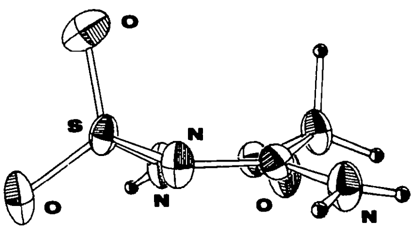

Fig. 1. Conformation bateau.

N(2), C(3), C(5) et N(6). Ces distances, exprimées en ångströms, sont en effet: S(1)–p0 = +0,456 (1); N(2)–p0 = +0,012 (3); C(3)–p0 = –0,012 (3); C(5)–p0 = +0,350 (3); C(5)–p0 = –0,012 (3); N(6)–p0 = +0,012 (3).

La configuration bateau (Fig. 1) est également mise en évidence par la mesure des angles entre le plan p0 et les plans p1 et p2 définis par les atomes N(2), S(1), N(6) d'une part et C(3), C(4), C(5) d'autre part. Ces angles sont respectivement de 27,5 (2) et 25,3 (3)°.

On relève plusieurs contacts intermoléculaires qui peuvent expliquer la densité élevée du cristal étudié comme le montrent les proximités minimums suivantes données en ångströms: N(8)···O(12$^{\rm i}$) = 2,893 (2), N(8)···O(11$^{\rm ii}$) = 3,005 (2), O(11)···H(82$^{\rm i}$) = 2,17 (2), O(12)···H(81$^{\rm ii}$) = 2,02 (2), les codes d'opérations de symétries étant: (i) x,y,z et (ii) x, 0,5–y, 0,5–z. Cependant aucun de ces contacts ne satisfait aux conditions angulaires permettant d'envisager des liaisons hydrogène (valeurs toujours très en dehors de la fourchette 170–175°), contrairement au sel de monopotassium déjà cité (Cabezuelo *et al.*, 1978). La Fig. 2 donne l'èmpilement cristallin.

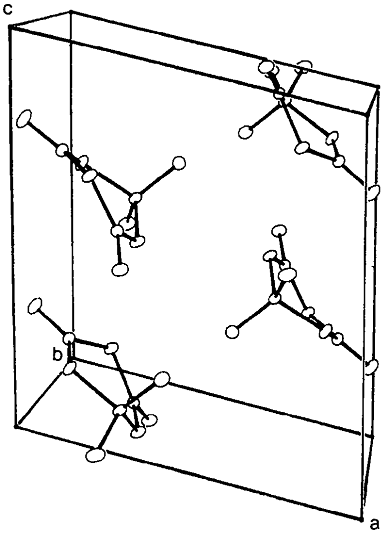

Fig. 2. Empilement cristallin.

Références

Cabezuelo, M. D., Foces-Foces, C., Cano, F. H. & García-Blanco, S. (1978). *Acta Cryst.* B**34**, 3069–3070.

Frenz, B. A. (1978). Dans *Computing in Crystallography*, edité par H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

International Tables for X-ray Crystallography (1974). Tome IV. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. de York, Angleterre, et Louvain, Belgique.

Acta Cryst. (1986). C**42**, 894–896

Molecular and Chiral Structure of (4*R*,6*S*,7*S*,11*S*)-5-Oxo-4β,6β,7α,11βH-germacran-1(10)-en-12,6-olide, a Derivative of Gallicin

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Abstract. $C_{15}H_{22}O_3$, $M_r = 250{\cdot}34$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}184$ (1), $b = 26{\cdot}236$ (6), $c = 6{\cdot}573$ (1) Å, $V = 1411{\cdot}3$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}18$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 0{\cdot}611$ mm^{-1}, $F(000) = 544$, $T = 295$ K, structure refined to $R = 0{\cdot}046$ including 600 observed Friedel pairs. Refinement and Bijvoet indices establish the molecular chirality. The conformation of the main ring is *CCC* and the molecular chirality is the same as that found in many other germacranolides. The five-membered ring is an envelope conformation.

Introduction. The present compound, (II), has been prepared by Professor A. Galindo and co-workers

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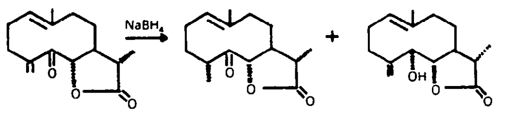
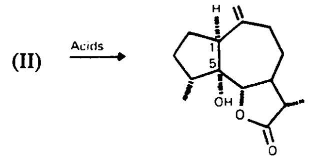
(Univ. of La Laguna, Spain) by reduction with $NaBH_4$ of compound (I), another gallicin ketone whose conformation and chiral structure have been described (González *et al.*, 1985). Alcohol (III) is also obtained in the same reaction.



(I) (II) (III)



(IV)

The main purpose of this study is to interpret the stereochemical cyclization process of the title compound to form guaiane derivatives of type (IV), and to study the relationship between the reactive conformation and the chiral structure of the chiral centres, C(1) and C(5), created in the process. Chemical data and the conformation of the title compound in solution will be published later.

Other work aimed at understanding 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), have been carried out. The conformations and chiral structures of several of these derivatives have been determined recently (Gómez-Rodríguez, 1984; González *et al.*, 1985), in solution and in the solid state.

Experimental. Samples of (II) were kindly supplied by Professor A. Galindo (Univ. of La Laguna, Spain). Colourless crystals, 0·4 × 0·5 × 0·5 mm. Philips PW 1100 automatic diffractometer, $\theta < 65°$, $\omega/2\theta$ scan technique. Cu $K\alpha$ radiation monochromatized by graphite. 2504 reflexions (hkl and $\bar{h}\bar{k}\bar{l}$) collected, $|h| < 9$, $|k| < 29$, $|l| < 7$, 1200 with $I > 2\sigma(I)$ used. Two standard intensity and orientation reflexions (080, 0$\bar{8}$0) measured every 90 min: no significant variation (<6%). Data corrected for absorption (Walker & Stuart, 1983) with minimum and maximum absorption corrections of 0·927 and 1·175, respectively, Lp correction. Lattice parameters determined by least-squares fit of the θ values for 25 reflexions ($15° < \theta < 30°$) measured at 295 K for both positive and negative Bragg angles (gravity centres of the peaks), using only the most accurate circle (ω) of the diffractometer. Structure solved by direct methods with *MULTAN*80 (Main *et al.*, 1980). Remaining calculations with *XRAY*70 (Stewart, Kundell & Baldwin, 1970). H atoms located in difference map. Refinement (non-H atoms anisotropic, H atoms fixed) by full-matrix least squares, minimizing $\sum w|\Delta F|^2$ with unit weights. Final $R = 0·046$, $wR = 0·045$ and $S = 0·900$. $(\Delta/\sigma)_{max} = 0·004$. Maximum height in $\Delta\rho$ map 0·2 e Å^{-3}, minimum −0·3 e Å^{-3}. Scattering factors for neutral atoms and anomalous-dispersion corrections for C and O atoms from *International Tables for X-ray Crystallography* (1974).

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

$U_{eq} = \frac{1}{3}[\sum U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j\cos(\mathbf{a}_i,\mathbf{a}_j)] \times 10^3$. Standard deviations in parentheses.

	x	y	z	U_{eq}(Å^2)
C(1)	0·5368 (8)	0·0368 (2)	0·5621 (9)	61 (2)
C(2)	0·4775 (9)	0·0172 (2)	0·3583 (12)	85 (3)
C(3)	0·3273 (11)	0·0451 (3)	0·2912 (3)	112 (4)
C(4)	0·3259 (9)	0·0990 (2)	0·2947 (9)	80 (3)
C(5)	0·3319 (8)	0·1215 (2)	0·5105 (9)	57 (2)
C(6)	0·4568 (6)	0·1642 (2)	0·5438 (8)	48 (2)
C(7)	0·5214 (7)	0·1694 (2)	0·7631 (8)	44 (2)
C(8)	0·6870 (7)	0·1457 (2)	0·8101 (9)	61 (2)
C(9)	0·6929 (8)	0·0872 (2)	0·8060 (9)	72 (3)
C(10)	0·6684 (8)	0·0641 (2)	0·6018 (10)	58 (2)
C(11)	0·5239 (7)	0·2275 (2)	0·7908 (7)	47 (2)
C(12)	0·3958 (7)	0·2461 (2)	0·6454 (9)	56 (2)
C(13)	0·4969 (7)	0·2467 (2)	1·0098 (9)	64 (2)
C(14)	0·1881 (8)	0·1252 (2)	0·1845 (9)	75 (3)
C(15)	0·7995 (7)	0·0753 (2)	0·4475 (10)	75 (3)
O(5)	0·2342 (5)	0·1114 (2)	0·6397 (7)	77 (2)
O(6)	0·3655 (5)	0·2107 (1)	0·5032 (6)	64 (1)
O(12)	0·3257 (5)	0·2866 (1)	0·6448 (6)	80 (2)

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

Standard deviations in parentheses.

C(1)—C(2)	1·515 (10)	C(7)—C(8)	1·524 (8)
C(1)—C(10)	1·321 (9)	C(7)—C(11)	1·534 (7)
C(2)—C(3)	1·498 (11)	C(8)—C(9)	1·535 (7)
C(3)—C(4)	1·414 (9)	C(9)—C(10)	1·486 (9)
C(4)—C(5)	1·537 (9)	C(10)—C(15)	1·505 (9)
C(4)—C(14)	1·507 (9)	C(11)—C(12)	1·500 (8)
C(5)—C(6)	1·533 (8)	C(11)—C(13)	1·541 (8)
C(5)—O(5)	1·196 (8)	C(12)—O(6)	1·342 (7)
C(6)—C(7)	1·541 (7)	C(12)—O(12)	1·207 (7)
C(6)—O(6)	1·454 (6)		

C(2)—C(1)—C(10)	128·3 (6)	C(8)—C(7)—C(11)	111·7 (4)
C(1)—C(2)—C(3)	111·0 (6)	C(7)—C(8)—C(9)	115·6 (5)
C(2)—C(3)—C(4)	119·4 (7)	C(8)—C(9)—C(10)	114·8 (5)
C(3)—C(4)—C(14)	117·0 (6)	C(1)—C(10)—C(9)	120·7 (6)
C(3)—C(4)—C(5)	113·5 (5)	C(9)—C(10)—C(15)	115·7 (5)
C(5)—C(4)—C(14)	107·0 (5)	C(1)—C(10)—C(15)	123·6 (6)
C(4)—C(5)—O(5)	123·3 (5)	C(7)—C(11)—C(13)	115·7 (4)
C(4)—C(5)—C(6)	115·7 (5)	C(7)—C(11)—C(12)	103·8 (4)
C(6)—C(5)—O(5)	120·4 (5)	C(12)—C(11)—C(13)	112·8 (5)
C(5)—C(6)—O(6)	104·1 (4)	C(11)—C(12)—O(12)	128·4 (5)
C(5)—C(6)—C(7)	115·3 (4)	C(11)—C(12)—O(6)	110·3 (5)
C(7)—C(6)—O(6)	105·9 (4)	O(6)—C(12)—O(12)	121·3 (5)
C(6)—C(7)—C(11)	101·7 (4)	C(6)—O(6)—C(12)	110·9 (4)
C(6)—C(7)—C(8)	117·3 (4)		

Discussion. Table 1 contains a list of atomic parameters.* 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. Torsional angles have been deposited.

The ten-membered ring has a *CCC* conformation (Hendrickson, 1967), although slightly distorted owing to the influence of the substituents, as can be seen from the least-squares-plane's calculations, and the torsion angles. The double bond C(1)=C(10) makes the C(2)—C(1) and C(9)—C(10) bonds *trans*. The substituent C(15) is β-axial, C(14) equatorial and O(5) α-axial. A projection of the main ring is shown in Fig. 2. The lactone ring, attached to C(6) and C(7) (Fig. 1), shows an envelope conformation, with C(7) at the flap, 0·420 (5) Å out of the plane defined by the other four atoms, although somewhat distorted in the sense of a half-chair conformation [$Q_2 = 0{\cdot}268\,(5)$ Å, $\varphi_2 = 44\,(1)°$] (Cremer & Pople, 1975).

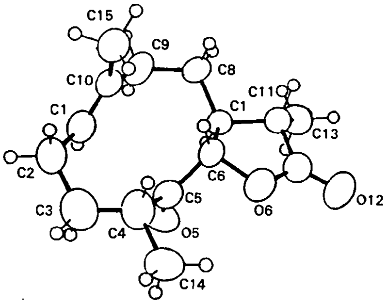


Fig. 1. Final X-ray model showing the structural chirality.

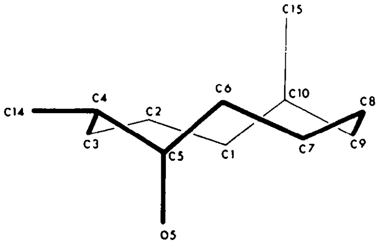


Fig. 2. Projection of the ten-membered ring onto the plane normal to the best ring plane.

The structural chirality was determined by comparing the 56 most relevant Bijvoet pairs with the conditions $F_o > 10\sigma(F_o)$ and $|\Delta F_c| > 0{\cdot}08$. The calculated Friedel differences for F_c show a very small anomalous-dispersion effect. Thus, the 56 most relevant Bijvoet pairs were carefully remeasured, using all equivalent reflexions and a very low scan speed (internal consistency 0·016). This led to an average Bijvoet difference: $\sum|[F_o(+h)-F_o(-h)]-[F_c(+h)-F_c(-h)]|/N$ of 0·119 (0·316 for the wrong enantiomer), and an average Bijvoet ratio: $1+\sum\big||F_o(+h)/F_o(-h)|/|F_c(+h)/F_c(-h)|-1\big|/N$ of 1·008 (1·021) and to $\sum|[F_o(+h)^2-F_o(-h)^2]-[F_c(+h)^2-F_c(-h)^2]|/\sum|F_o(+h)^2-F_o(-h)^2| = 0{\cdot}561$ (1·567) (Martínez-Ripoll & Fayos, 1980). Moreover, the technique of determining the chirality during the least-squares refinement, as suggested by Rogers (1981), has also been used. Thus, the f'' for the O atoms was allowed to vary in the last stages of refinement and converged to a value of $\eta = 1{\cdot}344\,(31)$. This chirality agrees with that found in other germacranolides (Gómez-Rodriguez, 1984).

Atoms C(1) and C(5) have their substituents in α-positions, as is found in the guaiane derivative (IV) obtained from the present compound.

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References

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Gómez-Rodríguez, M. A. (1984). Thesis. Univ. Complutense Madrid, Spain.

González, A. G., Bermejo, J., Mansilla, H., Galindo, A., Amaro, J. M. & Massanet, G. M. (1978). *J. Chem. Soc. Perkin Trans.* 1, pp. 1243–1246.

González, A. G., Galindo, A. & Mansilla, H. (1980). *Tetrahedron*, **36**, 2015–2017.

González, A. G., Galindo, A., Mansilla, H., Gutiérrez, A., Cabrera, I., Gómez-Rodriguez, M. A., Martínez-Ripoll, M. & García-Blanco, S. (1985). *J. Chem. Soc. Perkin Trans.* 2. In the press.

Hendrickson, J. B. (1967). *J. Am. Chem. Soc.* **89**, 7036.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Martínez-Ripoll, M. & Fayos, J. (1980). *Z. Kristallogr.* **152**, 189–194.

Rogers, D. (1981). *Acta Cryst.* A**37**, 734–741.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The *XRAY70* system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

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* Lists of structure factors, atomic parameters for H-atoms, torsional angles, anisotropic displacement parameters and Bijvoet pairs have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42838 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.