

of the molecule. The addition of a terminal *N*-methyl group in WR 151,327 does not affect the N...N distance. The intramolecular N...N distance of 4.48 Å in WR 151,327 is nearly identical to the N...N distance of 4.45 Å in WR 2721. However, the additional methylene group in WR 151,327 causes the N(4)...S distance of 5.19 Å and the N(8)...S distance of 9.41 Å to be considerably longer than the corresponding distances (3.49 Å and 7.14 Å, respectively) in the WR 2721 molecule. Radioprotection and toxicity studies (Sweeney, 1979) have demonstrated that these intramolecular distances, representing a separation of two or three C atoms between the S atom and the neighboring N atom and a separation of three C atoms between the N atoms, are optimal for radioprotection.

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Psilostachyin A

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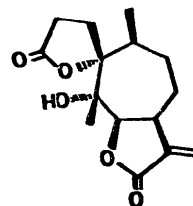
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Abstract. $C_{15}H_{20}O_5$, $M_r = 280.3$, orthorhombic, $P2_12_12_1$, $a = 7.516$ (1), $b = 12.817$ (1), $c = 14.238$ (2) Å, $V = 1371.7$ (3) Å³, $Z = 4$, $D_x = 1.357$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.95$ cm⁻¹, $F(000) = 600$, $T = 298$ K, $R = 0.045$ for 1577 observed reflections. The compound is a 4,5-seco-pseudo-guaianolide containing a spiro-lactone. The conformations of both the spiro-lactone and the *cis*-fused lactone ring at C(6)–C(7) approximate envelopes, while the seven-membered ring approximates a twist chair with the pseudodiad axis passing through C(7) and the C(1)–C(10) bond. Intermolecular hydrogen bonds of length 2.883 (2) Å join the hydroxy group and the spiro-lactone carbonyl O atom along the *b* direction.

Introduction. Psilostachyin A is a 4,5-seco-pseudo-guaianolide dilactone present in several species of the genus *Ambrosia* (Mabry, Miller, Kagan &

Renold, 1966; Geissman & Matsueda, 1968; Herz, Anderson, Gibaja & Raulais, 1969; Higo, Hammam, Timmermann, Yoshioka, Lee, Mabry & Payne, 1971; Herz, Raulais & Anderson, 1973). The structure analysis was undertaken in order to confirm the relative configuration of the chiral centers assigned by Mabry *et al.* (1966) from NMR data, as well as to study the effect of the unique spiro-lactone on the conformation of the seven-membered ring.



Experimental. Title compound provided by T. J. Mabry, isolated from *Ambrosia psilostachya* D.C., collected on Galveston Island, Texas. Tabular, colorless

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crystal, m.p. 488 K, size $0.52 \times 0.20 \times 0.32$ mm, space group by systematic absences $h00$ with h odd, $0k0$ with k odd, $00l$ with l odd. Cell dimensions from setting angles of 25 reflections with $13 < \theta < 14^\circ$. Data collection on Enraf–Nonius CAD-4 diffractometer, graphite monochromator, ω - 2θ scans designed to yield $I = 50\sigma(I)$, max. scan time 180 s. Scan rates 0.42 – $5.0^\circ \text{ min}^{-1}$. Data having $1 < \theta < 27^\circ$ [max. $(\sin\theta)/\lambda = 0.638 \text{ \AA}^{-1}$], h 0–9, k 0–16, l 0–18, measured and corrected for background, Lorentz, and polarization effects; 1731 unique reflections. Crystal decay and absorption negligible. Three standard reflections (200, 020, 006), 2.6% maximum variation.

Structure solved using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refined by full-matrix least squares based on F using 1577 data with $F_{\text{obs}} > 0$, $w = [\sigma^2(F) + 0.02F^2]^{-1}$, using *SHELX*76 (Sheldrick, 1976) and Enraf–Nonius *SDP* (Frenz & Okaya, 1980). Scattering factors of Cromer & Waber (1974). Non-H atoms anisotropic; H atoms located by ΔF map and refined isotropically. Final $R = 0.045$, $wR = 0.036$, and $S = 1.720$ for 261 variables. Max. $\Delta/\sigma = 0.02$ in final cycle, largest residual density 0.21 e \AA^{-3} [along the C(1)–C(5) bond], minimum 0.16 e \AA^{-3} . Absolute configuration not determined; assumed to correspond to that of other sesquiterpene lactones from higher plants: recent determinations: Nagumo, Kawai & Iitaka (1982), Baruah, Baruah, Sharma, Baruah, Herz, Watanabe & Blount (1982). Coordinates of non-H atoms and their equivalent isotropic thermal parameters are given in Table 1.*

Discussion. The structure deduced by Mabry *et al.* (1966) is confirmed, as depicted in Fig. 1.

The conformation of the five-membered lactone ring *cis*-fused at C(6)–C(7) most nearly approximates an envelope with flap at C(6): E^6 . The deviation from exact mirror symmetry of the envelope can be measured by $\Delta C_s = 0.8 (1)^\circ$ (Duax & Norton, 1975). A more precise measure is available in terms of the Cremer–Pople parameters (Cremer & Pople, 1975): the puckering amplitude q is $0.154 (2) \text{ \AA}$, and the pseudorotation angle φ is $3.8 (8)^\circ$, which is about 11% along the pseudorotation path toward twist conformation ${}^7T^6$. The conformation of the second lactone ring at C(1) approximates an envelope with C(2) at the flap, E^2 , with $\Delta C_s = 2.9 (2)^\circ$, $q = 0.181 (2) \text{ \AA}$, and $\varphi = 6.8 (6)^\circ$ (about 19% toward ${}^1T^2$).

* Lists of H-atom coordinates and thermal parameters, bond distances and angles, torsion angles, intermolecular contacts, anisotropic thermal parameters, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44837 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{\text{eq}} = \frac{4}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
O(1)	0.8209 (2)	0.37851 (10)	0.57327 (9)	3.91 (3)
O(2)	0.8005 (3)	0.52575 (12)	0.49176 (11)	6.85 (5)
O(3)	0.7043 (2)	0.13281 (8)	0.73893 (8)	2.84 (3)
O(4)	0.8993 (2)	0.00612 (10)	0.75812 (12)	4.99 (4)
O(5)	0.9150 (2)	0.30936 (9)	0.74257 (9)	3.22 (3)
C(1)	0.6445 (3)	0.2303 (1)	0.7848 (1)	2.47 (3)
C(2)	0.7271 (3)	0.2234 (1)	0.8839 (1)	3.35 (4)
C(3)	0.8727 (3)	0.1425 (2)	0.8765 (2)	4.04 (5)
C(4)	0.8339 (3)	0.0855 (1)	0.7877 (1)	3.34 (4)
C(5)	0.7279 (2)	0.3203 (1)	0.7259 (1)	2.33 (3)
C(6)	0.7043 (3)	0.3030 (1)	0.6192 (1)	2.71 (4)
C(7)	0.5209 (3)	0.3163 (1)	0.5714 (1)	3.11 (4)
C(8)	0.3521 (3)	0.3044 (2)	0.6300 (1)	3.54 (4)
C(9)	0.3476 (3)	0.2092 (2)	0.6930 (1)	3.56 (4)
C(10)	0.4400 (3)	0.2203 (1)	0.7885 (1)	2.94 (4)
C(11)	0.5393 (3)	0.4193 (2)	0.5217 (1)	3.98 (5)
C(12)	0.7286 (4)	0.4509 (2)	0.5256 (1)	4.43 (5)
C(13)	0.4191 (4)	0.4746 (2)	0.4763 (2)	6.07 (7)
C(14)	0.3493 (3)	0.3015 (2)	0.8518 (1)	4.07 (5)
C(15)	0.6694 (3)	0.4290 (1)	0.7566 (1)	2.93 (4)

Table 2. *Selected torsion angles ($^\circ$)*

C(12) O(1)	C(6) C(7)	16.3 (2)	C(1) C(5) C(6) C(7)	72.6 (2)
C(6) O(1)	C(12) C(11)	−9.8 (2)	O(1) C(6) C(7) C(11)	−15.4 (2)
H(O5)O(5)	C(5) C(6)	80.0 (14)	C(5) C(6) C(7) C(8)	−23.8 (2)
O(3) C(1)	C(2) C(3)	17.9 (2)	C(6) C(7) C(8) C(9)	−47.3 (2)
C(3) C(4)	O(3) C(1)	3.0 (2)	C(6) C(7) C(11) C(12)	10.3 (2)
C(4) O(3)	C(1) C(2)	−13.2 (2)	C(7) C(8) C(9) C(10)	83.9 (2)
C(10) C(1)	C(5) C(6)	−70.3 (2)	C(8) C(9) C(10) C(11)	−68.4 (2)
C(5) C(1)	C(10) C(9)	56.9 (2)	C(7) C(11) C(12) O(1)	−1.0 (2)
C(1) C(2)	C(3) C(4)	−16.4 (2)	C(13) C(11) C(12) O(2)	0.4 (4)
C(2) C(3)	C(4) O(3)	8.8 (2)		

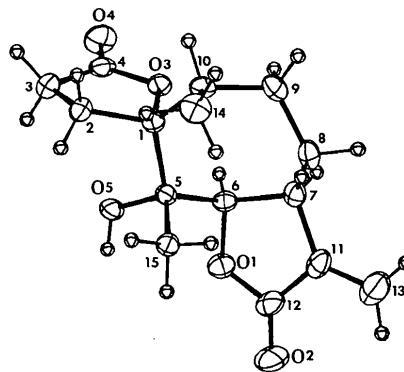


Fig. 1. Numbering scheme and thermal ellipsoids drawn at the 40% probability level. H atoms have arbitrary radius.

The conformation of the seven-membered ring is closest to a 'twist chair', with the diad axis through C(7) and the C(1)–C(10) bond. However, $\Delta C_2 = 14.9 (1)^\circ$. The Cremer–Pople parameters are: $q_2 = 0.444 (2) \text{ \AA}$, $\varphi_2 = 77.4 (2)^\circ$, $q_3 = 0.632 (2) \text{ \AA}$, $\varphi_3 = 83.7 (2)^\circ$. The spiro-lactone ring does not affect the conformation of the seven-membered ring appreciably, as this conformation is one of those also found in normal pseudo-

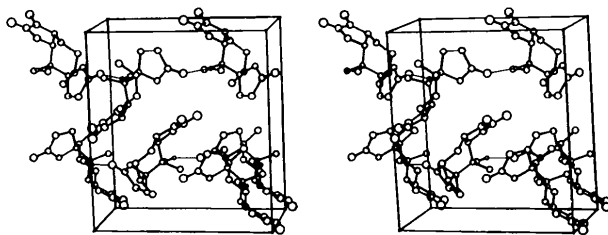


Fig. 2. Stereoscopic representation of the unit cell viewed slightly oblique to the a axis, with b horizontal, illustrating hydrogen bonds.

guaianolides of the ambrosanolide class, having five-membered rings *trans*-fused at C(1)–C(5). The r.m.s. difference between the seven endocyclic torsion angles found here (Table 2) and those of hysterin (Declercq, Germain, Van Meerssche, Demuynck, Declercq & Vandewalle, 1980) is 1.7° , with the largest individual difference $3.1 (5)^\circ$. Similar conformations are also found in bippinatin: r.m.s. deviation 7.2° and parthenin: r.m.s. deviation 9.3° (Fronczek, Vargas, Fischer, Chiari, Balza & Towers, 1988).

C–H distances range $0.89 (2)$ – $1.03 (2)$ Å and average $0.96 (4)$ Å, while the O–H distance is $0.83 (2)$ Å. Molecules interact in the crystal through a hydrogen bond, with hydroxyl group O(5) as donor and spiro-lactone carbonyl O(4) of a molecule related by the 2_1 axis at $1, y, \frac{3}{4}$ as acceptor. Geometrical parameters of this hydrogen bond are O...O $2.883 (2)$, H...O $2.09 (2)$ Å and O–H...O angle $161 (2)^\circ$. The spiral chains formed by this interaction are depicted in Fig. 2. No other intermolecular interactions shorter than 3.35 Å between heavy atoms exist.

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Structures of Two Semiconducting Charge-Salts Based on 4,5-Methylenedithio-4',5'-propylenedithiotetrathiafulvalene (MPT): (MPT)₂ClO₄(THF) and (MPT)₂PF₆(THF)

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Abstract. $2C_{10}H_8S_8^{1/2+}.ClO_4^-(C_4H_8O)$, $M_r = 940.933$, triclinic, $P\bar{1}$, $a = 9.110 (2)$, $b = 12.501 (4)$, $c = 16.611 (6)$ Å, $\alpha = 104.46 (2)$, $\beta = 88.47 (2)$, $\gamma =$

$102.42 (2)^\circ$, $V = 1788 (1)$ Å³, $Z = 2$, $D_x = 1.747$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.04$ mm⁻¹, $F(000) = 962$, $T = 298$ K, $R(F) = 0.088$ for 8261 observed reflections. $2C_{10}H_8S_8^{1/2+}.PF_6^-(C_4H_8O)$, $M_r = 986.446$, triclinic, $P\bar{1}$, $a = 9.215 (3)$, $b = 12.528 (4)$, $c = 17.110 (7)$ Å, $\alpha = 105.03 (3)$, $\beta = 91.14 (3)$, $\gamma = 103.56 (2)^\circ$, $V = 1848 (1)$ Å³, $Z = 2$, $D_x = 1.773$ Mg m⁻³, $\lambda(\text{Mo } K\alpha)$

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