

**(±)-Decahydro-4,5-dihydroxy-4a,8-dimethylazuleno[6,5-*b*]furan-2(3*H*)-one,
(3α,4α,4aβ,5α,7α,8α,9aβ)**

BY J. P. DECLERCQ, G. GERMAIN AND M. VAN MEERSSCHE

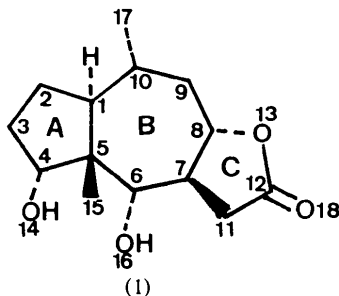
*Laboratoire de Chimie Physique et de Cristallographie de l'Université de Louvain, 1 place L. Pasteur,
B-1348 Louvain-la-Neuve, Belgium*

AND P. KOK, P. DE CLERCQ AND M. VANDEWALLE

*State University of Ghent, Department of Organic Chemistry, Laboratory of Organic Synthesis, Krijgslaan,
271 (S.4), B-9000 Ghent, Belgium*

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Abstract. C₁₄H₂₂O₄, monoclinic, *P*2₁/*a*, *a* = 10.666 (3), *b* = 14.593 (5), *c* = 9.423 (5) Å, β = 116.10 (3)°, *V* = 1317 (1) Å³, *D*_x = 1.28 Mg m⁻³ for *Z* = 4. The structure has been solved by direct methods (*MULTAN*) and refined to a final *R* value of 0.046 for 1365 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(4)*R*, C(5)*S*, C(6)*S*, C(7)*S*, C(8)*S* and C(10)*R*. Each ring of the tricyclic fragment exhibits approximate *m* symmetry with pseudo mirror planes passing through C(5), C(9) and C(7) for the *A*, *B* and *C* rings respectively. Hydrogen bonds, both intra- and intermolecular, are observed.

Introduction. In connection with a general programme of studies on synthetic hydroazulenic sesquiterpene lactones (Yoshioka, Mabry & Timmermann, 1973), we performed a stereoselective synthesis of the title compound (1), a valuable intermediate in our work (Kok, De Clercq, Vandewalle, Declercq, Germain & Van Meerssche, 1979). This lactone possesses all the characteristic structural features of the pseudo-guaianolides (Romo & Romo de Vivar, 1967) but lacks a C atom at C(11) [throughout this paper, instead of the IUPAC numbering given in the title, the numbering used is as shown in (1)].

Table 1. Atomic coordinates ($\times 10^4$; for H $\times 10^3$)

The isotropic thermal parameter for the H atoms is 5.6 Å².

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
C(1)	6479 (4)	5351 (3)	7757 (6)	3.1
C(2)	5807 (6)	5579 (4)	8863 (6)	4.3
C(3)	5743 (7)	6624 (4)	8923 (8)	5.3
C(4)	6424 (5)	6987 (4)	7920 (6)	4.0
C(5)	7416 (5)	6210 (3)	7936 (5)	3.2
C(6)	7974 (5)	6340 (3)	6667 (6)	3.4
C(7)	7550 (5)	5599 (3)	5412 (5)	3.1
C(8)	8213 (5)	4678 (3)	6099 (6)	3.3
C(9)	7393 (5)	4048 (3)	6640 (6)	3.8
C(10)	7155 (5)	4392 (3)	8028 (6)	3.4
C(11)	8038 (6)	5762 (4)	4146 (6)	4.2
C(12)	8294 (5)	4823 (4)	3695 (6)	4.3
O(13)	8398 (4)	4221 (2)	4817 (4)	4.5
O(14)	5330 (3)	7142 (2)	6356 (4)	4.4
C(15)	8683 (6)	6221 (4)	9575 (7)	4.6
O(16)	7595 (4)	7215 (2)	5919 (5)	5.7
C(17)	6273 (7)	3670 (4)	8360 (8)	5.1
O(18)	8439 (4)	4584 (3)	2549 (5)	6.0
H(C1)	575 (5)	536 (3)	667 (5)	
H(C2)	489 (5)	531 (3)	848 (5)	
H'(C2)	645 (5)	534 (3)	989 (6)	
H(C3)	487 (5)	689 (3)	857 (5)	
H''(C3)	622 (5)	684 (3)	999 (6)	
H(C4)	695 (5)	755 (3)	836 (5)	
H(C6)	900 (5)	631 (3)	723 (5)	
H(C7)	655 (5)	555 (3)	493 (5)	
H(C8)	920 (5)	476 (3)	695 (5)	
H(C9)	651 (5)	397 (3)	573 (5)	
H'(C9)	791 (4)	346 (3)	695 (5)	
H(C10)	801 (5)	440 (3)	894 (5)	
H(C11)	747 (5)	610 (3)	327 (6)	
H'(C11)	891 (5)	609 (3)	459 (5)	
H(O14)	584 (5)	735 (3)	568 (5)	
H(C15)	845 (5)	607 (3)	1041 (6)	
H'(C15)	916 (5)	680 (3)	980 (5)	
H''(C15)	941 (5)	574 (3)	958 (5)	
H(O16)	859 (5)	754 (3)	605 (5)	
H(C17)	531 (5)	366 (3)	750 (5)	
H'(C17)	620 (5)	380 (3)	937 (5)	
H''(C17)	665 (5)	305 (3)	839 (5)	

As such it is a potential precursor of helenanolides [α stereochemistry at C(10)], possessing a *trans*-fused five-membered lactone ring at C(7)–C(8) and α stereochemistry at C(8). The tricyclic fragment, with the relative stereochemistry at the ring fusions and at C(10) as shown in (1), is found in several naturally occurring pseudogaianolides (Yoshioka, Mabry & Timmermann, 1973).

In order to establish unequivocally its relative stereochemistry, a single-crystal X-ray diffraction analysis of (1) was undertaken. The compound was crystallized from chloroform–hexane (m.p. 460–461 K).

The intensities of 1950 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 $2\theta = 47^\circ$. 1365 reflections only were considered as observed [$I > 2.5\sigma(I)$] 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 22 H atoms were determined by a difference Fourier synthesis. They were introduced in the refinement with isotropic thermal parameters. At the end of the refinement process, the value of the conventional *R* index was 0.046.

Table 1* gives the final atomic positional parameters.

Discussion. The crystal is a racemate. Fig. 1 is a stereoview of the enantiomer mirror image of (1). Bond distances, bond angles and torsion angles are given in Tables 2, 3 and 4. The Newman projections of Fig. 2 show how the three *A*, *B* and *C* rings are fused along the C(5)–C(1) and C(7)–C(8) bonds.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34645 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

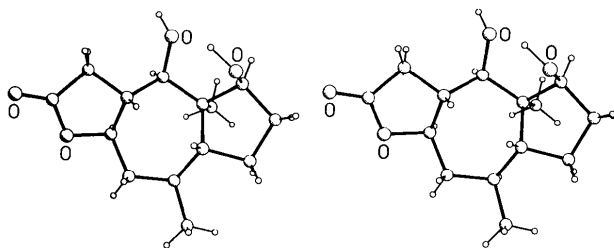


Fig. 1. Stereoview of the molecular configuration and conformation.

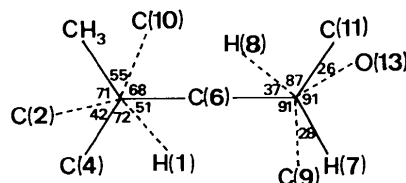


Fig. 2. Newman projections along the C(5)–C(1) bond (left) and the C(7)–C(8) bond (right).

Table 2. Interatomic distances (Å)

C(1)–C(2)	1.539 (4)	C(7)–C(8)	1.523 (4)
C(1)–C(5)	1.566 (4)	C(7)–C(11)	1.515 (4)
C(1)–C(10)	1.543 (4)	C(8)–C(9)	1.504 (4)
C(2)–C(3)	1.528 (5)	C(8)–O(13)	1.467 (3)
C(3)–C(4)	1.518 (4)	C(9)–C(10)	1.524 (4)
C(4)–C(5)	1.546 (4)	C(10)–C(17)	1.534 (4)
C(4)–O(14)	1.439 (3)	C(11)–C(12)	1.495 (4)
C(5)–C(6)	1.564 (4)	C(12)–O(13)	1.342 (4)
C(5)–C(15)	1.541 (4)	C(12)–O(18)	1.207 (3)
C(6)–C(7)	1.518 (4)	<C–H>	0.97 (3)
C(6)–O(16)	1.429 (3)	<O–H>	1.08 (3)

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

C(2)–C(1)–C(5)	102.7 (2)	C(7)–C(6)–O(16)	109.3 (2)
C(2)–C(1)–C(10)	114.0 (2)	C(6)–C(7)–C(8)	112.0 (2)
C(5)–C(1)–C(10)	118.6 (2)	C(6)–C(7)–C(11)	114.4 (2)
C(1)–C(2)–C(3)	106.4 (2)	C(8)–C(7)–C(11)	102.6 (2)
C(2)–C(3)–C(4)	106.5 (2)	C(7)–C(8)–C(9)	116.9 (2)
C(3)–C(4)–C(5)	104.5 (2)	C(7)–C(8)–O(13)	104.9 (2)
C(3)–C(4)–O(14)	107.4 (3)	C(9)–C(8)–O(13)	108.0 (2)
C(5)–C(4)–O(14)	111.6 (2)	C(8)–C(9)–C(10)	115.5 (2)
C(1)–C(5)–C(4)	100.6 (2)	C(1)–C(10)–C(9)	113.6 (2)
C(1)–C(5)–C(6)	117.0 (2)	C(1)–C(10)–C(17)	111.9 (2)
C(4)–C(5)–C(6)	113.1 (2)	C(9)–C(10)–C(17)	107.2 (3)
C(1)–C(5)–C(15)	110.6 (2)	C(7)–C(11)–C(12)	104.4 (2)
C(4)–C(5)–C(15)	107.3 (2)	C(11)–C(12)–O(13)	109.8 (2)
C(6)–C(5)–C(15)	107.7 (2)	C(11)–C(12)–O(18)	129.1 (3)
C(5)–C(6)–C(7)	115.3 (2)	O(13)–C(12)–O(18)	121.1 (3)
C(5)–C(6)–O(16)	111.4 (2)	C(8)–O(13)–C(12)	110.9 (2)

The stereochemistry of the molecule is as follows: C(1)– α H is *trans* to C(5)– β CH₃; C(7)– α H is *trans* to C(8)– β H; C(4)– α OH is *trans* to C(5)– β CH₃. Thus the *AB* and *BC* ring junctions are both *trans*. The H atoms attached to C(6) and C(10) are clearly on the β side of the molecule but O(16)H and C(17)H₃, bonded respectively to C(6) and C(10), are in positions best described as equatorial.

The conformations of the three fused rings given by the torsion angles in column (a) of Table 4 are described in another way with additional comments in Table 5. The torsion angles of the cyclopentane ring indicate a puckered envelope conformation like that of cyclopentane itself. For the latter molecule the puckering amplitude observed by electron diffraction (0.438 Å) leads to torsion angles of 0, ± 25 , and $\mp 40^\circ$ (Adams, Geise & Bartell, 1970).

Table 4. *Endocyclic torsion angles* (°)

	<i>a</i>	<i>b</i>	<i>c</i>
Ring <i>A</i> (cyclopentane)			
C(5)–C(1)–C(2)–C(3)	27.8	24.7	26.9
C(1)–C(2)–C(3)–C(4)	–2.3	3.4	–4.1
C(2)–C(3)–C(4)–C(5)	–24.7	–28.1	–23.9
C(3)–C(4)–C(5)–C(1)	41.2	44.3	40.4
C(4)–C(5)–C(1)–C(2)	–42.0	–40.5	–40.1
Ring <i>B</i> (seven-membered)			
C(10)–C(1)–C(5)–C(6)	68.4	69.4	64.0
C(1)–C(5)–C(6)–C(7)	–0.9	4.4	4.4
C(5)–C(6)–C(7)–C(8)	–66.9	–66.5	–61.9
C(6)–C(7)–C(8)–C(9)	91.4	90.2	76.0
C(7)–C(8)–C(9)–C(10)	–64.8	–66.1	–56.5
C(8)–C(9)–C(10)–C(1)	54.2	58.6	62.9
C(9)–C(10)–C(1)–C(5)	–77.5	–90.5	–86.1
Ring <i>C</i> (lactone)			
C(8)–C(7)–C(11)–C(12)	25.9	30.0	25.7
C(7)–C(11)–C(12)–O(13)	–17.4	–22.8	–18.5
C(11)–C(12)–O(13)–C(8)	0.0	7.7	2.3
C(12)–O(13)–C(8)–C(7)	16.5	10.8	14.6
O(13)–C(8)–C(7)–C(11)	–25.8	–24.8	–24.5
⟨σ⟩	0.3	3.0	3.0

(a) Our determination. (b), (c) The two symmetry independent molecules of 11,13-dibromopulchellin.

In the seven-membered ring the C_s (m) symmetrized absolute values of the torsion angles, *i.e.* 0, 67, 84, 59°, are in good agreement with those (0, 66, 84, 64°) proposed by Hendrickson (1967) for a cycloheptane molecule with equal bond lengths in a perfect chair conformation. In this ideal molecule the bond angles vary from 114 to 118° with an average of 116°. We observe the same average but a larger dispersion, from 112 to 119°.

The flatter lactone ring induces a more eclipsed conformation around the C(7)–C(8) bond (Fig. 2) and is probably responsible for high asymmetry at that level in the *B* ring.

The tricyclic fragment is in a very similar conformation, within one e.s.d., to that found by Sekita, Inayama & Iitaka (1971) in 11,13-dibromopulchellin, a pseudoguaianolide with an identical fused-ring system. For the 17 endocyclic torsion angles the r.m.s. difference Δ between the two tricyclic systems under comparison is: $\Delta(a - b/c) = 4.5^\circ$ (in 11,13-dibromopulchellin we take the mean angles of the two symmetry-independent molecules, columns *b* and *c* of Table 4). This value is lower than the r.m.s. difference between the two molecules (*b* vs *c*) in the pulchellin derivative: $\Delta(b - c) = 5.4^\circ$.

The molecules are linked together by hydrogen bonds between the O(14) and O(16) hydroxyl O atoms. O(14)H is a donor in an intramolecular bond with O(16) as acceptor, while O(16)H is a donor in an intermolecular bond with the O(14) atom of another molecule as the acceptor.

The hydrogen-bond dimensions are given in Table 6.

Table 5. *Ring conformation*

Ring	<i>A</i> (cyclopentane)	<i>B</i> (seven-membered)	<i>C</i> (lactone)
Description	Envelope	Deformed chair	Envelope
Approximate symmetry	C_s	C_s	C_s
Pseudo-symmetry element	m	m	m
from atom to the midpoint of bond	C(5) C(2)–C(3)	C(9) C(5)–C(6)	C(7) C(12)–O(13)
Average torsion angle magnitude	27.6°	60.6°	17.1°
Asymmetry parameter ΔC_s (Duax, Weeks & Rohrer, 1976)	2.5°	9.4°	0.8°

Table 6. *Hydrogen-bond dimensions*

Intramolecular		Intermolecular	
O(14)···O(16)	2.63 (1) Å	O(16)···O(14)	2.92 (1) Å
O(14)–H	1.05 (3)	O(16)–H	1.12 (3)
H···O(16)	1.79 (3)	H···O(14)	1.81 (3)
O(14)–H···O(16)	134 (3)°	O(16)–H···O(14)	177 (5)°

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