Dans les deux structures, il y a une liaison hydrogène intermoléculaire entre l'oxygène furannique d'une molécule et le groupement hydroxyle d'une autre molécule (Fig. 2). Les caractéristiques de ces liaisons hydrogène sont les suivantes:

	(1)	(2)
$O(8)\cdots O(1^{i})$	2,878 (2) Å	2,751 (2) Å
$O(8)–H(11)$	0,85 (4)	0,93 (3)
$H(11)\cdots O(1^{i})$	2,07 (4)	1,83 (3)
$O(8)–H(11)\cdots O(1^{i})$	160 (3)°	179 (2)°
(i) =	$x, \frac{1}{2}-y, z-\frac{1}{2}$	$1-x, \frac{1}{2}+y, \frac{3}{2}-z$.

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Structure of Longipilin

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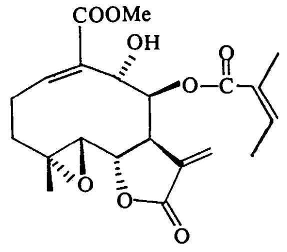
Abstract. $C_{21}H_{26}O_8$, $M_r = 406{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 13{\cdot}051\ (1)$, $b = 15{\cdot}894\ (2)$, $c = 10{\cdot}204\ (1)$ Å, $V = 2116{\cdot}6\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}275$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}92$ cm^{-1}, $F(000) = 864$, $T = 298$ K, $R = 0{\cdot}043$ for 1484 observations (out of 2131 unique data). Longipilin is a constituent of *Melampodium longipilum*. The conformation of the ten-membered ring is typical of melampolides, with no endocyclic torsion angles differing by more than 11° from those of enhydrin or alloschkuriolide. The epoxide is symmetric with an average C—O distance of 1·454 (4) Å.

Introduction. The sesquiterpene lactone analysis of *Melampodium longipilum*, collected 13 miles west of Rio Verde, San Luis Potosi, Mexico (plant material collected by Stuessy–Gardner, collection number 4062), yielded two known melampolides, longipilin (I) (Seaman & Fischer, 1978) and polymatin A (Le Van & Fischer, 1979), differing only by epoxidation at C(4)—C(5). We report here the structure of longipilin; the identity of polymatin A was established by comparison of its ^{1}H NMR spectrum with that of (I), and with literature parameters (Le Van & Fischer, 1979).



(I)

Experimental. Colorless crystal, dimensions 0·28 × 0·32 × 0·52 mm, space group from absences *h*00 with *h* odd, 0*k*0 with *k* odd, 00*l* with *l* odd, cell dimensions from setting angles of 25 reflections, 13 > θ > 12°.

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Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator, intensity data by ω–2θ scans designed for $I = 50\sigma(I)$, subject to max. scan time = 120 s, scan rates varied 0·48–5·0° min^{-1}. Data having $1 < \theta < 25°$, $0 \leq h \leq 15$, $0 \leq k \leq 18$, $0 \leq l \leq 12$ measured, corrected for background and Lorentz–polarization. Absorption and decay insignificant (200, 040, 004 standard reflections, 4·3% max. variation). 2131 unique data, 1484 observed $I > 3\sigma(I)$. Structure solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares based on F with weights $w = 4F_o^2[\sigma^2(I) + (0{\cdot}02F_o^2)^2]^{-1}$ using Enraf–Nonius *SDP* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974). Non-H atoms anisotropic, H atoms located from ΔF, included as fixed contributions. Final $R = 0{\cdot}043$ (0·086 all data), $wR = 0{\cdot}056$, $S = 1{\cdot}655$ for 263 variables. Max. $\Delta/\sigma = 0{\cdot}01$ in final cycle; max. residual density 0·21, min. −0·19 e Å^{-3}; extinction (Darwin, 1922), $g = 1{\cdot}0\,(1) \times 10^{-6}$ $\{|F_c| = |F_o|\,[1 + g(I_c)]\}$. Absolute configuration not determined.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* The structure of longipilin (I) is illustrated in Fig. 1. Its conformation is characterized by the torsion angles in Table 2. This conformation is very typical of a melampolide, and thus will not be discussed in detail here. Comparison of the ten endocyclic torsion angles with those of enhydrin (Kartha, Go & Joshi, 1972), in which the *trans* double bond is also epoxidized, reveals an average difference of 5·6° and a maximum difference of 11° about C(8)—C(9). Surprisingly, longipilin and alloschkuriolide (Rychlewska, 1983), which is not epoxidized, show an even closer conformational correspondence, with average difference 4·6° and largest difference 10° about C(4)—C(5). Except for torsional changes brought about by epoxidation at C(2)—C(3), longipilin also agrees well with the conformations of melampodin (Watkins, Fischer & Bernal, 1973) and melampodinin-A (Fronczek, Malcolm & Fischer, 1983). These similarities attest to the rigidity of the melampolide skeleton. The lactone ring of longipilin has a puckered conformation best described as a half chair with C(12) on the pseudo-twofold axis, with asymmetry parameter 3·5° (Duax & Norton, 1975). Bond distances, with standard deviations 0·003–0·005 Å (0·005–0·008 Å for the angelate substituent) are normal, and show good agreement with those of other melampolides. The endocyclic double bond C(1)—C(10) has length 1·343 (4) Å, and the exocyclic double bond of the lactone C(11)—C(13) has length 1·319 (5) Å. The epoxide is symmetric, with average C—O distance 1·454 (4) Å, and the C(9)—OH distance

Table 1. *Coordinates and equivalent isotropic thermal parameters*

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

	x	y	z	$B_{\rm eq}$(Å^2)
O(1)	−0·0478 (2)	0·4264 (1)	0·8846 (3)	4·64 (6)
O(2)	0·1430 (2)	0·4878 (2)	1·0190 (3)	4·66 (6)
O(3)	0·2884 (3)	0·5016 (2)	1·1301 (3)	7·56 (9)
O(4)	−0·0297 (2)	0·7904 (1)	0·7577 (3)	3·90 (5)
O(5)	0·1867 (2)	0·7467 (2)	0·6376 (3)	5·53 (7)
O(6)	0·1495 (3)	0·6647 (2)	0·4672 (3)	6·01 (8)
O(7)	0·0308 (2)	0·7180 (1)	1·0038 (2)	3·38 (8)
O(8)	0·1211 (3)	0·8351 (2)	1·0405 (3)	6·29 (8)
C(1)	−0·0243 (3)	0·6100 (2)	0·5823 (4)	4·12 (9)
C(2)	−0·1283 (3)	0·5783 (3)	0·6185 (4)	5·0 (1)
C(3)	−0·1297 (4)	0·4930 (3)	0·6855 (4)	5·1 (1)
C(4)	−0·0938 (3)	0·5009 (2)	0·8253 (4)	3·67 (8)
C(5)	0·0179 (3)	0·4960 (2)	0·8468 (4)	3·33 (8)
C(6)	0·0712 (3)	0·5430 (2)	0·9514 (3)	3·13 (7)
C(7)	0·1375 (3)	0·6158 (2)	0·8987 (3)	2·78 (7)
C(8)	0·0844 (3)	0·7011 (2)	0·8833 (3)	2·69 (7)
C(9)	0·0036 (3)	0·7057 (2)	0·7738 (3)	2·96 (7)
C(10)	0·0349 (3)	0·6663 (2)	0·6446 (3)	3·38 (8)
C(11)	0·2254 (3)	0·6155 (2)	0·9947 (4)	3·49 (8)
C(12)	0·2271 (3)	0·5323 (3)	1·0565 (4)	4·6 (1)
C(13)	0·2910 (3)	0·6751 (3)	1·0273 (4)	4·8 (1)
C(14)	0·1311 (3)	0·6966 (2)	0·5854 (4)	3·68 (8)
C(15)	−0·1653 (3)	0·5451 (3)	0·9204 (5)	5·3 (1)
C(16)	0·2423 (4)	0·6928 (4)	0·4016 (5)	7·1 (1)
C(17)	0·0551 (3)	0·7867 (2)	1·0735 (4)	4·16 (8)
C(18)	−0·0087 (4)	0·7897 (3)	1·1976 (4)	5·6 (1)
C(19)	−0·0577 (4)	0·7073 (3)	1·2452 (4)	6·7 (1)
C(20)	−0·0219 (7)	0·8601 (4)	1·2571 (6)	9·9 (2)
C(21)	0·0143 (9)	0·9439 (4)	1·2187 (7)	13·7 (3)

Table 2. *Selected torsion angles* (°)

C(1)—C(2)—C(3)—C(4)	74·8 (6)	O(2)—C(6)—C(7)—C(11)	−26·3 (4)
C(2)—C(3)—C(4)—C(5)	−86·5 (5)	C(6)—C(7)—C(11)—C(12)	20·5 (5)
C(3)—C(4)—C(5)—C(6)	147·1 (5)	C(7)—C(11)—C(12)—O(2)	−7·2 (5)
C(4)—C(5)—C(6)—C(7)	−108·8 (5)	C(11)—C(12)—O(2)—C(6)	−10·8 (5)
C(5)—C(6)—C(7)—C(8)	89·0 (4)	C(12)—O(2)—C(6)—C(7)	23·9 (4)
C(6)—C(7)—C(8)—C(9)	−69·3 (5)	O(3)—C(12)—C(11)—C(13)	−8·6 (6)
C(7)—C(8)—C(9)—C(10)	−44·7 (5)	C(1)—C(10)—C(14)—O(6)	1·8 (5)
C(8)—C(9)—C(10)—C(1)	128·7 (5)	C(6)—C(7)—C(8)—O(7)	48·8 (4)
C(9)—C(10)—C(1)—C(2)	3·0 (5)	O(7)—C(17)—C(18)—C(19)	20·0 (5)
C(10)—C(1)—C(2)—C(3)	−100·1 (6)	C(17)—C(18)—C(20)—C(21)	2·6 (7)

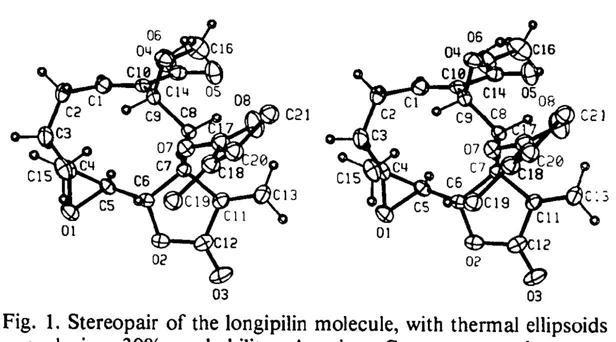

Fig. 1. Stereopair of the longipilin molecule, with thermal ellipsoids enclosing 30% probability. Angelate C atoms are drawn as spheres of arbitrary size, with H atoms omitted for clarity.

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* Lists of bond distances, bond angles, H-atom coordinates, anisotropic thermal parameters and structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42876 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is 1·424 (4) Å. The angelate substituent is nonplanar, with a twist of 20·0 (5)° about the central bond. The apparent thermal motion of C(21) is large (B_{eq} = 13·7 Å^2), and may be indicative of unresolved disorder. Molecules are linked in the solid by spiral H-bonded chains along the direction of the *a* axis. The H bond involves hydroxyl group O(4) as donor and epoxide O atom O(1) as acceptor, with O···O separation 2·794 (3) Å and O—H···O angle approximately 150°.

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Structure of *cis,cis,cis,cis*-1,2,3,4,5-Pentakis(methylsulfonyloxymethyl)cyclopentane Methanol Solvate

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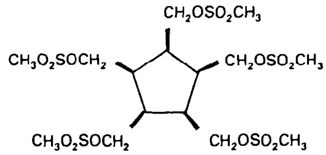
Abstract. $C_{15}H_{30}O_{15}S_5.0{\cdot}256\,(8)\,CH_3OH$, $M_r = 618{\cdot}9$, triclinic, $P\bar{1}$, $a = 11{\cdot}902\,(1)$, $b = 12{\cdot}994\,(1)$, $c = 9{\cdot}786\,(1)$ Å, $\alpha = 110{\cdot}00\,(1)$, $\beta = 109{\cdot}97\,(1)$, $\gamma = 92{\cdot}00\,(1)°$, $V = 1316{\cdot}9\,(3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}561$ g cm^{-3}, Mo $K\alpha$ (graphite monochromator), $\lambda = 0{\cdot}71073$ Å, $\mu = 4{\cdot}86$ cm^{-1}, $F(000) = 650{\cdot}32$, $T = 295\,(1)$ K, $R = 0{\cdot}050$ for 355 variables and 3159 unique reflections having $I > 3\sigma(I)$. The value of the dihedral angle describing the envelope conformation of the cyclopentane ring is 40·7 (5)°. Most bond lengths and angles fall within normal ranges. The $CH_2OSO_2CH_3$ groups are disposed in such a way that their unexpected resistance to nucleophilic attack is explained.

Introduction. The title compound (Gregory, 1983), hereafter PMMCP, undergoes elimination of methanesulfonic acid rather than nucleophilic displacement upon treatment with strong nucleophiles such as benzylthiolate. Inasmuch as substitution by sulfur constitutes an important component in the elaboration of PMMCP into dodecahedrane and other novel cage compounds (Tolbert, Gregory & Brock, 1985), we determined the crystal structure of PMMCP to evaluate the structural factors inhibiting the desired reaction.



Experimental. Colorless, thin tablet with pointed ends, 0·35 × 0·20 × 0·05 mm grown from methanol and mounted in air, bounding planes $\{100\}$, $\{01\bar{1}\}$, $\{10\bar{1}\}$, $\{1\bar{1}0\}$. Enraf–Nonius CAD-4/*F* diffractometer; 22 reflections having $12{\cdot}6 \le \theta \le 13{\cdot}3°$ used to determine lattice parameters; ω–2θ scans; transmission coefficients for absorption correction (Gaussian integration) 0·90–0·96; $\theta \le 27{\cdot}5°$; hemisphere of data with $0 \le h \le 15$, $-16 \le k \le 16$, $-11 \le l \le 10$. Average intensity loss for three control reflections 4·2% overall (not corrected). 6029 unique reflections measured; 3159 data having $I > 3\sigma(I)$ used for refinement. Structure solved using direct methods; computer programs as described previously (Brock & Webster, 1976). Scattering factors from Cromer & Waber (1974); anomalous terms included for S atoms.

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