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

O–C(16)	1·372 (4)	C(2)–C(3)–C(10)	109·6 (2)
N(1)–C(2)	1·505 (3)	C(2)–C(3)–C(14)	111·3 (2)
N(1)–C(5)	1·518 (4)	C(4)–C(3)–C(10)	111·8 (2)
N(1)–C(6)	1·497 (4)	C(4)–C(3)–C(14)	114·7 (2)
C(2)–C(3)	1·526 (4)	C(10)–C(3)–C(14)	108·8 (2)
C(3)–C(4)	1·534 (4)	C(3)–C(4)–C(5)	105·2 (2)
C(3)–C(10)	1·550 (4)	N(1)–C(5)–C(4)	105·5 (2)
C(3)–C(14)	1·525 (4)	N(1)–C(6)–C(7)	113·7 (2)
C(4)–C(5)	1·515 (4)	C(6)–C(7)–C(8)	121·1 (3)
C(6)–C(7)	1·490 (5)	C(6)–C(7)–C(9)	116·9 (3)
C(7)–C(8)	1·495 (5)	C(8)–C(7)–C(9)	59·7 (3)
C(7)–C(9)	1·494 (6)	C(7)–C(8)–C(9)	60·1 (3)
C(8)–C(9)	1·486 (6)	C(7)–C(9)–C(8)	60·2 (3)
C(10)–C(11)	1·537 (4)	C(3)–C(10)–C(11)	117·1 (3)
C(11)–C(12)	1·478 (7)	C(10)–C(11)–C(12)	112·3 (3)
C(11)–C(13)	1·502 (7)	C(10)–C(11)–C(13)	110·3 (3)
C(14)–C(15)	1·392 (4)	C(12)–C(11)–C(13)	107·9 (4)
C(14)–C(19)	1·393 (4)	C(3)–C(14)–C(15)	119·9 (3)
C(15)–C(16)	1·385 (4)	C(3)–C(14)–C(19)	121·4 (3)
C(16)–C(17)	1·384 (4)	C(15)–C(14)–C(19)	118·7 (3)
C(17)–C(18)	1·385 (5)	C(14)–C(15)–C(16)	120·6 (3)
C(18)–C(19)	1·393 (4)	O–C(16)–C(15)	117·7 (3)
C(2)–N(1)–C(5)	106·4 (2)	O–C(16)–C(17)	121·5 (3)
C(2)–N(1)–C(6)	115·7 (2)	C(15)–C(16)–C(17)	120·8 (3)
C(5)–N(1)–C(6)	112·1 (2)	C(16)–C(17)–C(18)	119·0 (3)
N(1)–C(2)–C(3)	104·7 (2)	C(17)–C(18)–C(19)	120·6 (3)
C(2)–C(3)–C(4)	100·4 (2)	C(14)–C(19)–C(18)	120·3 (3)

Hydrogen bonding

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N(1)–H(N)···Br	0·88 (3)	2·38 (3)	3·248 (2)	170 (3)
O–H(O)···Br′*	1·08 (4)	2·13 (4)	3·213 (3)	178 (4)

*Br′ at $\frac{1}{2}-x$, $1-y$, $z-\frac{1}{2}$.

In the pyrrolidine ring, the smallest torsion angle C(2)–N(1)–C(5)–C(4) is 2·1 (3)°, indicating near planarity for these four atoms, which deviate by a maximum of ±0·012 (3) Å from the mean plane through them. C(3) is −0·632 (2) Å from this plane. The pyrrolidine ring has the envelope conformation with the apex at C(3) [puckering parameters $q_2 = 0{\cdot}410$ Å and $\varphi_2 = 74{\cdot}8°$ (Cremer & Pople, 1975)]. The phenyl ring is planar with $\chi^2 = 5{\cdot}9$, and the O atom deviates from this plane by −0·028 (2) Å. The mean plane through the pyrrolidine ring makes dihedral angles of 56·7 (4)° with the cyclopropyl ring and 26·9 (4)° with the phenyl ring.

Molecules at (x,y,z) and ($\frac{1}{2}-x,1-y,\frac{1}{2}+z$) are interlinked through Br by two N–H(N)···Br···H(O)′–O′ hydrogen bonds into zigzag chains parallel to z. The geometry of these bonds is included in Table 3; angle H(N)···Br···H(O)′ is 93 (1)°. All other intermolecular distances are normal van der Waals interactions.

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Structure of (4βH,6βH,11αH)-3β,10β-Epoxy-8β-isobutyryloxy-1-oxogermacr-2-en-6,12-olide (Tetrahydrozexbrevin), $C_{19}H_{26}O_6$, a Sesquiterpenoid Lactone*

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Abstract. $M_r = 350{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}060$ (3), $b = 14{\cdot}080$ (3), $c = 14{\cdot}628$ (4) Å, $V = 1866$ (3) Å^3, $D_x = 1{\cdot}25$ Mg m^{-3}, $Z = 4$, $F(000) = 752$, $T = 293$ K, graphite-monochromated Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}723$ mm^{-1}, final $R = 0{\cdot}063$ for 1208 observed reflections. The cyclodecene ring adopts a chair–boat conformation with the C(4) and C(10) methyl groups oriented *anti* and is quasi-*trans* fused to the γ-lactone ring. The conformation of the 3(2*H*)-furanone ring is a flattened envelope with O(6) as the flap. Bond lengths are normal; bond angles indicate some strain in the molecule.

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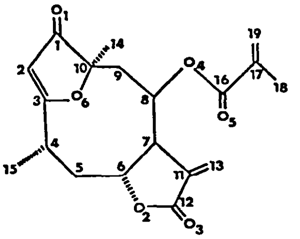
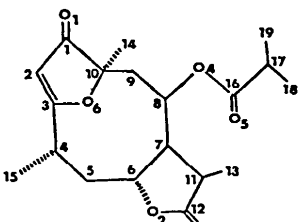
Introduction. The germacranolides are naturally occurring sesquiterpene lactones whose structure is based on 1-isopropyl-4,8-dimethylcyclodecane (germacrane) (Fischer, Olivier & Fischer, 1979). The structure and stereochemistry proposed for some of these have been confirmed, or partially revised, by X-ray crystallographic analysis (Herz & Blount, 1978). Zexbrevin is a heliangolide isolated from *Zexmenia brevifolia* (Romo de Vivar, Guerrero, Díaz & Ortega, 1970) and its structure (1) was deduced by chemical and spectroscopic means. Catalytic hydrogenation of zexbrevin (Pd/C, MeOH) gave the title compound (THZ) (2).



(1)



(2)

The 3(2*H*)-furanone moiety present in both (1) and (2) confers on them a high degree of conformational rigidity. It was of interest to study the crystal structure of THZ in order to ascertain its conformation and molecular geometry.

Experimental. Prismatic crystal $0{\cdot}14 \times 0{\cdot}16 \times 0{\cdot}28$ mm. Nicolet *R*3 four-circle diffractometer. Lattice parameters from 15 machine-centred reflections with $11{\cdot}6^\circ < 2\theta < 25{\cdot}3^\circ$. 1458 reflections with $3^\circ < 2\theta < 115^\circ$, 1208 independent with $I > 2{\cdot}5\sigma(I)$, index range h 0–9, k 0–15, l 0–15. ω-scan mode, variable scan speed, scan width $1{\cdot}0^\circ$ (θ). Two standard reflections monitored every 50 measurements. Lp correction, absorption ignored, anomalous-dispersion corrections applied to the scattering factors for the O and C atoms. Direct methods using *SHELXTL* (Sheldrick, 1981) gave the structure. Least-squares refinement of all non-H atoms treated anisotropically; H atoms riding on the bonded C with a fixed isotropic temperature factor, $U = 0{\cdot}06$ Å^2. $\sum w(\Delta F)^2$ minimized, $w = [\sigma^2(F_o) + G(F_o)^2]^{-1}$ with final $G = 0{\cdot}0040$. $(\Delta/\sigma)_{\max} < 0{\cdot}05$. Residual electron density within $\pm 0{\cdot}3$ e Å^{-3}. Isotropic-extinction parameter $X = 0{\cdot}012$. Final $R = 0{\cdot}063$, $wR = 0{\cdot}086$. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates are in Table 1.* A perspective molecular drawing of THZ is shown in Fig. 1. The bond lengths and angles for non-H atoms are listed in Table 2.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2 $\times 10^3$)

$$U_{\rm eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	$U_{\rm eq}$
O(1)	7333 (5)	11120 (3)	3100 (3)	62 (2)
O(2)	4621 (5)	9028 (3)	−616 (3)	61 (2)
O(3)	4576 (7)	7561 (4)	−1145 (4)	85 (2)
O(4)	5834 (4)	9386 (3)	1878 (3)	48 (1)
O(5)	6338 (5)	8487 (4)	3094 (3)	68 (2)
O(6)	7918 (4)	10962 (3)	723 (3)	48 (1)
C(1)	7264 (7)	11161 (4)	2264 (4)	45 (2)
C(2)	6168 (7)	11564 (4)	1681 (4)	49 (2)
C(3)	6574 (7)	11385 (4)	806 (4)	46 (2)
C(4)	5770 (7)	11476 (4)	−69 (4)	54 (2)
C(5)	5891 (8)	10493 (4)	−570 (4)	49 (2)
C(6)	5490 (6)	9640 (4)	8 (4)	43 (2)
C(7)	6753 (7)	8998 (4)	361 (4)	41 (2)
C(8)	7142 (6)	9068 (4)	1394 (4)	43 (2)
C(9)	8489 (7)	9629 (4)	1685 (4)	48 (2)
C(10)	8445 (7)	10717 (4)	1637 (4)	45 (2)
C(11)	6304 (8)	7995 (4)	61 (4)	54 (2)
C(12)	5119 (8)	8135 (5)	−639 (4)	61 (2)
C(13)	5666 (11)	7318 (5)	764 (5)	88 (3)
C(14)	4209 (8)	11809 (5)	66 (5)	72 (3)
C(15)	9920 (7)	11155 (5)	1791 (4)	62 (2)
C(16)	5567 (7)	9048 (5)	2720 (4)	58 (2)
C(17)	4208 (9)	9524 (7)	3118 (5)	87 (3)
C(18)	2908 (9)	9267 (9)	2609 (7)	118 (5)
C(19)	4127 (10)	9485 (7)	4110 (5)	94 (4)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O(1)–C(1)	1·225 (7)	O(2)–C(6)	1·483 (7)
O(2)–C(12)	1·336 (9)	O(3)–C(12)	1·200 (9)
O(4)–C(8)	1·451 (7)	O(4)–C(16)	1·343 (7)
O(5)–C(16)	1·188 (8)	O(6)–C(3)	1·360 (7)
O(6)–C(10)	1·462 (7)	C(1)–C(2)	1·427 (9)
C(1)–C(10)	1·542 (9)	C(2)–C(3)	1·355 (8)
C(3)–C(4)	1·478 (9)	C(4)–C(5)	1·569 (8)
C(4)–C(14)	1·503 (10)	C(5)–C(6)	1·513 (8)
C(6)–C(7)	1·546 (8)	C(7)–C(8)	1·555 (8)
C(7)–C(11)	1·534 (9)	C(8)–C(9)	1·515 (8)
C(9)–C(10)	1·534 (8)	C(10)–C(15)	1·489 (9)
C(11)–C(12)	1·497 (10)	C(11)–C(13)	1·516 (10)
C(16)–C(17)	1·518 (11)	C(17)–C(18)	1·439 (12)
C(17)–C(19)	1·454 (11)		
C(6)–O(2)–C(12)	112·5 (5)	C(8)–O(4)–C(16)	119·0 (5)
C(3)–O(6)–C(10)	108·3 (4)	O(1)–C(1)–C(2)	130·7 (6)
O(1)–C(1)–C(10)	122·6 (6)	C(2)–C(1)–C(10)	106·8 (5)
C(1)–C(2)–C(3)	107·6 (6)	O(6)–C(3)–C(2)	114·1 (5)
O(6)–C(3)–C(4)	113·7 (5)	C(2)–C(3)–C(4)	131·9 (6)
C(3)–C(4)–C(5)	107·1 (5)	C(3)–C(4)–C(14)	112·2 (5)
C(5)–C(4)–C(14)	113·7 (6)	C(4)–C(5)–C(6)	114·9 (5)
O(2)–C(6)–C(5)	104·2 (4)	O(2)–C(6)–C(7)	105·0 (4)
C(5)–C(6)–C(7)	118·2 (5)	C(6)–C(7)–C(8)	117·0 (5)
C(6)–C(7)–C(11)	104·3 (5)	C(8)–C(7)–C(11)	113·3 (5)
O(4)–C(8)–C(7)	108·0 (4)	O(4)–C(8)–C(9)	111·1 (5)
C(7)–C(8)–C(9)	119·3 (5)	C(8)–C(9)–C(10)	119·1 (5)
O(6)–C(10)–C(1)	102·8 (5)	O(6)–C(10)–C(9)	106·6 (4)
C(1)–C(10)–C(9)	113·3 (5)	O(6)–C(10)–C(15)	109·5 (5)
C(1)–C(10)–C(15)	111·4 (5)	C(9)–C(10)–C(15)	112·6 (5)
C(7)–C(11)–C(12)	105·3 (5)	C(7)–C(11)–C(13)	119·0 (5)
C(12)–C(11)–C(13)	105·9 (6)	O(2)–C(12)–O(3)	120·7 (7)
O(2)–C(12)–C(11)	110·4 (6)	O(3)–C(12)–C(11)	128·8 (7)
O(4)–C(16)–O(5)	123·5 (6)	O(4)–C(16)–C(17)	110·0 (6)
O(5)–C(16)–C(17)	126·4 (6)	C(16)–C(17)–C(18)	110·8 (7)
C(16)–C(17)–C(19)	114·0 (7)	C(18)–C(17)–C(19)	117·7 (8)

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39374 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The molecule consists of a cyclodecene ring incorporating a bridgehead enol ether system [C(3)—O(6)—C(10)] and a γ-lactone ring quasi-*trans* fused at C(6) and C(7).

The molecule is strained and distortion of bond angles is the key factor in strain relief. The average bond length and valence angle in the ten-membered ring are 1·503 (8) Å and 115·3 (5)°. The internal angles in the fragment from C(6) to C(9) reflect a deformation which may be due to the strain caused by the quasi-*trans* fusion of the γ-lactone.

The stereochemistry of THZ is described as follows: C(1)—βO(1) *cis* to C(10)—αCH_3; C(6)—βH *trans* to C(7)—αH; C(7)—αH *trans* to C(11)—βCH_3; C(7)—αH *trans* to C(8)—β(isobutyrate); *anti* relationship of methyl groups [C(14) and C(15)].

The cyclodecene ring adopts a chair–boat conformation. This type of conformation has been observed in X-ray studies of dihydroheliangine (Nishikawa, Kamiya, Takabatake, Oshio, Tomiie & Nitta, 1966) and in eupaformonin (McPhail & Onan, 1976).

The conformation of the 3(2*H*)-furanone ring can best be described as a flattened envelope with O(6) as the flap. The envelope is flattened by the planar α,β-unsaturated ketone moiety involving the endocyclic double bond [torsion angle O(1)—C(1)—C(2)—C(3) = 177·2 (5)°]. The mean of the five endocyclic torsion-angle moduli is 4·4° and the asymmetry parameter (Duax, Weeks & Rohrer, 1976) $\Delta C_s = 1{\cdot}9°$.

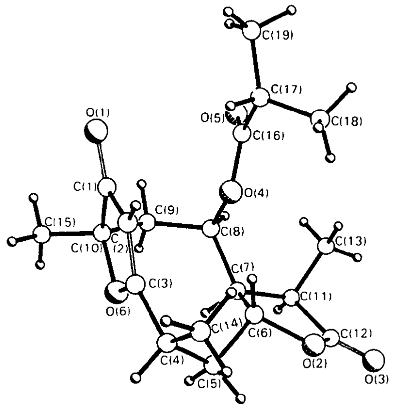

Fig. 1. A molecule of THZ showing the atom labelling.

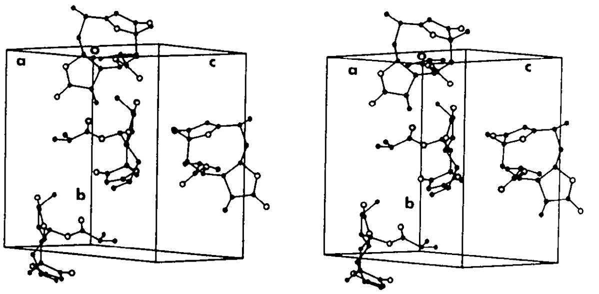

Fig. 2. Stereoscopic view of the molecular conformation and packing.

The γ-lactone ring approximates more closely to a half-chair conformation than to an envelope. A pseudo-diad runs through O(2) and the midpoint of the C(7)—C(11) bond. The mean of the five endocyclic torsion-angle moduli is 10·3° and the asymmetry parameter $\Delta C_2 = 2{\cdot}8°$.

The isobutyrate group is almost perpendicular to the ten-membered ring; the pertinent torsion angles are C(16)—O(4)—C(8)—C(9) = −82·7 (6), C(16)—O(4)—C(8)—C(7) = 144·7 (5) and C(16)—O(4)—C(8)—H(8) = 30°, placing the C=O group *syn* to the C(8)—H bond (Mathieson, 1965; Chothia & Pauling, 1970). It is interesting to note that O(4) is so oriented that one of its electron pairs in the sp^2-hybridized orbitals points towards H(6) [O(4)···H(6) 2·20 Å and C(6)—H(6)···O(4) 117·7°]. There is another short C—H···O contact involving C(7), which is 3·01 Å from O(6). The H(7)···O(6) distance of 2·64 Å together with the C(7)—H(7)···O(6) angle of 102·9° suggest that a weak C—H···O bond may occur. These interactions internally stabilize the conformation of the molecule.

The molecular packing is shown in Fig. 2. The arrangement of molecules in the crystal appears to be determined by van der Waals interactions.

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