoms β oriented, with O—C—C=C torsion angles of −136.9(3) and −134.5(3)°. The epoxide is asymmetric, with mean C—O distances of 1.436(2) and 1.464(2) Å.

Comment

Calodendrolide, (1), a highly degraded limonoid, was first isolated from the root bark of *Calodendrum capense* Thunb (Rutaceae) (Cassady & Liu, 1972). The crystal structure of (1) was determined in order to confirm the relative configurations at the chiral centers and to probe the conformation of the pyran ring. A description of the isolation and characterization of (1) is given by Cassady & Liu (1972) and the synthesis of DL-calodendrolide has been reported by Tokoroyama *et al.* (1990), and Rajab & Guyo (1993). Drewes *et al.* (1985) confirmed the configuration of calodendrolide at the C atom bearing the furan ring.



(1)

† Alternative name: 1-(3-furyl)-1,7,8,8a-tetrahydro-5a,8-dimethyl-4,4a-epoxy-2-benzopyran-3(4H)-one.

Three independent molecules are present in the asymmetric unit of (1); they are illustrated in Fig. 1, in which all three are shown in the same orientation, rather than in proper orientation with respect to one another. Space group $P2_12_12_1$ with $Z' = 3$ is uncommon, occurring in only 0.2% of cases in that space group in the Brock & Dunitz (1994) compilation, and 0.4% in the compilation of Chernikova *et al.* (1991) for homomolecular organics. The three molecules differ principally in the conformation of the 3'-furyl group with respect to the remainder of the molecule, as shown in Fig. 1 and as described by the tabulated O1—C17—C20—C21 torsion angles. Endocyclic torsion angles in the two six-membered rings exhibit excellent agreement across molecules A, B and C (tabulated for molecule A in Table 1). The maximum spread of any of these 12 torsion angles is only 2.3(4)°, between the A and B molecules for C17—C13—C14—C15. The conformation of the cyclohexene ring is a half chair, with the local twofold axis bisecting the double bond. The pyran ring has the twist conformation observed in 1,3-cyclohexadiene (Oberhammer & Bauer, 1969), with near-zero torsion angles about C14—C15 and O1—C16, and a torsion angle of 21.3(2)° (mean of three) about the bond joining them. The closely related compound DL-*epi*-pyroangolensolide, which is racemic, epimeric to (1)

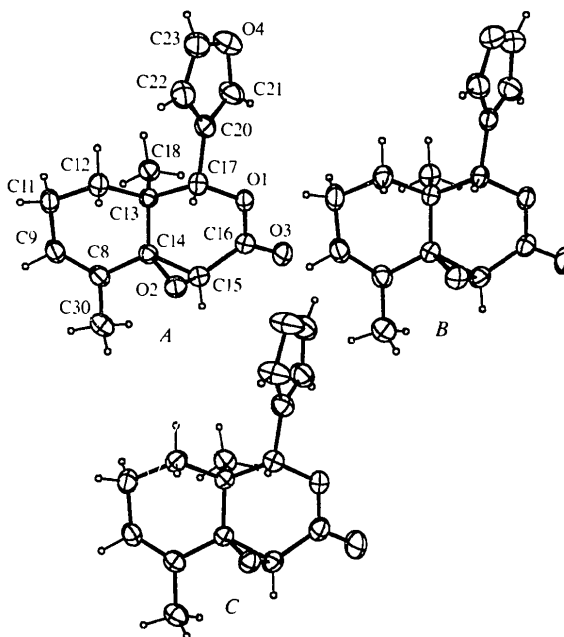


Fig. 1. The three independent molecules, with displacement ellipsoids drawn at the 30% probability level and H atoms represented as small circles of arbitrary radii. Each molecule has been placed in the same orientation for comparison.

at C17, and lacks the epoxide at C14—C15, has been determined (Drewes *et al.*, 1985). It appears to have a similar conformation for the six-membered ring system, but coordinates have not been reported. The epoxide of (1) is slightly asymmetric, with the mean value for the O2—C14 distance 0.028 (3) Å longer than that for O2—C15.

Experimental

Compound (1) was isolated from the root bark of *Calodendrum capense* Thunb (Rutaceae) which was collected in Eldoret, Uasin Gishu District, Kenya. Crystals were grown from acetone-hexane.

Crystal data

$C_{15}H_{16}O_4$	Cu $K\alpha$ radiation
$M_r = 260.29$	$\lambda = 1.54184 \text{ \AA}$
Orthorhombic	Cell parameters from 25 reflections
$P2_12_12_1$	$\theta = 20\text{--}25^\circ$
$a = 9.0230 (5) \text{ \AA}$	$\mu = 0.74 \text{ mm}^{-1}$
$b = 17.894 (2) \text{ \AA}$	$T = 299 \text{ K}$
$c = 24.469 (2) \text{ \AA}$	Needle
$V = 3950 (1) \text{ \AA}^3$	$0.58 \times 0.10 \times 0.10 \text{ mm}$
$Z = 12$	Colorless
$D_x = 1.313 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Enraf-Nonius CAD-4 diffractometer	4232 reflections with $I > 0$
$\omega/2\theta$ scans	$\theta_{\max} = 75^\circ$
Absorption correction: ψ scans (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 11$
$T_{\min} = 0.911$, $T_{\max} = 0.929$	$k = 0 \rightarrow 22$
4558 measured reflections	$l = 0 \rightarrow 30$
4558 independent reflections	3 standard reflections frequency: 120 min intensity decay: 2.1%

Refinement

Refinement on F^2	Extinction correction: isotropic (Zachariasen, 1963)
$R(F) = 0.052$	Extinction coefficient: $5.1 (2) \times 10^{-7}$
$wR(F^2) = 0.044$	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
$S = 1.557$	Absolute structure: assumed to correspond to that of methyl angolensate (Cassady & Liu, 1972)
4232 reflections	
527 parameters	
H atoms: see below	
$w = 4F_o^2 / [\sigma^2(F_o^2) + 0.0004F_o^4]$	
$(\Delta/\sigma)_{\max} = 0.005$	
$\Delta\rho_{\max} = 0.14 \text{ e \AA}^{-3}$	
$\Delta\rho_{\min} = -0.08 \text{ e \AA}^{-3}$	

Table 1. Selected geometric parameters (Å, °)

O2A—C14A	1.467 (3)	C8B—C9B	1.324 (4)
O2A—C15A	1.441 (3)	C20B—C22B	1.414 (4)
C8A—C9A	1.332 (4)	O2C—C14C	1.455 (3)
C20A—C22A	1.412 (4)	O2C—C15C	1.431 (3)
O2B—C14B	1.469 (3)	C8C—C9C	1.323 (4)
O2B—C15B	1.435 (3)	C20C—C22C	1.417 (4)

C14A—O2A—C15A	60.7 (2)	O2B—C15B—C14B	60.7 (2)
O2A—C14A—C15A	58.8 (2)	C14C—O2C—C15C	60.8 (2)
O2A—C15A—C14A	60.5 (2)	O2C—C14C—C15C	58.8 (2)
C14B—O2B—C15B	60.8 (2)	O2C—C15C—C14C	60.4 (2)
O2B—C14B—C15B	58.4 (2)		
		C17A—O1A—C16A—C15A	−1.2 (4)
		C16A—O1A—C17A—C13A	−38.4 (3)
		C14A—C8A—C9A—C11A	1.7 (4)
		C9A—C8A—C14A—C13A	−19.8 (4)
		C8A—C9A—C11A—C12A	−13.9 (4)
		C9A—C11A—C12A—C13A	42.6 (3)
		C11A—C12A—C13A—C14A	−58.3 (3)
		C12A—C13A—C14A—C8A	47.3 (3)
		C17A—C13A—C14A—C15A	−38.6 (3)
		C14A—C13A—C17A—O1A	56.7 (3)
		C13A—C14A—C15A—C16A	1.5 (4)
		C14A—C15A—C16A—O1A	21.2 (4)
		O1A—C17A—C20A—C21A	30.7 (4)
		O1B—C17B—C20B—C21B	−136.9 (3)
		O1C—C17C—C20C—C21C	−134.5 (3)

The numbering scheme chosen corresponds to the standard nomenclature for undegraded limonoids. H atoms on the epoxidized C15A, C15B and C15C atoms were refined isotropically. Other H atoms were placed in calculated positions, guided by difference maps for the methyl groups. C—H distances for calculated H atoms were 0.95 Å, with $B_{\text{iso}} = 1.3B_{\text{eq}}$ of the attached C atom. Assignment of atom types for C23 and O4 of the 3'-fury ring was made based upon visibility of the C23 H atom in difference maps. C20—C22 distances corresponding to a single bond opposite O4 and refinement of displacement parameters to unrealistic values when assignments were reversed.

Data collection: *CAD-4 Operations Manual* (Enraf-Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *PROCESS MolEN* (Fair, 1990). Program(s) used to solve structure: direct methods *SIR* (Burla *et al.*, 1989). Program(s) used to refine structure: *LSFM MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *BTABLE PTABLE CIF IN MolEN*.

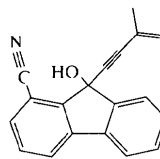
The purchase of the diffractometer was made possible by a National Science Foundation chemical instrumentation grant, which we gratefully acknowledge. Improvements to the LSU X-ray Crystallography Facility were supported by Grant No. LEQSF(1996-97)-ENH-TR-10, administered by the Louisiana Board of Regents.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1000). Services for accessing these data are described at the back of the journal.

References

- Brock, C. P. & Dunitz, J. D. (1994). *Chem. Mater.* **6**, 1118–1127.
- Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.
- Cassady, J. M. & Liu, C.-S. (1972). *J. Chem. Soc. Chem. Commun.* pp. 86–87.
- Chernikova, N. Yu., Bel'skii, V. K. & Zorkii, P. M. (1991). *J. Struct. Chem.* **31**, 661–666.
- Drewes, S. E., Grieco, P. A. & Huffman, J. C. (1985). *J. Org. Chem.* **50**, 1309–1311.
- Enraf-Nonius (1977). *CAD-4 Operations Manual*. Enraf-Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.

- Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Oberhammer, H. & Bauer, S. H. (1969). *J. Am. Chem. Soc.* **91**, 10–16.
- Rajab, M. S. & Guyo, P. M. (1993). *Bull. Chem. Soc. Ethiop.* **8**, 35–38.
- Tokoroyama, T., Kotsuji, T., Matsuyama, H., Shimura, T., Yokotani, K. & Fukuyama, Y. (1990). *J. Chem. Soc. Perkin Trans. 1*, pp. 1745–1752.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.



(1)

The C15—C16 bond distance in the title molecule [1.191 (2) Å] is in agreement with those of related alkynol compounds: 3,3-diphenyl-1-propyn-3-ol [1.169 (2) Å; Garcia *et al.*, 1995], 1,1-bis(2,4-dimethylphenyl)-2-propyn-1-ol, 1,1-bis(2,4-dimethylphenyl)-2-butyn-1-ol and 9-hydroxy-9-(1-propynyl)fluorene [1.208 (5), 1.189 (6) and 1.16 (2) Å, respectively; Toda *et al.*, 1985], 1,6,9,14-tetrahydroxy-1,6,9,14-tetra-*tert*-butylcyclohexadeca-2,4,7,10,12,15-hexayne [1.168 (6) Å; Toda *et al.* 1988], and also with those of related alkyne compounds: phenyl-(2-trimethylsilylethynyl)-phenylmethanone and (2-trimethylsilylethynyl)benzaldehyde [1.199 (3) and 1.192 (3) Å, respectively; Garcia *et al.*, 1996], 2,3,5,6-tetra[1-ethynyl-2(trimethylsilyl)]pyridine [1.190 (4) and 1.191 (4) Å; Garcia *et al.*, 1997], 2,3,5,6-tetra[1-ethynyl-2-(trimethylsilyl)]pyrazine [1.198 (5) and 1.199 (6) Å; Garcia *et al.*, 1997], 2,3,4,5-tetra[1-ethynyl-2-(trimethylsilyl)]thiophene [1.190 (4) and 1.190 (4) Å; Garcia *et al.*, 1997], 3,4-dibromo-2,5-di[1-ethynyl-2-(trimethylsilyl)]-*N*-methylpyrrole [1.189 (5) and 1.194 (4) Å; Garcia *et al.*, 1997]. The C14—N1 bond in the title molecule [1.143 (2) Å] is similar in length to that of 2-cyanobenzophenone [1.130 (5) Å; Preut *et al.*, 1992].

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9-Hydroxy-9-(3-methylbut-3-en-1-ynyl)-9H-fluorene-1-carbonitrile

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Abstract

The N atom in the title compound, C₁₉H₁₃NO, lies −0.0365 (14) Å from the plane formed by the fluorene system, and the C≡N distance is 1.143 (2) Å. The C≡C distance is 1.191 (2) Å, and the ethynyl group deviates slightly from linearity, with C—C≡C—C bond angles of 172.0 (1) and 176.1 (2)°. Terminal CH₂ and CH₃ groups are 50:50 disordered, with equal C—C distances of 1.408 (3) and 1.406 (3) Å.

Comment

The determination of the crystal structure of the title compound, (I), was undertaken as part of an on-going program of structure analyses of some novel intermediates in the synthesis of potentially bio-active compounds bearing a conjugated acetylenic functionality. The nitrile unit is nearly coplanar with the fluorene ring system; the torsion angles N1—C14—C3—C2, N1—C14—C3—C4 and C14—C3—C2—C1 are 162.3 (3), −17.1 (3) and 0.9 (2)°, respectively.

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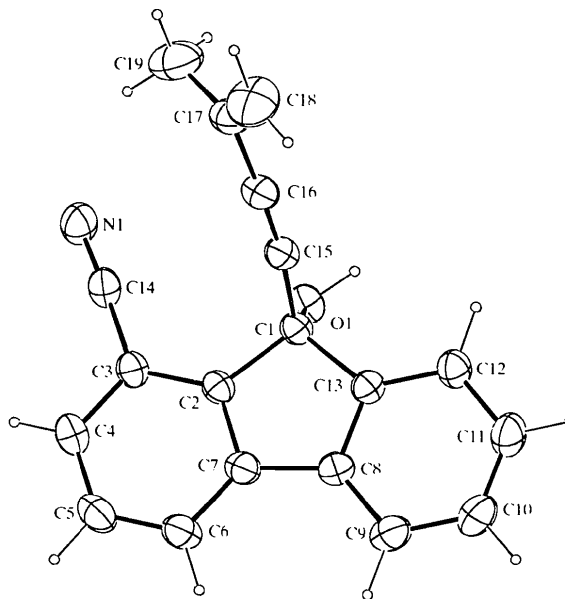


Fig. 1. The title molecule with ellipsoids drawn at the 30% probability level and H atoms shown with arbitrary radii. Only one set of the partially populated H-atom positions is illustrated for C18 and C19.