

SHORT STRUCTURAL PAPERS

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Chloromycorrhizin A

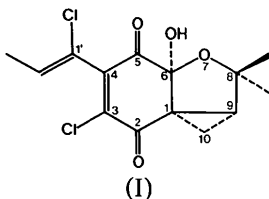
BY CLAES STÅLHANDSKE, CHRISTER SVENSSON AND CHRISTER SÄRNSTRAND

Inorganic Chemistry 2, Chemical Center, University of Lund, PO Box 740, S-220 07 Lund 7, Sweden

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Abstract. $C_{14}H_{14}O_4Cl_2$, orthorhombic, space group $P2_12_12_1$, $a = 8.250$ (1), $b = 12.652$ (4), $c = 13.629$ (3) Å, $V = 1422.7$ Å³, $Z = 4$, F.W. 317.18, $D_x = 1.481$ g cm⁻³, $\mu(\text{Mo } K\alpha_1) = 4.1$, $\mu(\text{Cu } K\alpha_1) = 40.5$ cm⁻¹. The structure and absolute configuration have been determined for the title compound, which is a novel fungicide isolated from a mycorrhizal fungus of *Monotropa hypopitys* L.

Introduction. The compound (1*S*,6*S*,9*R*)-3-chloro-6-hydroxy-8,8-dimethyl-4-(1-chloroprop-1-ene)tricyclo[4.4.0.0^{1,9}]-7-oxadec-3-ene-2,5-dione (I) was isolated from a mycorrhizal fungus of *Monotropa hypopitys* L. and chemically investigated by Trofast & Wickberg (1977).



It was given the trivial name chloromycorrhizin A and is a strong antagonist of the root-rot fungus *Fomes annosus* (Fr.) Cke. An X-ray investigation was undertaken to elucidate the molecular structure and absolute configuration.

The crystal used had been recrystallized from a mixture of chloroform and cyclohexane. It was pale yellow, stout, prismatic a with dimensions $0.21 \times 0.15 \times 0.16$ mm. The cell dimensions were determined from 45 reflexions with θ between 5 and 18°, $\lambda(\text{Mo } K\alpha_1) = 0.70930$ Å.

The intensities were collected on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation, and the ω - 2θ scan technique with variable scan speeds and a maximum time spent on each reflexion of 5 min. 1278 of the 1894 reflexions with $\theta < 27.5^\circ$ in one octant of reciprocal space had $I > 2.5\sigma(I)$. These observed data were

corrected for Lorentz–polarization and absorption effects.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). The H atoms were located from difference maps. A refinement of the non-

Table 1. Atomic parameters

(a) Non-hydrogen atoms. Atomic coordinates ($\times 10^4$) with e.s.d.'s in parentheses

	x	y	z
Cl(1)	6302 (1)	4922 (1)	1035 (1)
Cl(2)	1936 (1)	4127 (1)	-873 (1)
O(1)	5630 (3)	6788 (2)	2202 (2)
O(2)	290 (3)	5594 (2)	707 (2)
O(3)	2334 (3)	7294 (2)	-368 (2)
O(4)	673 (3)	7756 (2)	885 (2)
C(1)	2947 (8)	2172 (3)	368 (4)
C(2)	3236 (5)	3269 (3)	735 (3)
C(3)	2870 (4)	4151 (3)	284 (2)
C(4)	3114 (4)	5233 (2)	669 (2)
C(5)	4503 (4)	5604 (2)	1050 (2)
C(6)	4615 (4)	6634 (3)	1582 (2)
C(7)	3346 (4)	7405 (3)	1331 (2)
C(8)	2028 (4)	7126 (2)	627 (2)
C(9)	1651 (4)	5941 (3)	687 (2)
C(10)	3701 (6)	8588 (3)	1417 (3)
C(11)	2574 (5)	8084 (3)	2125 (3)
C(12)	774 (5)	8109 (3)	1904 (3)
C(13)	-118 (6)	7349 (5)	2559 (3)
C(14)	49 (8)	9208 (5)	1931 (5)

(b) Hydrogen atoms. Atomic coordinates ($\times 10^3$) and thermal parameters with e.s.d.'s in parentheses

	x	y	z	B
H(1A)	374 (7)	197 (5)	-8 (5)	7 (2)
H(1B)	295 (7)	173 (4)	82 (4)	6 (1)
H(1C)	221 (11)	223 (7)	-4 (7)	11 (3)
H(2)	362 (4)	330 (3)	136 (3)	3 (1)
H(10A)	465 (5)	877 (3)	162 (3)	2 (1)
H(10B)	328 (5)	909 (3)	90 (3)	3 (1)
H(11)	295 (4)	802 (3)	270 (2)	2 (1)
H(13A)	-8 (6)	768 (4)	321 (4)	6 (1)
H(13B)	-117 (7)	721 (4)	239 (4)	6 (1)
H(13C)	46 (7)	658 (4)	258 (3)	5 (1)
H(14A)	66 (7)	967 (4)	148 (4)	6 (1)
H(14B)	7 (8)	951 (4)	256 (4)	6 (1)
H(14C)	-112 (8)	921 (4)	185 (5)	7 (2)
H(O3)	304 (5)	748 (3)	-43 (3)	2 (1)

hydrogen atoms with anisotropic temperature factors and the form factors of Doyle & Turner (1968), and the H atoms with isotropic temperature factors and the form factors of Stewart, Davidson & Simpson (1965), converged to $R = 0.030$, $R_w = 0.038$ and $S = 1.12$. The function minimized was $\sum w_i(|F_o| - |F_c|)^2$, with $w_i^{-1} = \sigma^2(F_o) + 0.027 |F_o|^2$. The final parameters are given in Table 1.*

In order to determine the absolute configuration another set of intensities was collected with the same crystal and the same experimental conditions but with Cu K α radiation. The full sphere of data was sampled

* A list of structure factors and anisotropic thermal parameters has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32249 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Comparison of ratios between pairs of Friedel reflexions

<i>hkl</i>	Observed values				Calculated values
	$ F(hkl) $ $ F(\bar{h}\bar{k}\bar{l}) $	$ F(h\bar{k}l) $ $ F(\bar{h}kl) $	$ F(\bar{h}kl) $ $ F(h\bar{k}l) $	$ F(\bar{h}\bar{k}\bar{l}) $ $ F(hkl) $	$ F(hkl) $ $ F(\bar{h}\bar{k}\bar{l}) $
125	1.29	1.19	1.13	1.15	1.18
227	0.90	0.90	0.89	0.90	0.87
235	1.25	1.17	1.11	1.14	1.14
137	1.15	1.12	1.11	1.12	1.13
344	0.92	0.92	0.88	0.89	0.90
412	1.12	1.15	1.08	1.09	1.11
424	1.14	1.10	1.08	1.09	1.11
414	1.18	1.16	1.13	1.09	1.11
316	0.93	0.92	0.88	0.92	0.91
141	1.14	1.06	1.07	1.05	1.08
324	1.11	1.08	1.06	1.01	1.08
243	0.95	0.95	0.92	0.93	0.93
242	0.95	0.94	0.92	0.95	0.93
314	0.97	0.92	0.92	0.91	0.93
136	1.12	1.06	1.06	1.07	1.07

out to $\theta = 27^\circ$. The same corrections as above were applied. 15 reflexions with the largest relative differences $|1 - |F_c(hkl)|/|F_c(\bar{h}\bar{k}\bar{l})||$ were selected from

Table 3. Bond lengths (Å) and angles (°)

C(1)–C(2)	1.494 (6)	C(1)–C(2)–C(3)	126.7 (4)
C(2)–C(3)	1.309 (5)	C(2)–C(3)–C(4)	126.2 (3)
C(3)–Cl(2)	1.756 (3)	C(2)–C(3)–Cl(2)	120.5 (3)
C(3)–C(4)	1.479 (5)	Cl(2)–C(3)–C(4)	113.2 (2)
C(4)–C(5)	1.343 (5)	C(3)–C(4)–C(5)	125.2 (3)
C(4)–C(9)	1.504 (5)	C(3)–C(4)–C(9)	116.6 (3)
C(5)–Cl(1)	1.716 (3)	C(5)–C(4)–C(9)	118.1 (3)
C(5)–C(6)	1.495 (5)	C(4)–C(5)–C(6)	123.1 (3)
C(6)–O(1)	1.205 (4)	C(4)–C(5)–Cl(1)	123.9 (3)
C(6)–C(7)	1.472 (5)	Cl(1)–C(5)–C(6)	113.0 (2)
C(7)–C(8)	1.493 (4)	C(5)–C(6)–C(7)	114.9 (3)
C(8)–O(3)	1.396 (4)	C(5)–C(6)–O(1)	121.6 (3)
C(8)–C(9)	1.533 (5)	O(1)–C(6)–C(7)	123.4 (3)
C(9)–O(2)	1.205 (4)	C(6)–C(7)–C(8)	120.7 (3)
C(7)–C(10)	1.529 (5)	C(6)–C(7)–C(10)	119.6 (3)
C(7)–C(11)	1.520 (5)	C(6)–C(7)–C(11)	120.5 (3)
C(10)–C(11)	1.484 (6)	C(10)–C(7)–C(11)	58.2 (2)
C(11)–C(12)	1.515 (5)	C(10)–C(7)–C(8)	114.9 (3)
C(12)–C(13)	1.504 (6)	C(11)–C(7)–C(8)	106.6 (3)
C(12)–C(14)	1.514 (7)	C(7)–C(8)–C(9)	110.2 (3)
C(12)–O(4)	1.461 (4)	C(7)–C(8)–O(3)	117.2 (3)
O(4)–C(8)	1.417 (4)	C(7)–C(8)–O(4)	106.3 (2)
C(1)–H(1A)	0.93 (6)	C(9)–C(8)–O(3)	103.7 (2)
C(1)–H(1B)	0.83 (6)	C(9)–C(8)–O(4)	112.1 (3)
C(1)–H(1C)	0.83 (9)	O(3)–C(8)–O(4)	107.4 (3)
C(2)–H(2)	0.91 (4)	C(8)–C(9)–C(4)	114.8 (3)
C(10)–H(10A)	0.86 (4)	C(8)–C(9)–O(2)	123.1 (3)
C(10)–H(10B)	1.01 (4)	O(2)–C(9)–C(4)	122.1 (3)
C(11)–H(11)	0.85 (3)	C(7)–C(10)–C(11)	60.6 (2)
C(13)–H(13A)	0.99 (6)	C(7)–C(11)–C(10)	61.2 (2)
C(13)–H(13B)	0.92 (6)	C(7)–C(11)–C(12)	106.3 (3)
C(13)–H(13C)	1.08 (5)	C(10)–C(11)–C(12)	118.4 (3)
C(14)–H(14A)	0.99 (6)	C(11)–C(12)–C(13)	110.4 (3)
C(14)–H(14B)	0.93 (6)	C(11)–C(12)–C(14)	113.7 (4)
C(14)–H(14C)	0.97 (7)	C(11)–C(12)–O(4)	103.8 (3)
O(3)–H(O3)	0.64 (4)	C(13)–C(12)–C(14)	112.3 (4)
		C(13)–C(12)–O(4)	109.9 (3)
		C(14)–C(12)–O(4)	106.3 (3)
		C(12)–O(4)–C(8)	111.3 (2)

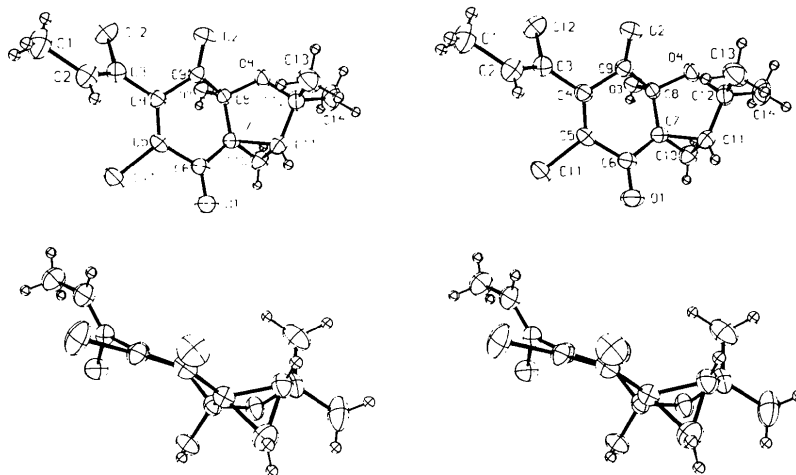


Fig. 1. A stereo view of the chloromycorrhizin A molecule in two orientations.

Table 4. *Torsion angles* ($^{\circ}$)

C(1)–C(2)–C(3)–C(4)	177.9 (4)	C(6)–C(7)–C(8)–C(9)	30.9 (4)	C(8)–C(7)–C(10)–C(11)	94.8 (3)
C(1)–C(2)–C(3)–Cl(2)	0.2 (6)	C(6)–C(7)–C(8)–O(3)	–87.4 (4)	C(6)–C(7)–C(11)–C(10)	108.1 (4)
C(2)–C(3)–C(4)–C(5)	50.3 (5)	C(6)–C(7)–C(8)–O(4)	152.6 (3)	C(6)–C(7)–C(11)–C(12)	–138.0 (3)
C(2)–C(3)–C(4)–C(9)	–125.7 (4)	C(10)–C(7)–C(8)–C(9)	–173.7 (3)	C(8)–C(7)–C(11)–C(10)	–109.4 (3)
Cl(2)–C(3)–C(4)–C(5)	–131.9 (3)	C(10)–C(7)–C(8)–O(3)	68.1 (4)	C(8)–C(7)–C(11)–C(12)	4.5 (4)
Cl(2)–C(3)–C(4)–C(9)	52.2 (4)	C(10)–C(7)–C(8)–O(4)	–52.0 (4)	C(10)–C(7)–C(11)–C(12)	113.9 (3)
C(3)–C(4)–C(5)–C(6)	–169.3 (3)	C(11)–C(7)–C(8)–C(9)	–111.5 (3)	C(7)–C(10)–C(11)–C(12)	–93.9 (4)
C(3)–C(4)–C(5)–Cl(1)	7.3 (5)	C(11)–C(7)–C(8)–O(3)	130.2 (3)	C(7)–C(11)–C(12)–C(13)	100.8 (4)
C(9)–C(4)–C(5)–C(6)	6.6 (5)	C(11)–C(7)–C(8)–O(4)	10.2 (3)	C(7)–C(11)–C(12)–C(14)	–132.0 (4)
C(9)–C(4)–C(5)–Cl(1)	–176.8 (2)	C(7)–C(8)–C(9)–C(4)	–47.4 (4)	C(7)–C(11)–C(12)–O(4)	–16.9 (4)
C(4)–C(5)–C(6)–C(7)	–23.8 (5)	C(7)–C(8)–C(9)–O(2)	135.5 (3)	C(10)–C(11)–C(12)–C(13)	166.4 (4)
C(4)–C(5)–C(6)–O(1)	152.8 (3)	O(3)–C(8)–C(9)–C(4)	78.9 (3)	C(10)–C(11)–C(12)–C(14)	–66.3 (5)
Cl(1)–C(5)–C(6)–C(7)	159.3 (2)	O(3)–C(8)–C(9)–O(2)	–98.2 (4)	C(10)–C(11)–C(12)–O(4)	48.7 (4)
Cl(1)–C(5)–C(6)–O(1)	–24.1 (4)	O(4)–C(8)–C(9)–C(4)	–165.6 (3)	C(11)–C(12)–O(4)–C(8)	24.8 (4)
C(5)–C(6)–C(7)–C(8)	2.6 (4)	O(4)–C(8)–C(9)–O(2)	17.3 (4)	C(13)–C(12)–O(4)–C(8)	–93.3 (4)
C(5)–C(6)–C(7)–C(10)	–151.7 (3)	C(8)–C(9)–C(4)–C(3)	–153.4 (3)	C(14)–C(12)–O(4)–C(8)	145.0 (3)
C(5)–C(6)–C(7)–C(11)	139.9 (3)	C(8)–C(9)–C(4)–C(5)	30.4 (4)	C(12)–O(4)–C(8)–C(7)	–22.3 (3)
O(1)–C(6)–C(7)–C(8)	–174.0 (3)	O(2)–C(9)–C(4)–C(3)	23.8 (5)	C(12)–O(4)–C(8)–C(9)	98.2 (3)
O(1)–C(6)–C(7)–C(10)	31.8 (5)	O(2)–C(9)–C(4)–C(5)	–152.4 (3)	C(12)–O(4)–C(8)–O(3)	–148.5 (3)
O(1)–C(6)–C(7)–C(11)	–36.7 (5)	C(6)–C(7)–C(10)–C(11)	–109.5 (3)		

Table 5. *Deviations* (\AA) *from the least-squares planes through the six- and five-membered rings*

C(4)	0.048	C(7)	0.011
C(5)	0.164	C(8)	–0.093
C(6)	–0.148	O(4)	0.141
C(7)	–0.059	C(12)	–0.124
C(8)	0.265	C(11)	0.065
C(9)	–0.270		
O(1)	–0.508		
O(2)	–0.853		

reflexions with $I > 100\sigma(I)$. The anomalous dispersion parameters of Cromer & Liberman (1970) were used. The ratios $|F_o(hkl)|/|F_c(h\bar{k}l)|$ are compared with the corresponding observed ratios in Table 2. They all confirm that the correct absolute configuration is (1*S*,6*S*,9*R*) (Cahn, Ingold & Prelog, 1966), as given by the coordinates in Table 1.

Discussion. A stereoscopic view of the molecule is given in Fig. 1, also showing our arbitrary atomic num-

bering. Bond distances and angles are given in Table 3 and torsion angles in Table 4. The six- and five-rings are *cis*-fused. Both rings deviate from planarity (Table 5). The six-ring has a flattened boat or twist conformation with both keto groups on the same side of the least-squares plane. The conformation of the five-ring is an envelope; the O atom projects out of the plane of the other four atoms. The angle between the cyclopropane ring and the best plane through the five-ring is $74(5)^{\circ}$.

The chloropropene side chain has the *cis* conformation and is stretched so that the angles C(1)–C(2)–C(3) and C(2)–C(3)–C(4) are 126.7 and 126.2° . The short C(2)–C(3) bond, 1.309 \AA , indicates only weak conjugation with the enone moiety. Owing to steric hindrance, C(2)–C(3) cannot be coplanar with C(4)–C(5). The torsion angle C(2)–C(3)–C(4)–C(5) is 50.3° , with intramolecular van der Waals con-

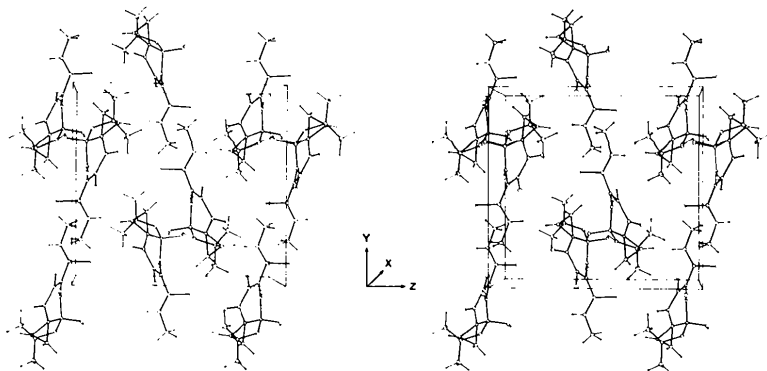


Fig. 2. Packing of the molecules in the crystal. Hydrogen bonds are indicated by thin lines.

tacts Cl(1)···C(2) 3.31, Cl(1)···H(2) 3.05 and Cl(2)···O(2) 3.15 Å. Presumably the barrier to internal rotation around C(3)—C(4) permits the separation of diastereoisomers with opposite axial chirality. The compound examined would then have the absolute configuration (1*S*,6*S*,9*R*,1',4-*aR*). The ring system does not allow independent inversions at the 1 and 9 asymmetry centres; if one is *R* the other must be *S*.

The packing of the molecules is shown in Fig. 2. Adjacent molecules are connected along *x* by weak O(3)—H(O3)···O(4) hydrogen bonds of 2.845 (4) Å with O(3)—H(O3) 0.64 (4) and H(O3)···O(4) 2.28 (4) Å. The angle O(3)—H(O3)—O(4) is 150 (5)°. There are no other intermolecular distances significantly shorter than the sum of the van der Waals radii.

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N-Benzylphenothiazine

BY SHIRLEY S. C. CHU

School of Engineering and Applied Science, Southern Methodist University, Dallas, Texas 75275, USA

AND DICK VAN DER HELM

Department of Chemistry, The University of Oklahoma, Norman, Oklahoma 73069, USA

(Received 7 July 1976; accepted 9 September 1976)

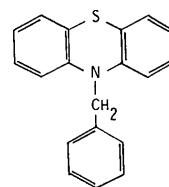
Abstract. C₁₉H₁₅NS, triclinic, $P\bar{1}$, $Z = 4$, $M_r = 289.40$, $a = 11.274$ (7), $b = 11.504$ (7), $c = 13.404$ (9) Å, $\alpha = 90.873$ (6), $\beta = 91.824$ (7), $\gamma = 120.484$ (6)°, $V = 1496.39$ Å³, $D_x = 1.284$, $D_m = 1.27$ g cm⁻³ (by flotation), $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 17.83$ cm⁻¹. Final residual $R = 0.048$.

Introduction. Samples of *N*-benzylphenothiazine (I) were obtained through the courtesy of Dr Edward R. Biehl of the Chemistry Department of Southern Methodist University. Single crystals in the form of clear prisms were grown from acetone solutions. The unit-cell parameters were obtained from the measurement of '+' and '-' 2θ values of 28 reflections and the intensity data were collected on a Nonius CAD-4 automatic diffractometer. An $\omega/2\theta$ scanning mode with Ni-filtered Cu $K\alpha$ radiation was used to measure 5668 independent reflections with 2θ values below 140°, of which 4671 reflections were considered as observed by the criterion $I > 2.0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure factors, and no absorption corrections were applied.

Thanks are due to J. Trofast for providing the crystals.

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(I)

The structure was determined by the heavy-atom method. There are two crystallographically independent molecules in one asymmetric unit of the crystal. The refinement was carried out by the full-matrix least-squares method with isotropic temperature factors and block-diagonal least-squares method with anisotropic temperature factors. All the H atoms were located by difference Fourier syntheses. The isotropic temperature factors were used for the H atoms in the refinement. The weight of the reflection was assigned as $1/[\sigma(F)]^2$ for observed reflections and zero for unobserved reflections, where $\sigma(F)$ was calculated from counting statistics. The quantity $\Sigma w\{|F_o| - |F_c|\}^2$ was