

(±)-Decahydro-4-hydroxy-4a,8-dimethylazuleno[6,5-*b*]furan-2,5(3*H*)-dione
(3α, 4α, 4β, 7α, 8α, 9αβ)

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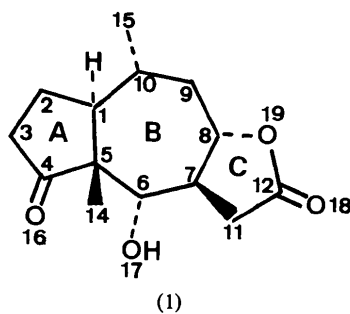
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Abstract. C₁₄H₂₀O₄, orthorhombic, *Pbca*, *a* = 14.724 (9), *b* = 15.203 (7), *c* = 11.666 (4) Å, *V* = 2611 (2) Å³, *D_x* = 1.28 Mg m⁻³ for *Z* = 8. The structure has been solved by direct methods (*MULTAN*) and refined to a final *R* value of 0.048 for 862 observed reflections. The stereochemistry of the title compound is as depicted for one enantiomer in (1); the relative configuration of the asymmetric carbons can be specified as C(1)*S*, C(5)*R*, C(6)*S*, C(7)*S*, C(8)*S* and C(10)*R*. The lactone ring of the tricyclic fragment is in an envelope conformation while the two other rings exhibit approximate *m* symmetry, the different symmetry elements passing through C(4), C(6) and C(7) for the *A*, *B* and *C* rings respectively.



Introduction. In the course of synthetic studies directed towards the pseudoguaianolide (±)-carpesiolin (Maruyama & Omura, 1977) we needed to establish unequivocally the relative stereochemistry of the different chiral centers in one of our synthetic intermediates. We therefore undertook a single-crystal X-ray diffraction study of lactone (1), which possesses the same relative configuration as (±)-carpesiolin (Kok, De Clercq & Vandewalle, 1980); the nor-derivative (1) is an immediate precursor of (±)-carpesiolin. It has a melting point of 444–445 K.

Table 1. Atomic coordinates ($\times 10^4$; $\times 10^3$ for H atoms) and B_{eq} values (Å²)

The isotropic thermal parameter for the H atoms is 4.8 Å².

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
C(1)	11961 (3)	2900 (3)	8700 (5)	2.9
C(2)	12741 (4)	3577 (4)	8694 (6)	4.0
C(3)	13533 (4)	3102 (4)	8122 (6)	4.1
C(4)	13382 (3)	2146 (4)	8365 (5)	3.5
C(5)	12439 (3)	2000 (3)	8891 (4)	2.8
C(6)	11970 (3)	1197 (4)	8339 (5)	3.0
C(7)	10931 (3)	1254 (4)	8314 (5)	2.9
C(8)	10471 (4)	1606 (4)	9390 (6)	3.7
C(9)	10338 (4)	2596 (4)	9410 (6)	4.2
C(10)	11203 (4)	3149 (4)	9537 (5)	3.8
C(11)	10469 (4)	366 (4)	8138 (6)	3.9
C(12)	9557 (4)	490 (4)	8699 (6)	4.3
C(14)	12656 (4)	1826 (5)	10175 (5)	3.9
C(15)	10926 (5)	4122 (5)	9442 (8)	5.9
O(16)	13934 (3)	1566 (3)	8210 (4)	5.2
O(17)	12213 (2)	1088 (3)	7152 (3)	4.4
C(18)	8886 (3)	33 (3)	8619 (4)	5.6
O(19)	9572 (2)	1193 (3)	9391 (4)	4.7
H(C1)	1168 (3)	286 (3)	789 (5)	
H(C2)	1294 (3)	371 (3)	953 (5)	
H'(C2)	1254 (3)	411 (3)	827 (4)	
H(C3)	1353 (3)	321 (3)	731 (5)	
H'(C3)	1420 (3)	332 (3)	836 (4)	
H(C6)	1212 (3)	65 (3)	875 (4)	
H(C7)	1077 (3)	170 (3)	766 (5)	
H(C8)	1079 (3)	141 (3)	1008 (5)	
H(C9)	1003 (4)	274 (3)	872 (4)	
H'(C9)	990 (4)	271 (3)	1009 (5)	
H(C10)	1143 (3)	305 (3)	1031 (4)	
H(C11)	1079 (3)	-14 (3)	855 (4)	
H'(C11)	1038 (3)	18 (3)	740 (4)	
H(C14)	1296 (3)	235 (4)	1057 (4)	
H'(C14)	1310 (3)	131 (3)	1017 (4)	
H''(C14)	1212 (4)	167 (4)	1056 (5)	
H(C15)	1036 (3)	421 (4)	989 (4)	
H'(C15)	1078 (3)	422 (3)	858 (4)	
H''(C15)	1143 (3)	441 (3)	980 (4)	
H(O17)	1275 (4)	80 (3)	725 (4)	

The intensities of 1929 independent reflections were collected on a Syntex P2₁ diffractometer using graphite-monochromatized Mo K α radiation ($\lambda = 0.7107$ Å) and the ω -scan technique up to $2\theta = 47^\circ$. 862 reflections only were considered as observed [$I \geq 2.5\sigma(I)$] and included in the refinement.

The structure was solved by direct methods using the MULTAN 78 computer system (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). An *E* map showed clearly all non-hydrogen atomic positions of the molecule.

The refinement was carried out by the program SHELX 76 (Sheldrick, 1976) with anisotropic thermal parameters for the non-hydrogen atoms. The positions of the 20 H atoms were determined by a difference Fourier synthesis. They were introduced in the refinement with an overall isotropic temperature factor. At the end of the refinement process, the value of the conventional *R* index was 0.048.

Table 1* gives the final atomic positional parameters, following the numbering shown in (1) instead of the IUPAC numbering given in the title.

Discussion. Fig. 1 is a stereoview of the enantiomer depicted in (1). Bond distances, bond angles and

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34897 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

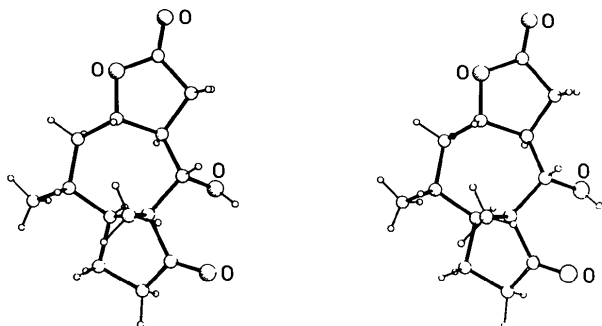


Fig. 1. Stereoscopic view of the molecule.

Table 2. Interatomic distances (Å)

C(2)—C(1)	1.541 (7)	C(8)—C(7)	1.524 (7)
C(5)—C(1)	1.556 (7)	C(11)—C(7)	1.525 (7)
C(10)—C(1)	1.530 (7)	C(9)—C(8)	1.517 (8)
C(3)—C(2)	1.525 (7)	O(19)—C(8)	1.465 (6)
C(4)—C(3)	1.497 (8)	C(10)—C(9)	1.533 (8)
C(5)—C(4)	1.534 (7)	C(15)—C(10)	1.540 (8)
O(16)—C(4)	1.212 (6)	C(12)—C(11)	1.505 (8)
C(6)—C(5)	1.543 (7)	O(18)—C(12)	1.212 (6)
C(14)—C(5)	1.555 (7)	O(19)—C(12)	1.339 (7)
C(7)—C(6)	1.533 (6)	O(17)—H(O17)	0.91 (5)
O(17)—C(6)	1.439 (6)	<C—H>	1.00 (5)

Table 3. Bond angles ($^\circ$)

C(5)—C(1)—C(2)	104.5 (4)	O(17)—C(6)—C(7)	103.6 (4)
C(10)—C(1)—C(2)	112.4 (4)	C(8)—C(7)—C(6)	116.7 (4)
C(10)—C(1)—C(5)	117.1 (4)	C(11)—C(7)—C(6)	113.5 (5)
C(3)—C(2)—C(1)	104.8 (4)	C(11)—C(7)—C(8)	102.9 (4)
C(4)—C(3)—C(2)	105.3 (5)	C(9)—C(8)—C(7)	114.8 (5)
C(5)—C(4)—C(3)	110.5 (5)	O(19)—C(8)—C(7)	104.6 (4)
O(16)—C(4)—C(3)	125.3 (5)	O(19)—C(8)—C(9)	108.0 (4)
O(16)—C(4)—C(5)	124.1 (5)	C(10)—C(9)—C(8)	116.0 (5)
C(4)—C(5)—C(1)	103.0 (4)	C(9)—C(10)—C(1)	114.1 (5)
C(6)—C(5)—C(1)	115.8 (4)	C(15)—C(10)—C(1)	112.6 (5)
C(6)—C(5)—C(4)	110.6 (4)	C(15)—C(10)—C(9)	107.4 (5)
C(14)—C(5)—C(1)	112.4 (4)	C(12)—C(11)—C(7)	103.3 (5)
C(14)—C(5)—C(4)	102.9 (4)	O(18)—C(12)—C(11)	128.5 (6)
C(14)—C(5)—C(6)	111.1 (5)	O(19)—C(12)—C(11)	110.3 (5)
C(7)—C(6)—C(5)	114.2 (4)	O(19)—C(12)—O(18)	121.2 (5)
O(17)—C(6)—C(5)	112.4 (5)	C(12)—O(19)—C(8)	110.9 (4)

Table 4. Endocyclic torsion angles ($^\circ$)

Ring A (cyclopentanone)	
C(5)—C(1)—C(2)—C(3)	−35.3
C(1)—C(2)—C(3)—C(4)	27.6
C(2)—C(3)—C(4)—C(5)	−9.7
C(3)—C(4)—C(5)—C(1)	−11.8
C(4)—C(5)—C(1)—C(2)	28.5
Ring B (seven-membered)	
C(10)—C(1)—C(5)—C(6)	−85.6
C(1)—C(5)—C(6)—C(7)	34.0
C(5)—C(6)—C(7)—C(8)	41.9
C(6)—C(7)—C(8)—C(9)	−89.7
C(7)—C(8)—C(9)—C(10)	69.9
C(8)—C(9)—C(10)—C(1)	−50.0
C(9)—C(10)—C(1)—C(5)	69.2
Ring C (lactone)	
C(8)—C(7)—C(11)—C(12)	−26.4
C(7)—C(11)—C(12)—O(19)	16.9
C(11)—C(12)—O(19)—C(8)	0.0
C(12)—O(19)—C(8)—C(7)	−18.1
O(19)—C(8)—C(7)—C(11)	27.2
< σ >	0.6

torsion angles are given in Tables 2, 3 and 4. The conformations of the three fused rings given by the torsion angles are described in another way with some additional comments in Table 5. The cyclopentanone ring takes *C*₂ (2) symmetry corresponding to the half-chair conformation preferred by the free molecule and its derivatives as well as when in a fused ring (Fuchs, 1978). In the seven-membered ring the *C*₂-symmetrized values of the torsion angles, *i.e.* −50, 70, −88, 38°, are in good agreement with those (−54, 72, −88, 39°) proposed by Hendrickson (1967) for a cycloheptane molecule with equal bond lengths and in a perfect twist-chair conformation.

The lactone ring is in an envelope conformation with C(7) at the flap and all other atoms, including O(18), strictly in a plane.

Table 5. *Ring conformation*

Ring Description	A (cyclo-pentanone) Half-chair	B (seven-membered) Twist-chair	C (lactone) Envelope
Approximate symmetry	C ₂	C ₂	C _s
Pseudo-symmetry element from atom	2	2	<i>m</i>
to the midpoint of bond	C(4)	C(6)	C(7)
Average torsion angle magnitude	C(1)–C(2) 22.8°	C(9)–C(10) 63.1°	C(12)–O(19) 17.6°
Asymmetry parameter ΔC (Duax, Weeks & Rohrer, 1976)	1.6°	5.2°	1.0°

The conformation in the *A* and *B* parts of the tricyclic system differs from that observed in decahydro-4,5-dihydroxy-4a,8-dimethylazuleno[6,5-*b*]furan-2(3*H*)-one (Declercq, Germain, Van Meerssche, Kok, De Clercq & Vandewalle, 1980) due to the change of hybridization from *sp*² to *sp*³ at the C atom in the 5 position [C(4) in our numbering]. In the latter molecule both the *A* and *B* rings possess C_s (*m*) symmetry with pseudo-mirror planes passing through C(5) and C(9).

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References

- DECLERCQ, J. P., GERMAIN, G., VAN MEERSSCHE, M., KOK, P., DE CLERCQ, P. & VANDEWALLE, M. (1980). *Acta Cryst.* **B36**, 190–192.
- DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Stereochemistry*, Vol. 9, edited by N. L. ALLINGER & E. L. ELIEL. New York: John Wiley.
- FUCHS, B. (1978). *Top. Stereochem.* **10**, 27.
- HENDRICKSON, J. B. (1967). *J. Am. Chem. Soc.* **89**, 7036–7043.
- KOK, P., DE CLERCQ, P. & VANDEWALLE, M. (1980). *J. Org. Chem.* In the press.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MARUYAMA, M. & OMURA, S. (1977). *Phytochemistry*, **16**, 782–783.
- SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Forme Stable du Dichloro-3,4 Phénol

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Abstract. C₆H₄Cl₂O exists in two crystalline forms with a monotropic transition. The stable form is tetragonal, *I*4₁/*a*, *a* = *b* = 26.27 (5) Å, *c* = 3.859 (5) Å, *Z* = 16, *D*_c = 1.6 Mg m⁻³. An *R* of 0.06 was obtained for 943 reflexions after least-squares refinement. The molecules are linked by hydrogen bonds in infinite chains; the shortest intermolecular Cl⋯Cl distances of 3.27 and 3.48 Å are significantly shorter than the usually quoted van der Waals distance of 3.6 Å.

Introduction. L'étude du dichloro-3,4 phénol entre dans le cadre d'un travail entrepris au laboratoire sur les structures de phénols substitués et les phénomènes de polymorphisme rencontrés chez certains d'entre eux (Bavoux & Perrin, 1973; Perrin & Michel, 1973;

Bavoux & Thozet, 1973, 1976; Bavoux & Michel, 1974; Perrin & Thozet, 1974; Perrin, Michel & Perrin, 1975; Perrin, Bavoux & Thozet, 1977). Le dichloro-3,4 phénol en surfusion donne, suivant les conditions expérimentales, des cristaux ayant la forme de prismes hexagonaux (*T*_F: 316 K) (phase II), ou des aiguilles (*T*_F: 338 K) (phase I). Alors que le passage de la phase (II) à la phase (I) se fait à n'importe quelle température, la transformation inverse (I → II) n'a jamais été observée; le polymorphisme serait donc de type monotrope. Nous étudions ici la structure de la phase (I), la plus stable. Les cristaux utilisés pour l'étude aux rayons X ont été obtenus par évaporation lente vers 278 K d'une solution saturée dans le pentane; ils sont très hygroscopiques et ont été placés dans des tubes de