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Molecular and Chiral Structure of (6*R*,7*S*,10*R*,11*S*)-1-Oxo-6*β*,7*α*,10*β*,11*β* H-germacr-4-en-6,12-olide, a Ketone Derivative of Gallicin

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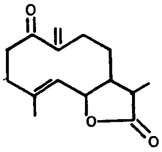
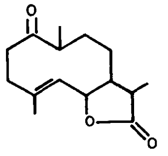
Abstract. $C_{15}H_{22}O_3$, $M_r = 250{\cdot}34$, orthorhombic, $P2_12_12_1$, $a = 14{\cdot}012\,(1)$, $b = 12{\cdot}986\,(1)$, $c = 7{\cdot}7028\,(3)$ Å, $V = 1401{\cdot}6\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}19$ g cm^{-3}, Cu $K\bar{\alpha}$, $\lambda = 1{\cdot}54178$ Å, $\mu = 6{\cdot}15$ cm^{-1}, $F(000) = 544$, $T = 295$ K. The structure was refined to an R factor of 0·045 including 1250 observed Friedel pairs. Refinement and Bijvoet indices establish the molecular chirality, which agrees with that of other germacranolides. The ten-membered ring has the conformation *CCC* typical of many germacranolides, although it is slightly distorted because of the substituents. The lactone ring has an envelope conformation.

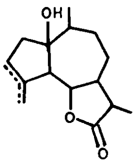
Introduction. This work forms part of a series of structural studies aimed at understanding the biogenetic-type cyclization processes of the natural product gallicin (González, Bermejo, Mansilla, Galindo, Amaro & Massanet, 1978) and its derivatives, to form germacranolides and guaianolides (González, Galindo & Mansilla, 1980).



(I)



(II)



(III)

The title compound, (II), results from the reduction with $NaBH_4$ of (I), another gallicin ketone whose conformation and absolute configuration have been determined in solution (González, Galindo, Mansilla & Palenzuela, 1983) and in the solid state (González *et al.*, 1985). The present structural study is justified in order to interpret the synthesis of guaianolides of type (III); this will aid in the understanding of the processes used in the biogenesis of guaianolides.

Experimental. Samples of (II) were kindly supplied by Professor A. Galindo (Univ. of La Laguna, Spain). Colourless crystals, 0·3 × 0·4 × 0·2 mm, Philips PW 1100 automatic diffractometer, $\omega/2\theta$ scan, graphite-monochromated Cu $K\bar{\alpha}$, 2804 (hkl and $\bar{h}\bar{k}\bar{l}$) reflexions up to $\theta = 65$, $|h| < 16$, $|k| < 15$, $|l| < 9$, 2500 with $I > 2\sigma(I)$, Lp corrections, absorption ignored. Two standard reflexions (440, $\bar{4}\bar{4}0$) monitored periodically showed <6% intensity variations. Lattice parameters determined by LS fit of θ values for 25 reflexions ($15 < \theta < 30°$) measured at 295 K for positive and negative Bragg angles (gravity centres of peaks), using only the most accurate circle (ω) of the diffractometer; errors associated with these values are obviously underestimates of real standard deviations, which may be as much as ten times those figures. Scattering factors for neutral atoms and anomalous-dispersion corrections for C and O atoms from *International Tables for X-ray Crystallography* (1974). Direct methods [*MULTAN*80 (Main *et al.*, 1980)], anisotropic full-matrix refinement on F, H atoms (from ΔF synthesis) isotropic, convenient weighting scheme to obtain flat dependence in $\langle w\Delta^2F\rangle$ *vs* $\langle F_o\rangle$ and *vs* $\langle \sin\theta/\lambda\rangle$ (Martínez-Ripoll & Cano, 1975), $w = w1 \times w2$, $w1 = k/(a + b|F_o|)^2$, $w2 = 1/(c + d\sin\theta/\lambda)$, $k = 0{\cdot}57$, $a = 0{\cdot}43$ and $b = -0{\cdot}07$ for $F_o < 5{\cdot}0$, $a = 1{\cdot}10$ and $b = -0{\cdot}22$ for $5{\cdot}0 < F_o < 8{\cdot}5$, $a = 0{\cdot}03$ and $b = 0{\cdot}05$ for $F_o > 8{\cdot}5$, $c = 2{\cdot}15$ and $d = -2{\cdot}63$. Final $R = 0{\cdot}045$ and $wR = 0{\cdot}056$. Max. $\Delta/\sigma = 0{\cdot}04$, max., min. height in $\Delta\rho$ map 0·2, −0·3 e Å^{-3}. The structural chirality was determined by comparing the $N = 45$ most relevant Bijvoet pairs with the conditions $I > 10\sigma(I)$ and $\Delta F_c > 0{\cdot}07$, average Bijvoet difference $\sum|[F_o(+h) - F_o(-h)] - [F_c(+h) - F_c(-h)]|/N$ of 0·222 (0·282 for the wrong enantiomer), average Bijvoet ratio $1 + \sum\big||F_o(+h)/F_o(-h)|/|F_c(+h)/F_c(-h)|-1\big|/N$ of 1·014 (1·024) and $\sum|[F_o(+h)^2 - F_o(-h)^2] - [F_c(+h)^2 - F_c(-h)^2]|/\sum|F_o(+h)^2 - F_o(-h)^2|$ of 0·952 (1·081) (Martínez-Ripoll & Fayos, 1980). Most programs from *XRAY*70 (Stewart, Kundell & Baldwin, 1970). Table 1 shows the final atomic parameters.*

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* Lists of structure factors, atomic parameters for H atoms, torsion angles, anisotropic thermal parameters and Bijvoet pairs have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42224 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. Fig. 1 is a perspective drawing (Johnson, 1965) of the final X-ray model, showing its structural chirality. A list of bond lengths and bond angles is given in Table 2. Torsion angles have been deposited as supplementary material.

The conformation of the ten-membered ring is *CCC* (Hendrickson, 1967), slightly distorted owing to the influence of the substituents. A projection of the ring is shown in Fig. 2. The double bond C(4)=C(5) makes the C(3)—C(4) and C(5)—C(6) bonds *trans*, the substituent C(14) is β-axial, C(15) equatorial and O(1) α-axial. The lactone ring, attached to C(6) and C(7) (Fig. 1), shows an envelope conformation, with C(7) at the flap, 0·577 (1) Å out of the plane defined by the other four atoms, although somewhat distorted towards a half-chair conformation [$Q_2 = 0{\cdot}364\ (2)$, $\varphi_2 = 30{\cdot}6\ (3)°$] (Cremer & Pople, 1975).

The conformation and structural chirality described for (II) agree with those found in (I) and in other germacranolides (Gómez-Rodríguez, 1984).

Table 1. *Atomic parameters for* $C_{15}H_{22}O_3$

$U_{eq} = \frac{1}{3}\{\sum[U_{ij}a^*_i a^*_j a_i a_j \cos(a_i,a_j)]\}$. Standard deviations are in parentheses.

	x	*y*	*z*	U_{eq}(Å$^2 \times 10^4$)
C(1)	0·3918 (1)	0·7091 (1)	0·4889 (3)	584 (6)
C(2)	0·3030 (1)	0·6494 (2)	0·5397 (3)	703 (7)
C(3)	0·2713 (1)	0·5836 (2)	0·3834 (3)	735 (7)
C(4)	0·3539 (1)	0·5187 (1)	0·3254 (3)	593 (6)
C(5)	0·4092 (1)	0·5528 (1)	0·1979 (2)	499 (5)
C(6)	0·5067 (1)	0·5163 (1)	0·1548 (2)	487 (5)
C(7)	0·5838 (1)	0·5976 (1)	0·1827 (2)	448 (5)
C(8)	0·6180 (1)	0·6107 (2)	0·3709 (2)	616 (6)
C(9)	0·5760 (1)	0·6984 (2)	0·4783 (3)	642 (6)
C(10)	0·4838 (1)	0·6793 (1)	0·5779 (2)	477 (5)
C(11)	0·6611 (1)	0·5595 (1)	0·0559 (2)	491 (5)
C(12)	0·6018 (1)	0·5124 (1)	−0·0881 (2)	524 (5)
C(13)	0·7320 (1)	0·6386 (2)	−0·0068 (3)	638 (6)
C(14)	0·3731 (2)	0·4242 (2)	0·4303 (3)	864 (9)
C(15)	0·4832 (2)	0·7396 (2)	0·7497 (3)	641 (7)
O(1)	0·3888 (1)	0·7787 (1)	0·3846 (3)	937 (7)
O(6)	0·5127 (1)	0·4924 (1)	−0·0314 (2)	554 (4)
O(12)	0·6249 (1)	0·4946 (1)	−0·2350 (2)	717 (5)

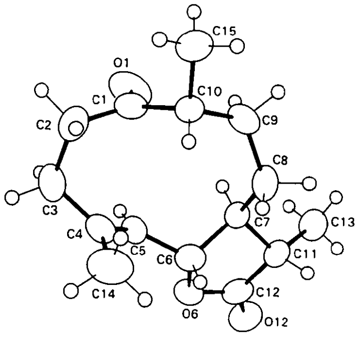

Fig. 1. Final X-ray model showing the structural chirality.

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Table 2. *Bond lengths* (Å) *and bond angles* (°) *for* $C_{15}H_{22}O_3$

Standard deviations are in parentheses.

C(1)—C(2)	1·517 (3)	C(7)—C(8)	1·536 (2)
C(1)—C(10)	1·510 (3)	C(7)—C(11)	1·540 (2)
C(1)—O(1)	1·210 (3)	C(8)—C(9)	1·526 (3)
C(2)—C(3)	1·542 (3)	C(9)—C(10)	1·523 (3)
C(3)—C(4)	1·500 (3)	C(10)—C(15)	1·537 (3)
C(4)—C(5)	1·327 (3)	C(11)—C(12)	1·515 (2)
C(4)—C(14)	1·494 (3)	C(11)—C(13)	1·509 (3)
C(5)—C(6)	1·483 (2)	C(12)—O(6)	1·348 (2)
C(6)—C(7)	1·526 (2)	C(12)—O(12)	1·200 (2)
C(6)—O(6)	1·470 (2)		
C(10)—C(1)—O(1)	121·5 (2)	C(8)—C(7)—C(11)	115·5 (1)
C(2)—C(1)—O(1)	121·6 (2)	C(7)—C(8)—C(9)	118·4 (2)
C(2)—C(1)—C(10)	116·9 (2)	C(8)—C(9)—C(10)	118·6 (2)
C(1)—C(2)—C(3)	108·6 (2)	C(1)—C(10)—C(9)	117·0 (2)
C(2)—C(3)—C(4)	108·7 (2)	C(9)—C(10)—C(15)	110·8 (2)
C(3)—C(4)—C(14)	116·0 (2)	C(1)—C(10)—C(15)	104·9 (2)
C(3)—C(4)—C(5)	118·9 (2)	C(7)—C(11)—C(13)	116·6 (1)
C(5)—C(4)—C(14)	124·7 (2)	C(7)—C(11)—C(12)	102·0 (1)
C(4)—C(5)—C(6)	126·6 (2)	C(12)—C(11)—C(13)	113·7 (2)
C(5)—C(6)—O(6)	109·8 (1)	C(11)—C(12)—O(12)	128·3 (2)
C(5)—C(6)—C(7)	113·5 (1)	C(11)—C(12)—O(6)	110·4 (1)
C(7)—C(6)—O(6)	104·1 (1)	O(6)—C(12)—O(12)	121·3 (2)
C(6)—C(7)—C(11)	100·7 (1)	C(6)—O(6)—C(12)	109·2 (1)
C(6)—C(7)—C(8)	115·5 (1)		

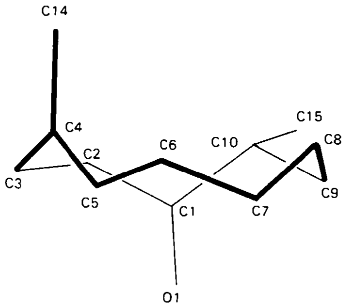

Fig. 2. Projection of the ten-membered ring onto the plane normal to the best ring plane.

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6-Diethylamino-1-dimethylthiocarbamoyl-5-methyl-3-phenyl-1*H*-pyridazin-4-one (I), $C_{18}H_{24}N_4OS$, and 5-Diethylthiocarbamoyl-6-dimethylamino-5-methyl-3-phenyl-5*H*-pyridazin-4-one (II), $C_{18}H_{24}N_4OS$*

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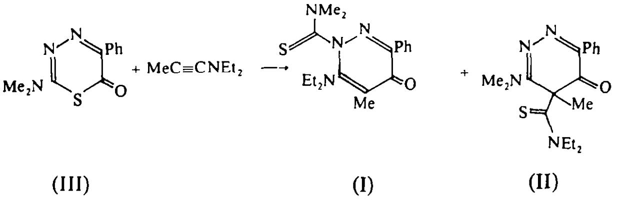
Abstract. (I): $M_r = 344{\cdot}5$, monoclinic, $P2_1/c$, $a = 13{\cdot}210\,(1)$, $b = 10{\cdot}353\,(1)$, $c = 14{\cdot}386\,(1)$ Å, $\beta = 110{\cdot}586\,(3)°$, $V = 1841{\cdot}8\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}242$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 1{\cdot}61$ mm^{-1}, $F(000) = 736$, $T = 293\,(1)$ K, final $R = 0{\cdot}069$ for 2432 significant reflections. (II): $M_r = 344{\cdot}5$, monoclinic, $P2_1/n$, $a = 11{\cdot}154\,(1)$, $b = 14{\cdot}943\,(1)$, $c = 11{\cdot}066\,(1)$ Å, $\beta = 102{\cdot}239\,(3)°$, $V = 1802{\cdot}5\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}269$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 1{\cdot}65$ mm^{-1}, $F(000) = 736$, $T = 293\,(1)$ K, final $R = 0{\cdot}054$ for 2446 significant reflections. Both compounds are formed by the reaction of 2-dimethylamino-5-phenyl-1,3,4-thiadiazin-6-one with 1-(diethylamino)propyne. Whereas in (I) the six-membered heterocyclic ring is planar, in (II), with a tetrahedral C atom at the 5-position, there is considerable ring puckering and incomplete conjugation over the remaining ring atoms is quite pronounced.

Introduction. We recently reported (Baydar, Boyd & Lindley, 1981) that the novel 1,3,4-thiadiazinone (III) reacted with 1-(diethylamino)propyne to yield a mixture of the rearranged adducts (I) and (II). Compound (II) is particularly interesting, as it is not fully conjugated; such 5*H*-pyridazin-4-ones have not been described previously. We now give details of the X-ray analyses and molecular structures of the two isomeric adducts.



(III) (I) (II)

Experimental. X-ray data collection and refinement details are listed in Table 1. Details of the preparation of compounds (I) and (II) and spectroscopic data have

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* IUPAC names: (I) 6-Diethylamino-*N*,*N*,5-trimethyl-4-oxo-3-phenyl-1,4-dihydro-1-pyridazinecarbothioamide. (II) 3-Dimethylamino-*N*,*N*-diethyl-4-methyl-5-oxo-6-phenyl-4,5-dihydro-4-pyridazinecarbothioamide.

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