

Structure of the Germacrane Furanosesquiterpenoid Linderane

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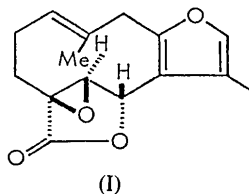
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Abstract. [1a*S*-(1a*R**,4*E*,10*R**,10a*R**)]-3,6,10,10a-Tetrahydro-5,9-dimethyl-2*H*-10,1a-(epoxymethano)-oxireno[4,5]cyclodeca[1,2-*b*]furan-12-one, C₁₅H₁₆O₄, *M_r* = 260.3, orthorhombic, *P*2₁2₁2₁, *a* = 13.633 (3), *b* = 9.102 (2), *c* = 10.153 (2) Å, *V* = 1259.8 (4) Å³, *Z* = 4, *D_x* = 1.373 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 0.93 cm⁻¹, *F*(000) = 552, *T* = 295 K, *R* = 0.057, *wR* = 0.052 for 1088 observed reflections [*I* ≥ σ(*I*)]. The molecule consists of a macrocyclic ten-membered ring and its fused associated epoxide, furan and γ-lactone rings. The conformation of the ten-membered ring is such that the methyl group and γ-lactone ring lie *syn* on the α face of the molecule, and C4—C5 and C1a—C10a (IUPAC numbering) bonds are in a crossed orientation. The γ-lactone ring, *cis*-fused at C1a and C10, is approximately perpendicular to the mean plane of the ten-membered ring [85.8 (2)°] and the epoxide ring makes an angle of 103.1 (4)° with the γ-lactone ring. The plane of C4, C5, C6 and the methyl C atom on C5 is approximately perpendicular to the ten-membered ring [81.7 (3)°].

Experimental. Linderane, a germacrane furanosesquiterpenoid isolated from the root of *Lindera strychnifolia* Vill, can be represented by the formula (I).



Crystals of (I) were prepared and recrystallized from acetone–light petroleum solution as colorless needles, m.p. 463–464 K, elongated along the *b* axis. The unit-cell dimensions were obtained by least-squares refinement of the setting angles of 20 reflec-

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) with *e.s.d.*'s in parentheses

$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
O(1)	0.5940 (3)	0.2435 (4)	0.0860 (4)	3.9 (2)
O(2)	0.6444 (3)	0.6900 (4)	-0.0636 (4)	4.1 (2)
O(3)	0.7580 (3)	0.8593 (5)	-0.0253 (5)	5.2 (2)
O(4)	0.5224 (3)	0.8831 (4)	0.0699 (5)	4.9 (2)
C(1)	0.7060 (4)	0.6583 (7)	0.3015 (6)	3.6 (3)
C(2)	0.7386 (5)	0.8154 (7)	0.3024 (7)	4.5 (3)
C(3)	0.6590 (5)	0.9120 (7)	0.2415 (7)	4.0 (3)
C(4)	0.6169 (4)	0.8383 (6)	0.1196 (6)	3.5 (3)
C(5)	0.5376 (5)	0.7324 (6)	0.1111 (7)	3.7 (3)
C(6)	0.5538 (4)	0.6352 (6)	-0.0030 (7)	3.6 (3)
C(7)	0.5624 (4)	0.4722 (5)	0.0206 (5)	2.9 (2)
C(8)	0.6125 (4)	0.3893 (6)	0.1071 (6)	3.6 (3)
C(9)	0.6779 (6)	0.4102 (8)	0.2231 (8)	4.7 (3)
C(10)	0.7362 (4)	0.5522 (6)	0.2266 (6)	3.1 (2)
C(11)	0.5052 (4)	0.3711 (7)	-0.0588 (6)	3.6 (3)
C(12)	0.5277 (5)	0.2372 (7)	-0.0151 (7)	4.0 (3)
C(13)	0.4335 (6)	0.4076 (9)	-0.1653 (8)	4.7 (4)
C(14)	0.8231 (6)	0.5537 (10)	0.1387 (9)	5.2 (4)
C(15)	0.6824 (4)	0.8040 (6)	0.0050 (6)	3.6 (3)

tions (5.0 ≤ 2θ ≤ 26.7°) measured on the automatic diffractometer. Intensity data were collected on a Hilger & Watts automatic four-circle Y 290 diffractometer controlled by a PDP 8 computer. Integrated intensities were measured for 2θ < 55° by the ω–2θ scan technique with Mo *K*α radiation. Three standard reflections (022, 120, 201) were monitored every 100 reflections and showed no significant variation over the data collection. 1669 independent reflections (0 ≤ *h* ≤ 17, 0 ≤ *k* ≤ 11, 0 ≤ *l* ≤ 13) were recorded, of which 1088 intensities having *I* ≥ σ(*I*) were considered observed. Intensities were corrected for Lorentz and polarization factors. No absorption corrections were applied since the specimen was considered to be sufficiently small (0.20 × 0.23 × 0.30 mm).

The structure was solved by direct methods, using the program *DIRECTER* (Koyama & Okada, 1975; Okada & Koyama, 1991) for automatic structure analysis. The H atoms were found on the difference Fourier map. Full-matrix least-squares refinement using the program *LSBF* (Okada, Okada & Koyama, 1990; Okada & Koyama, 1991) decreased

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Table 2. Bond distances (Å), bond angles (°) and torsion angles (°) with *e.s.d.*'s in parentheses

O(1)—C(8)	1.367 (7)	C(4)—C(5)	1.450 (8)
O(1)—C(12)	1.369 (8)	C(4)—C(15)	1.500 (8)
O(2)—C(6)	1.467 (7)	C(5)—C(6)	1.475 (9)
O(2)—C(15)	1.353 (7)	C(6)—C(7)	1.508 (8)
O(3)—C(15)	1.187 (8)	C(7)—C(8)	1.344 (8)
O(4)—C(4)	1.442 (7)	C(7)—C(11)	1.451 (8)
O(4)—C(5)	1.448 (7)	C(8)—C(9)	1.489 (10)
C(1)—C(2)	1.498 (9)	C(9)—C(10)	1.518 (9)
C(1)—C(10)	1.296 (8)	C(10)—C(14)	1.483 (10)
C(2)—C(3)	1.526 (10)	C(11)—C(12)	1.333 (9)
C(3)—C(4)	1.521 (9)	C(11)—C(13)	1.495 (10)
C(8)—O(1)—C(12)	106.3 (5)	C(6)—C(7)—C(8)	134.1 (5)
C(6)—O(2)—C(15)	111.5 (4)	C(6)—C(7)—C(11)	119.6 (5)
C(4)—O(4)—C(5)	60.2 (4)	C(8)—C(7)—C(11)	106.3 (5)
C(2)—C(1)—C(10)	128.4 (6)	O(1)—C(8)—C(7)	110.4 (5)
C(1)—C(2)—C(3)	109.7 (6)	O(1)—C(8)—C(9)	111.0 (6)
C(2)—C(3)—C(4)	110.1 (5)	C(7)—C(8)—C(9)	138.5 (6)
O(4)—C(4)—C(3)	119.8 (5)	C(8)—C(9)—C(10)	116.2 (6)
O(4)—C(4)—C(5)	60.1 (4)	C(1)—C(10)—C(9)	118.8 (5)
O(4)—C(4)—C(15)	108.7 (5)	C(1)—C(10)—C(14)	126.9 (6)
C(3)—C(4)—C(5)	128.5 (6)	C(9)—C(10)—C(14)	114.3 (6)
C(3)—C(4)—C(15)	119.9 (5)	C(7)—C(11)—C(12)	105.7 (5)
C(5)—C(4)—C(15)	105.0 (5)	C(7)—C(11)—C(13)	127.8 (6)
O(4)—C(5)—C(4)	59.7 (3)	C(12)—C(11)—C(13)	126.5 (6)
O(4)—C(5)—C(6)	111.3 (6)	O(1)—C(12)—C(11)	111.3 (5)
C(4)—C(5)—C(6)	109.5 (5)	O(2)—C(15)—O(3)	121.6 (6)
O(2)—C(6)—C(5)	104.5 (5)	O(2)—C(15)—C(4)	109.3 (5)
O(2)—C(6)—C(7)	109.6 (4)	O(3)—C(15)—C(4)	129.0 (6)
C(5)—C(6)—C(7)	118.5 (6)		
C(1)—C(2)—C(3)—C(4)	-42.3 (7)	C(2)—C(1)—C(10)—C(14)	11.6 (10)
C(2)—C(3)—C(4)—C(5)	86.6 (8)	C(15)—C(4)—C(5)—C(6)	0.6 (8)
C(3)—C(4)—C(5)—C(6)	-150.2 (8)	C(4)—C(5)—C(6)—O(2)	-1.3 (6)
C(4)—C(5)—C(6)—C(7)	121.0 (7)	O(1)—C(8)—C(7)—C(11)	2.0 (6)
C(5)—C(6)—C(7)—C(8)	-46.7 (9)	C(6)—C(7)—C(11)—C(13)	-1.2 (8)
C(6)—C(7)—C(8)—C(9)	4.1 (11)	O(1)—C(8)—C(9)—C(10)	156.5 (7)
C(7)—C(8)—C(9)—C(10)	-27.6 (10)	O(2)—C(6)—C(7)—C(11)	-109.2 (6)
C(8)—C(9)—C(10)—C(1)	101.5 (8)	O(2)—C(6)—C(7)—C(8)	73.1 (8)
C(9)—C(10)—C(1)—C(2)	-167.1 (9)	C(5)—C(6)—C(7)—C(11)	131.0 (7)
C(10)—C(1)—C(2)—C(3)	106.4 (8)	C(3)—C(4)—C(15)—O(3)	-23.5 (8)
C(8)—C(9)—C(10)—C(14)	-77.4 (8)	C(5)—C(4)—C(15)—O(2)	0.4 (7)

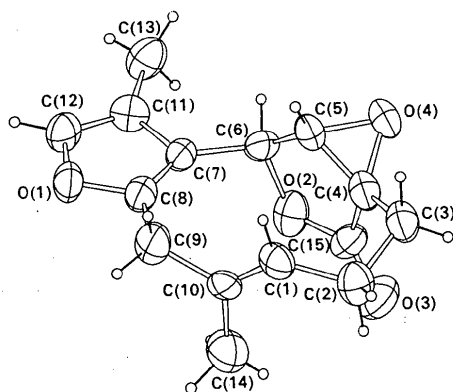


Fig. 1. View of the molecule with the atom-numbering scheme. Thermal ellipsoids of the C and O atoms are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

R to 0.057, with $wR = 0.052$ and $S = 0.88$ for the 1088 observed reflections with $I \geq \sigma(I)$, maximum (Δ/σ) was 0.46. The function minimized was $\sum w[F_o(\mathbf{h}) - F_c(\mathbf{h})]^2$ with unit weights for 236 variables. All H atoms were included in the final refinement with isotropic temperature factors. No further appropriate weighting scheme could be found from an analysis of ΔF values. Final difference Fourier map showed maximum and negative features of 0.11

and $-0.03 \text{ e} \text{ \AA}^{-3}$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were carried out with an NEC PC-9801RA personal computer using *DS*SYSTEM* (Okada, Okada & Koyama, 1990; Okada & Koyama, 1991).

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.† The configuration of the molecule with atom-numbering scheme is illustrated in Fig. 1, drawn with the version of *ORTEPII* (Johnson, 1976) included in the *DS*SYSTEM*. Molecular packing is displayed in Fig. 2. Bond distances, angles and torsion angles are given in Table 2.

Related literature. Linderane of the germacrane type has been assigned a structure on the basis of chemical and spectroscopic investigation (Takeda, Minato & Horibe, 1963). The absolute configuration of the molecule has been determined (Takeda, Horibe, Teraoka & Minato, 1968, 1969). Most of the observed bond distances and angles of the ten-membered ring are comparable to those observed in the related structures: dihydroelephantopin (Watson, Zabel, Mabry & Yabuta, 1982), tanacetols A and B (Calleri, Chiari & Viterbo, 1983), shiromodiol 8-*O*-angelate (Appendino, Calleri & Chiari, 1986) and shiromodiol 6-*O*-acetate 8-*O*-*p*-bromobenzoate (Sim, 1987). The torsion angles of the ten-membered ring are similar to those in dihydroelephantopin and costunolide (Bovill, Cox, Cradwick, Guy, Sim & White, 1976), though ω^{6-7} , ω^{7-8} and ω^{8-9} are shifted. The transannular distance $C(1) \cdots C(5)$ [3.075 (9) Å] is considerably less than the sum of the van der Waals radii [3.40 Å], as seen in shiromodiol 8-*O*-angelate. The C—C bond distance [1.450 (8) Å] in the epoxide

† Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond lengths and angles involving H atoms and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55470 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0584]

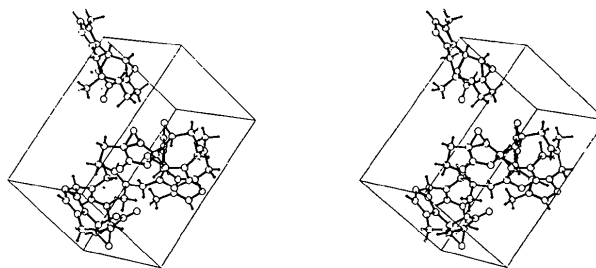


Fig. 2. A stereodiagram of the linderane molecules in the unit cell, drawn with the version of *PLUTO78* (Motherwell & Clegg, 1978) included in *DS*SYSTEM* (Okada, Okada & Koyama, 1990; Okada & Koyama, 1991).

ring is shorter than expected for a single bond (1.552–1.560 Å) and hence may be inferred to show partial double-bond character. The angle C(7)—C(8)—C(9) [138.5 (6)°] is an indication of strain imposed at the junction between the furan ring and the ten-membered ring.

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Structure of 3-Benzoylamino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydrocoumarin

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Abstract. C₁₈H₁₇NO₄, $M_r = 311.34$, monoclinic, $P2_1/n$, $a = 6.782$ (2), $b = 18.496$ (3), $c = 12.439$ (3) Å, $\beta = 99.34$ (1)°, $V = 1539.7$ (8) Å³, $Z = 4$, $D_x = 1.343$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.890$ cm⁻¹, $F(000) = 656$, $T = 293$ (2) K, final $R = 0.044$ and $wR = 0.063$ for 1821 observed reflections. The overall shape of the molecule is planar. The dihedral angle between the phenyl ring and the planar part of the coumarin group is 6.0 (7)°. The bond lengths and angles agree with expected values. This derivative of coumarin is a valuable material in the synthesis of the novel heterocyclic system 2*H*-, 5*H*-pyrano[3,2-*c*]azepine and its derivatives.

Experimental. Plate-like colourless single crystal, 0.45 × 0.35 × 0.20 mm, sealed in glass capillary. Cell dimensions were determined from the angular settings of 25 reflections with 10 < θ < 12° measured on an Enraf-Nonius CAD-4 diffractometer. Space group $P2_1/n$ was determined from the systematic absences. Intensity data were collected in the range 1 < 2 θ < 56° with variable-speed ω -2 θ scans using graphite-monochromated Mo $K\alpha$ radiation; max. scan time 60 s, scan width (0.8 + 0.3tan θ)°, background measured for 0.25 of scan time at each scan

limit. Three reflections were monitored every 300 reflections. Orientation was checked every 2 h. Data were corrected for intensity variation (–3.4%) and Lp effects; absorption was ignored. 7421 reflections ($\pm h$, $\pm k$, $\pm l$) were collected. On averaging ($R_{int} = 2.8\%$), 1821 reflections were considered observed [$I > 3\sigma(I)$; $\sigma(I)$ based on counting statistics] out of 3481 unique reflections; range of hkl : $h - 8$ to 8, $k 0$ to 24, $l 0$ to 16. The structure was solved with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The initial structural model was refined by full-matrix least squares, minimizing the function $\sum w(|F_o| - |F_c|)^2$ with *SHELX76* (Sheldrick, 1976). Final R and wR values were 0.044 and 0.063, respectively, with $w = 1.0/[\sigma^2(F_o) + 0.0094(F_o)^2]$ and 209 variables; H-atom positions were found in the final difference synthesis and included in the refinement with constraint imposed only on the C—H bonds. A common isotropic displacement parameter U for all H atoms was 0.077 (2) Å². A final difference Fourier map showed residual electron density within +0.18 and –0.31 e Å⁻³. $(\Delta/\sigma)_{max}$ at convergence was 0.011 (overall scale factor). Scattering factors for C, N and O atoms were taken from *International Tables for*