

Fig. 1. The molecular structure and atom numbering.

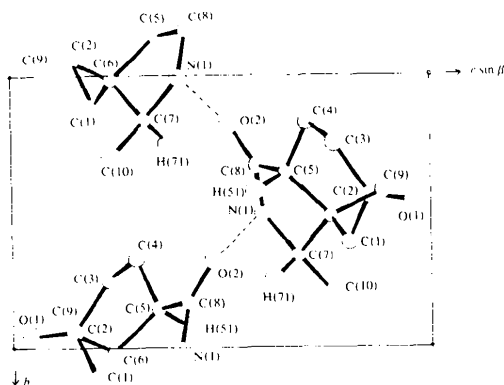


Fig. 2. The unit-cell contents projected down a. Hydrogen bonds are shown by broken lines.

molecule has a chair conformation in the six-membered ring *trans*-fused to a five-membered lactam. The structure also indicates that there is considerable steric interaction between the two *cis*-methyl groups, C(9)···C(10) [2.94 (3) Å]. The lactam ring reveals the expected shortening of the N(1)–C(8) amide bond

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## Thieleanine

BY VOLKER ZABEL AND WILLIAM H. WATSON\*

*FASTBIOS Laboratory, Department of Chemistry, Texas Christian University, Fort Worth, TX 76129, USA*

AND SANDRA ALVARADO, JOSE F. CICCIO AND JOSE CALZADA

*Escuela de Química, Universidad de Costa Rica, San José, Costa Rica*

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**Abstract.** C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>, *M<sub>r</sub>* = 246.13, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 6.843 (2), *b* = 28.219 (10), *c* = 6.789 (3) Å, *V* = 1311.0 (8) Å<sup>3</sup>, *Z* = 4, *d<sub>c</sub>* = 1.247 Mg m<sup>-3</sup>, λ(Cu *K*α) = 1.54178 Å. Full-matrix least-squares

refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1324 reflexions led to a final *R* of 0.055. Thieleanine is a guaianolide-type sesquiterpene lactone composed of fused five- and seven-membered rings and a *trans*-fused α,β-unsaturated γ-lactone. The five- and seven-membered rings occur in flattened

Table 3. Bond angles (°) and their *e.s.d.*'s

C(2)–C(1)–C(6)	108.7 (22)	C(5)–C(6)–C(7)	100.0 (9)
C(1)–C(2)–C(3)	118.2 (9)	C(5)–C(6)–C(9)	113.0 (21)
C(1)–C(2)–O(1)	120.9 (24)	C(7)–C(6)–C(9)	110.1 (8)
C(3)–C(2)–O(1)	120.8 (24)	C(6)–C(7)–C(10)	118.0 (7)
C(2)–C(3)–C(4)	115.1 (13)	C(6)–C(7)–N(1)	100.9 (21)
C(3)–C(4)–C(5)	108.3 (21)	C(10)–C(7)–N(1)	111.8 (8)
C(4)–C(5)–C(6)	113.2 (9)	C(5)–C(8)–N(1)	106.8 (19)
C(4)–C(5)–C(8)	121.6 (22)	C(5)–C(8)–O(2)	125.7 (21)
C(6)–C(5)–C(8)	102.7 (12)	N(1)–C(8)–O(2)	127.5 (10)
C(1)–C(6)–C(5)	107.6 (9)	C(7)–N(1)–C(8)	113.6 (10)
C(1)–C(6)–C(7)	116.1 (21)		
C(1)–C(6)–C(9)	109.8 (6)		

[1.32 (3) Å] compared with the normal N(1)–C(7) single-bond [1.49 (3) Å]. All other bonds and angles are as expected.

We thank Dr D. R. Russell for assistance in the data collection and for use of the diffractometer at Leicester University.

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\* To whom correspondence should be addressed.

envelope and twist-chair conformations while the  $\alpha,\beta$ -unsaturated  $\gamma$ -lactone exhibits a flattened half-chair conformation. The molecules are held together by van der Waals interactions.

**Introduction.** *Decachaeta* is a small genus of 16 known species and belongs to the family Compositae and the tribe Eupatorieae. The genus is primarily restricted to Mexico and Central America. The relationships between members of the genus and the relationships with other genera can be assessed through phytochemical investigations. *Decachaeta thieleana* (Klatt) R. M. King & H. Robinson was collected in Turrucare, Alajuela, Costa Rica. The new sesquiterpene thieleanine was isolated (Alvarado, Ciccio, Calzada, Zabel & Watson, 1979), and the structure established by X-ray diffraction techniques.

A crystal of dimensions 0.4 × 0.1 × 0.6 mm was used to collect intensity data on a Syntex P2<sub>1</sub> diffractometer system by the  $\theta:2\theta$  scanning technique

Table 1. Atomic positional parameters ( $\times 10^4$ , for H  $\times 10^3$ ) and isotropic thermal parameters

	x	y	z	$U_{eq}/U(\text{\AA}^2)^*$
C(1)	5769 (3)	787 (1)	6559 (3)	3.8
C(2)	4231 (4)	510 (1)	6111 (4)	4.8
C(3)	2861 (4)	501 (1)	7760 (4)	5.0
O(3)	1237 (3)	320 (1)	7746 (5)	7.8
C(4)	3792 (4)	744 (1)	9496 (4)	4.9
C(5)	5554 (3)	1012 (1)	8585 (3)	3.7
C(6)	5285 (4)	1552 (1)	8528 (3)	4.1
C(7)	6700 (3)	1810 (1)	7162 (3)	4.0
C(8)	6280 (4)	1696 (1)	4988 (3)	4.1
O(8)	6589 (3)	2136 (1)	3904 (3)	5.4
C(9)	7532 (4)	1311 (1)	4112 (4)	5.2
C(10)	7573 (4)	857 (1)	5351 (4)	4.5
C(11)	6487 (4)	2341 (1)	7194 (4)	4.9
C(12)	6559 (4)	2510 (1)	5133 (5)	5.2
O(12)	6592 (4)	2910 (1)	4530 (4)	7.0
C(13)	6215 (7)	2632 (1)	8684 (6)	6.9
C(14)	8018 (6)	428 (1)	4066 (5)	6.5
C(15)	2353 (8)	1011 (1)	10730 (8)	8.4
H(2)	404 (5)	30 (1)	491 (6)	6.0
H(4)	448 (4)	46 (1)	1040 (4)	4.0
H(5)	680 (5)	97 (1)	927 (5)	4.6
H(6a)	406 (5)	165 (1)	808 (5)	4.5
H(6b)	543 (6)	165 (1)	979 (6)	6.1
H(7)	812 (5)	171 (1)	729 (5)	5.3
H(8)	487 (5)	161 (1)	472 (5)	4.3
H(9a)	885 (8)	149 (1)	426 (8)	8.5
H(9b)	658 (6)	113 (1)	279 (6)	7.5
H(10)	859 (6)	93 (1)	612 (5)	5.1
H(13a)	655 (11)	292 (3)	917 (11)	12.2
H(13b)	646 (9)	253 (2)	989 (3)	9.7
H(14a)	703 (6)	45 (3)	329 (9)	17.0
H(14b)	771 (8)	15 (2)	444 (8)	9.5
H(14c)	926 (10)	50 (2)	332 (2)	11.2
H(15a)	169 (5)	127 (1)	997 (5)	5.1
H(15b)	279 (10)	117 (2)	1157 (1)	10.5
H(15c)	125 (9)	78 (2)	1095 (8)	9.0

$$* U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}.$$

using a variable scan speed and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 reflexions whose angles were measured by a centering routine associated with the Syntex diffractometer. Systematic absences were consistent with space group  $P2_12_12_1$ . A periodically monitored reflexion showed no significant change in intensity. Of the 1393 independent reflexions measured, 60 had intensities less than  $2\sigma(I)$  and were not used in the refinement. Nine additional reflexions showed significant secondary extinction and were dropped from the final refinement. Lorentz and polarization corrections were applied, but no absorption corrections were made.

The direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) was used to calculate phases for the 300  $|E|$  values greater than 1.22. The phase set with the largest combined figure of merit was selected, and the  $E$  map calculated with these phases revealed the positions of 18 atoms. After several cycles of full-matrix least-squares refinement, H atoms were located by a difference Fourier calculation. Least-squares refinement was terminated at a final  $R$  of 0.055 where  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . The function minimized in the refinement was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma(I)$  was determined from counting statistics. H atom thermal parameters were refined isotropically.

A final difference map showed no peaks larger than  $0.25 e \text{\AA}^{-3}$  and during the final cycle of refinement no shift in heavy-atom positional parameters was greater than  $0.5\sigma$ . Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Atomic positional parameters are given in Table 1.\*

**Discussion.** Fig. 1 is an *ORTEP* drawing (Johnson, 1965) of thieleanine. Bond lengths, valence angles and torsion angles are shown in Figs. 2 and 3.

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35458 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

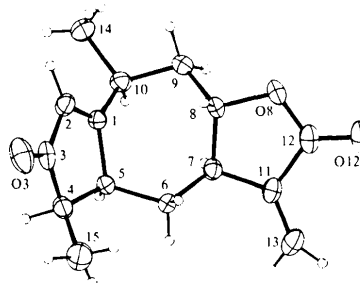


Fig. 1. *ORTEP* drawing of thieleanine. Thermal ellipsoids are shown at the 35% probability level. H atoms are represented by circles of arbitrary size.

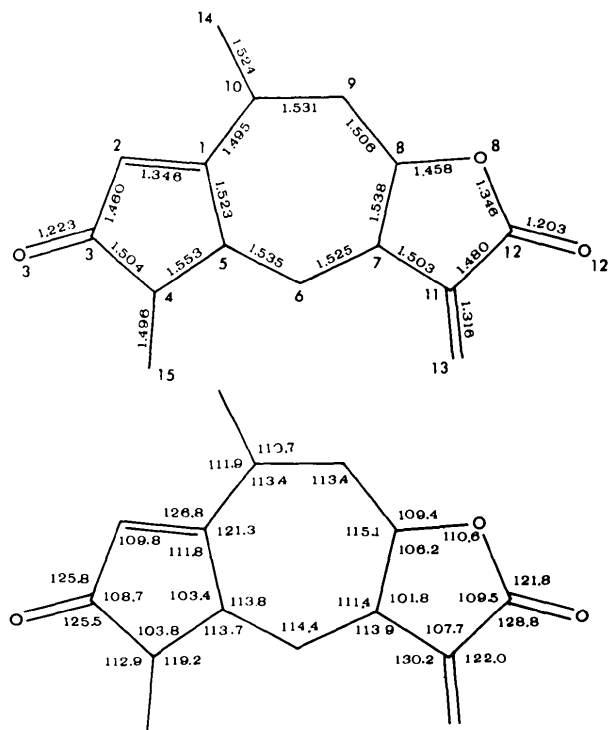


Fig. 2. Interatomic distances (Å) and valence angles (°) for thieleanine. Standard deviations in distances average 0.004 Å while those for angles average 0.2°.

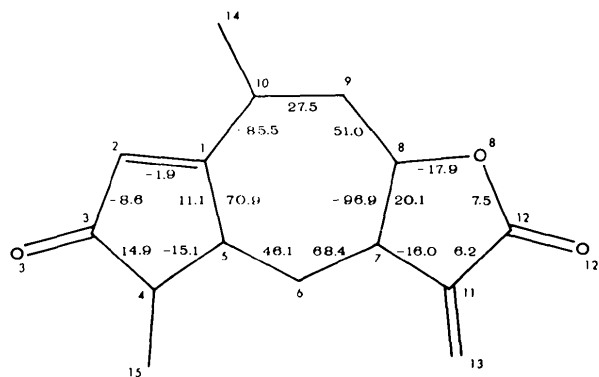


Fig. 3. Torsion angles (°) for thieleanine. Standard deviations average 0.3°.

Unlike the ten-membered rings of the germacranolide-type sesquiterpene lactones, the seven-membered rings of the guaianolides and pseudoguaianolides exhibit a variety of conformations. This is in part related to the existence of both *cis* and *trans* ring fusions and to the position of the double bond in the five-membered carbocyclic ring. However, autumnolide (Von Dreele, Pettit, Cragg & Ode, 1975) and bromohelenalin (Mazhar-ul-Haque & Caughlan, 1969), which differ only in the replacement of the double bond by an epoxide and the substitution of a Br atom, exhibit

significantly different conformations. The seven-membered ring of autumnolide is described as a symmetric boat while that of bromohelenalin most closely approximates a deformed chair. Intermolecular packing interactions and, in particular, hydrogen bonding are frequently the most important factors in determining ring conformations.

Thieleanine contains no hydroxyl function and van der Waals interactions are the only type of intermolecular contacts. The seven-membered ring adopts a twist-chair conformation. The sesquiterpene 4,11-dihydroxy-10-norguaian-10-one (Taira, Watson, Silva & Sammes, 1976) contains no  $\gamma$ -lactone ring and the carbocyclic five-membered ring contains no double bond; however, the C(10) methyl group has been replaced by a keto function which serves the same conformational role as the C(1)–C(2) double bond. The conformation of the seven-membered ring is similar to that of thieleanine. Since the substituents on these molecules differ significantly, the twist-chair conformation may represent a favored conformation for seven-membered rings containing one  $sp^2$ -hybridized C atom. There are no significant intramolecular interactions across the seven-membered ring.

The  $\gamma$ -lactone ring system is *trans*-fused to the seven-membered ring and exhibits a flattened half-chair conformation. The exocyclic double bond and the carbonyl group form a planar system, C(13)C(11)–C(12)O(12) = 8.2°. The C( $sp^2$ )–C( $sp^2$ ) bond between C(11) and C(12) is 1.480 (5) Å, which is normal for exocyclic  $\alpha,\beta$ -unsaturated carbonyl functions.

The five-membered carbocyclic ring adopts a flattened envelope conformation with C(4) as the flap. The envelope is flattened by the planar  $\alpha,\beta$ -unsaturated ketone moiety involving the endocyclic double bond, C(1)C(2)C(3)O(3) = 172.5°. The C( $sp^2$ )–C( $sp^2$ ) single bond between C(2)–C(3) is reduced to 1.460 (4) Å. The C(1)–C(2) and C(3)–O(3) distances of 1.346 (3) and 1.223 (3) Å are significantly longer than the C(13)–C(11) and C(12)–O(12) distances of 1.316 (5) and 1.202 (3) Å. This is consistent with an increased delocalization in the ring system with the endocyclic double bond.

Biogenetic considerations lead to the prediction that H(5) and H(7) exhibit the  $\alpha$  configuration, *i.e.* (5*S*,7*R*) (Fischer, Olivier & Fischer, 1979). The enantiomer consistent with the above assignment was used in the least-squares refinement and is shown in Fig. 1.

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### (3-Chloro-2-hydroxy-5-nitrophenyl)(2'-chlorophenyl)iodonium Hydroxide, Inner Salt\*

BY CAMDEN R. HUBBARD, VICKY L. HIMES† AND ALAN D. MIGHELL

*National Measurement Laboratory, National Bureau of Standards, Washington, DC 20234, USA*

AND SAMUEL W. PAGE

*Bureau of Foods, Food and Drug Administration, Washington, DC 20204, USA*

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**Abstract.**  $C_{12}H_6Cl_2INO_3$ ,  $M_r = 410.00$ , monoclinic,  $P2_1/n$ ,  $a = 15.928$  (9),  $b = 4.623$  (2),  $c = 18.271$  (6) Å,  $\beta = 105.58$  (2)°,  $Z = 4$ ,  $D_x = 2.101$ ,  $D_m = 2.11$  Mg m<sup>-3</sup>;  $R$  on  $F^2 = 0.055$  (2302 unique reflections). The molecule exists as a zwitterion with an intramolecular  $I^+ \cdots O^-$  distance of 2.755 (4) Å. The I–C bond distances were found to be 2.106 (6) and 2.105 (5) Å, with a C–I–C angle of 98.4 (2)°. Intermolecular ionic attraction between  $I^+$  and  $O^-$  causes the formation of infinite chains along the  $y$  axis of the cell.

**Introduction.** The title compound is an intermediate in the preparation of *o*-iododiphenyl ethers. The preparation, NMR data and other chemical information for  $C_{12}H_6Cl_2INO_3$  have been reported by Page, Mazzola, Mighell, Himes & Hubbard (1979). Transparent yellow needle-shaped crystals suitable for X-ray analysis were prepared by recrystallization from formic acid. Analysis: calculated for  $C_{12}H_6Cl_2INO_3$ : C 35.16, H 1.48, N 3.42, Cl 17.30, I 30.95%; composition found: C 35.63, H 1.48, N 3.65, Cl 17.59, I 31.30%. The density was measured by the flotation method using a mixture of halogenated organic liquids. A crystal of dimensions 0.15 × 0.04 × 0.06 mm was

mounted on a four-circle diffractometer (graphite-monochromated Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å). Cell dimensions were determined by a least-squares refinement of 15 reflections with  $2\theta$  values ranging between 17 and 32°. The monoclinic symmetry was verified by reduction procedures (*International Tables for X-ray Crystallography*, 1969) and the space group  $P2_1/n$ , which was initially assigned by analysis of precession photographs, was confirmed on the diffractometer by checking 310 systematically absent positions.

Diffraction intensities were measured in the bisecting mode with  $4^\circ \leq 2\theta \leq 50^\circ$ . The peaks were scanned over a  $2\theta$  range of ( $K\alpha_1 - 1.0^\circ$ ) to ( $K\alpha_2 + 1.0^\circ$ ) using variable scan rates of 1.0 to 29.3° min<sup>-1</sup> depending on the intensity of the preliminary count. Background counts were taken at each end of the scan with a ratio of total background time to scan time of 1.0. Three standard reflections, which were measured periodically, showed a gradual loss of intensity of approximately 9% over the course of data collection. The intensity data were corrected for the drop in the standard reflections. The estimated standard deviation in intensity,  $\sigma(I)$ , was calculated from  $\sigma^2(I) = TC + (0.016TC)^2$ , where TC is the total observed counts and the constant was derived from a statistical analysis of the intensity distributions of the three standard reflections. Corrections were applied for Lorentz and polarization factors and for absorption ( $\mu = 2.860$  mm<sup>-1</sup>). Of the 2696 reflections measured, there were 2302 unique reflections with 367 measured more than once. One reflection was either

\* IUPAC name: 6-chloro-2-(2-chlorophenyl)iodonio-4-nitro-1-phenolate.

† Food and Drug Administration – NBS summer student; currently a student at the Catholic University of America, Washington, DC 20064, and a participant in the NBS Graduate Cooperative Education Program.