$C_{22}H_{32}N_2O_3$

conformation chaise avec toutefois une agitation thermique importante des atomes appartenant à ce dernier (Tableau 1). Le Tableau 2 rassemble les distances et les angles les plus significatifs de la molécule. Tous sont en bon accord avec les valeurs habituellement rencontrées. L'organisation est représentée sur la Fig. 2. Elle montre l'existence de chaînes moléculaires en escalier se développant dans la direction de l'axe *b*. Aucune liaison hydrogène n'a été mise en évidence, la cohésion cristalline étant exclusivement assurée par des interactions de type van der Waals.

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A Guaianolide Sesquiterpene Lactone

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Abstract. (5*S*,6*S*,7*R*,8*R*,2'*R*,3'*R*)-8-(2',3'-Epoxy-angeloyloxyguaia-1(10),3,11(13)-trien-2-one-6,7-olide. (3a*R*,4*R*,9a*S*,9b*S*,2'*R*,3'*R*)-2,3,3a,4,5,7,9a,9b-Octahydro-6,9-dimethyl-3-methylene-2,7-dioxoazuleno[5,4-*b*]fur-4-yl 2-methyl-2,3-epoxybutenoate. $C_{20}H_{22}O_6$, $M_r = 358 \cdot 40$, orthorhombic, $P2_12_12_1$, $a = 10 \cdot 1953$ (9), $b = 12 \cdot 531$ (1), $c = 14 \cdot 342$ (1) Å, $V = 1832 \cdot 2$ (2) Å^3, $Z = 4$, $D_x = 1 \cdot 299$ g cm^{-3}, λ(Cu $K\alpha$) = 1 \cdot 54178 Å, $\mu = 7 \cdot 55$ cm^{-1}, $F(000) = 760$, $T = 300$ K, $R = 0 \cdot 039$ for 1362 unique reflections. The absolute configuration of the guaianolide sesquiterpene is determined. The cyclopentenone ring exhibits a flattened envelope conformation, the cycloheptene ring a chair conformation while the γ-lactone is intermediate between half-chair and envelope.

Introduction. Most members of the important sunflower genus *Helianthus* produce sesquiterpene lactones (for example, see Herz & Kumar, 1981; Gershenzon & Mabry, 1984; Gao, Wang & Mabry, 1986). Recently, guaianolide-type sesquiterpene lactones bearing epoxyangelate side chains were reported from the two closely related species *H. glaucophyllus* and *H. microcephalous* (Gao, Wang & Mabry, 1987). While the structures of these new compounds could be determined by NMR techniques, the stereochemistry of the epoxyangelate

side chain could not be established even by nuclear Overhauser enhancement (NOE) experiments. The absolute stereochemistry of one of the new sesquiterpene lactones, (1), is reported herein.
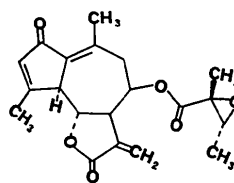
(1)

Experimental. A transparent crystal of dimensions $0 \cdot 35 \times 0 \cdot 35 \times 0 \cdot 40$ mm; Nicolet $R3m/\mu$ update of $P2_1$ diffractometer; data collected in the Wyckoff mode (2θ fixed, ω varied) ($4 \leq 2\theta \leq 120°$), graphite-monochromated Cu $K\alpha$ radiation, lattice parameters from a least-squares refinement of 25 reflections ($42 \cdot 74 \leq 2\theta \leq 82 \cdot 11°$); angles measured by a centering routine; systematic absences ($h00$, $h = 2n+1$, $0k0$, $k = 2n+1$, $00l$, $l = 2n+1$) consistent with space group $P2_12_12_1$; Laue symmetry *mmm*; monitored reflections 104 and $\bar{1}22$ showed no variation greater than 3σ; 1439 independent reflections with Friedel pairs measured ($0 \leq h \leq 10$, $0 \leq k \leq 11$, $0 \leq l \leq 15$); 1362 unique reflections with intensities greater than $2 \cdot 5\sigma(I)$;

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

	x	y	z	U^*_{eq}
C(1)	2707 (4)	766 (3)	718 (2)	74 (1)
C(2)	1681 (5)	413 (4)	17 (2)	99 (2)
O(2)	1591 (5)	754 (3)	−781 (2)	140 (2)
C(3)	869 (5)	−377 (4)	473 (3)	100 (2)
C(4)	1214 (4)	−510 (3)	1342 (3)	85 (1)
C(15)	659 (6)	−1311 (3)	1988 (4)	126 (2)
C(5)	2331 (4)	227 (2)	1611 (2)	66 (1)
C(6)	2009 (3)	1082 (2)	2319 (2)	56 (1)
O(6)	1173 (2)	709 (2)	3083 (2)	67 (1)
C(12)	1417 (4)	1300 (3)	3851 (2)	66 (1)
O(12)	720 (3)	1251 (2)	4524 (2)	93 (1)
C(11)	2612 (3)	1952 (2)	3696 (2)	59 (1)
C(13)	3003 (5)	2702 (3)	4277 (3)	80 (1)
C(7)	3204 (3)	1549 (2)	2805 (2)	55 (1)
C(8)	4048 (3)	2272 (2)	2217 (2)	61 (1)
C(9)	4644 (4)	1724 (3)	1377 (3)	75 (1)
C(10)	3700 (4)	1437 (3)	594 (2)	78 (1)
C(14)	4008 (6)	1948 (4)	−329 (3)	114 (2)
O(8)	3269 (2)	3163 (1)	1867 (2)	61 (1)
C(16)	3670 (3)	4152 (2)	2039 (2)	51 (1)
O(16)	4521 (2)	4378 (2)	2578 (2)	76 (1)
C(17)	2903 (3)	4938 (2)	1467 (2)	52 (1)
O(17)	3397 (2)	6000 (2)	1537 (2)	71 (1)
C(18)	2154 (4)	5762 (2)	1945 (2)	67 (1)
C(19)	2032 (4)	5889 (3)	2981 (3)	91 (2)
C(20)	2506 (4)	4583 (3)	505 (2)	78 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

C(1)–C(2)	1·517 (6)	C(1)–C(5)	1·498 (5)
C(1)–C(10)	1·329 (6)	C(2)–O(2)	1·226 (5)
C(2)–C(3)	1·446 (6)	C(3)–C(4)	1·305 (6)
C(4)–C(15)	1·479 (6)	C(4)–C(5)	1·516 (5)
C(5)–C(6)	1·512 (4)	C(6)–O(6)	1·465 (4)
C(6)–C(7)	1·521 (4)	O(6)–C(12)	1·351 (4)
C(12)–O(12)	1·200 (5)	C(12)–C(11)	1·484 (5)
C(11)–C(13)	1·318 (5)	C(11)–C(7)	1·501 (4)
C(7)–C(8)	1·508 (4)	C(8)–C(9)	1·514 (5)
C(8)–O(8)	1·459 (4)	C(9)–C(10)	1·521 (5)
C(10)–C(14)	1·503 (6)	O(8)–C(16)	1·328 (3)
C(16)–O(16)	1·195 (4)	C(16)–C(17)	1·502 (4)
C(17)–O(17)	1·426 (3)	C(17)–C(18)	1·455 (4)
C(17)–C(20)	1·504 (4)	O(17)–C(18)	1·428 (4)
C(18)–C(19)	1·500 (5)		

C(2)–C(1)–C(5)	105·0 (3)	C(2)–C(1)–C(10)	128·4 (3)
C(5)–C(1)–C(10)	126·6 (3)	C(1)–C(2)–O(2)	124·7 (4)
C(1)–C(2)–C(3)	107·2 (3)	O(2)–C(2)–C(3)	128·1 (4)
C(2)–C(3)–C(4)	111·3 (4)	C(3)–C(4)–C(15)	125·6 (4)
C(3)–C(4)–C(5)	111·6 (3)	C(15)–C(4)–C(5)	122·7 (4)
C(1)–C(5)–C(4)	104·4 (3)	C(1)–C(5)–C(6)	108·0 (3)
C(4)–C(5)–C(6)	116·1 (3)	C(5)–C(6)–O(6)	113·7 (2)
C(5)–C(6)–C(7)	114·0 (3)	O(6)–C(6)–C(7)	104·2 (2)
C(6)–O(6)–C(12)	109·2 (2)	O(6)–C(12)–O(12)	121·3 (3)
O(6)–C(12)–C(11)	109·3 (3)	O(12)–C(12)–C(11)	129·4 (3)
C(12)–C(11)–C(13)	123·1 (3)	C(12)–C(11)–C(7)	105·8 (2)
C(13)–C(11)–C(7)	131·1 (3)	C(6)–C(7)–C(11)	101·4 (2)
C(6)–C(7)–C(8)	115·5 (2)	C(11)–C(7)–C(8)	120·2 (2)
C(7)–C(8)–C(9)	113·7 (3)	C(7)–C(8)–O(8)	110·0 (2)
C(9)–C(8)–O(8)	107·0 (3)	C(8)–C(9)–C(10)	116·1 (3)
C(1)–C(10)–C(9)	122·1 (3)	C(1)–C(10)–C(14)	123·2 (4)
C(9)–C(10)–C(14)	114·7 (4)	C(8)–O(8)–C(16)	118·8 (2)
O(8)–C(16)–O(16)	124·4 (3)	O(8)–C(16)–C(17)	110·5 (2)
O(16)–C(16)–C(17)	125·1 (3)	C(16)–C(17)–O(17)	112·9 (2)
C(16)–C(17)–C(18)	118·8 (2)	O(17)–C(17)–C(18)	59·4 (2)
C(16)–C(17)–C(20)	116·5 (2)	O(17)–C(17)–C(20)	115·8 (2)
C(18)–C(17)–C(20)	120·0 (3)	C(17)–O(17)–C(18)	61·3 (2)
C(17)–C(18)–O(17)	59·3 (2)	C(17)–C(18)–C(19)	125·8 (3)
O(17)–C(18)–C(19)	117·2 (3)		

Lorentz–polarization corrections; ψ-scan empirical absorption correction (transmission factors 0·399 to 0·440); structure solved by direct-methods techniques; block-cascade least-squares refinement; H atoms found in difference Fourier map, allowed to ride on attached atom, isotropic temperature parameters refined several cycles, then fixed; final $R = 0\cdot039$, $wR = 0\cdot045$, 236 parameters refined, $S = 1\cdot35$, $(\Delta/\sigma)_{max} = 0\cdot012$, largest peaks in the final difference Fourier map 0·19 and $-0\cdot14$ e Å^{-3}; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0\cdot0008 F_o^2]^{-1}$; free variable for absolute configuration refined to 1·1(1) (Rogers, 1981). $[\alpha]_D^{26\cdot'C} = -54\cdot5°$ (CHCl$_3$, c 0·33). All computer programs supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configuration (Nicolet Instrument Corporation, 1986); atomic scattering factors and anomalous-dispersion corrections contained in the program (*International Tables for X-ray Crystallography*, 1974). Table 1 lists atomic positional parameters while Table 2 lists interatomic distances and valence angles.*

Discussion. Fig. 1 is a thermal-ellipsoid drawing of the absolute configuration of (1). The absolute configuration is that normally observed for guaianolides (Klyne & Buckingham, 1974, 1978) although the opposite configuration at C(6) occurs in some plant genera (Pinar, Rodriguez, Rico, Peralez & Fayos, 1983). The cyclopentenone ring is in a highly flattened envelope conformation (Toromanoff, 1980) with a root-mean-square deviation from the plane of 0·03 Å. The cycloheptene ring is in a slightly distorted chair conformation with torsion angles at the juncture of the

* Lists of structure factors, H-atom parameters, anisotropic thermal parameters and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44137 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
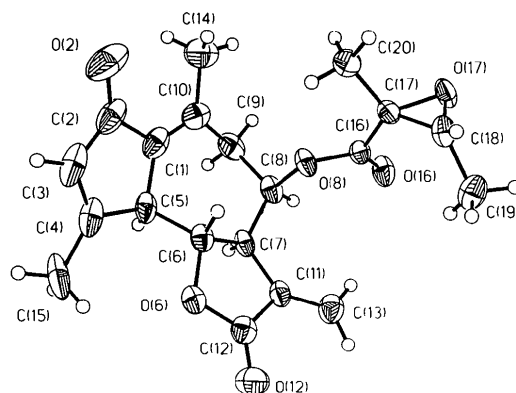

Fig. 1. Thermal-ellipsoid plot of (1). Thermal ellipsoids are drawn at the 35% probability level. H atoms are represented by spheres of arbitrary size.

two rings being 6·9 (4) and 60·4 (5)°. The γ-lactone ring is intermediate between envelope and half-chair conformations with torsion angles at the juncture with the seven-membered ring being −31·4 (3) and 72·4 (3)°. Several atoms exhibit relatively large thermal motion which may be rationalized in terms of a short $O(2)\cdots C(14)$ contact of 2·954 (6) Å. Librational corrections lead to increases in bond lengths of 0·006 to 0·009 Å.

Lactucin (Ruban, Zabel, Gensch & Smalla, 1978) is similar to (1) except for the substituent at C(8) being an α-hydroxyl with a second hydroxyl group attached to C(15). Lactucin has extensive hydrogen bonding in the crystal which leads to small but significant changes in torsion angles and in some distances compared to those observed in (1). The molecules of (1) are held together in the crystal by van der Waals forces leaving sufficient room for thermal motion of methyl groups and substituents.

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Structure of 1-Thia-5-azacyclononan-6-one

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Abstract. $2(C_7H_{13}NOS)$, $M_r = 318·50$, orthorhombic, Pbca, $a = 9·613$ (3), $b = 14·468$ (4), $c = 23·707$ (5) Å, $V = 3297·0$ (15) Å^3, $Z = 8$, $D_x = 1·283$ Mg m^{-3} at 130 K, $\lambda(Mo\,K\alpha) = 0·71069$ Å, $\mu = 0·31$ mm^{-1}, $F(000) = 1376$, $T = 130$ (1) K, $R = 0·037$ for 1677 observed reflections. The asymmetric unit contains two molecules linked by a hydrogen bond. Values of bond lengths and angles are normal.

Introduction. Transannular interactions between functional groups in medium-sized ring systems can be manifested by the observation of unusual spectroscopic properties or enhanced chemical reactivity. An interaction between the amine and ketone functions in 6-hydroxy-1-methyl-1-azacyclononan-5-one was revealed by a lowering of its carbonyl stretching frequency (Leonard, Fox & Oki, 1954). An interaction between a thioether and a sulfoxide was revealed by

X-ray analysis and manifested in the rapid reduction of 3-methoxy-1,5-dithiacyclooctane 1-oxide by HI to 3-methoxy-1,5-dithiacyclooctane (Doi, Kessler, DeLeeuw, Olmstead & Musker, 1983). In our recent studies of the oxidation of thioethers with aqueous iodine (Doi, Goodrow & Musker, 1986), we found that a transannular amide group in the nine-membered ring 1-thia-5-azacyclononan-6-one increased the rate of thioether oxidation by a factor of 100 relative to a simple thioether (Doi, Bharadwaj & Musker, 1987). To see whether a transannular interaction was partially responsible for this rate acceleration, the structure of this amide-thioether was determined.

Experimental. The title compound was obtained by Beckmann rearrangement (Nace & Watterson, 1966) of 5-thiacyclooctanone oxime p-toluenesulfonate (Wise, Morrison, Egan & Lattime, 1971) on alumina, m.p. 359–360 K. Suitable crystals were grown from toluene solution. Colorless rectangular plate 0·31 × 0·23 ×