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Structure and Absolute Configuration of (23*R*)-6 α -Chloro-5 β ,17 β -dihydroxy-12 β -methoxy-1-oxo-12,22-epoxyergosta-2,24-dien-23,26-olide, a New Withanolide from *Jaborosa magellanica*

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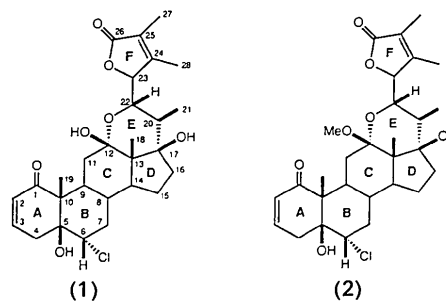
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Abstract. C₂₉H₃₉ClO₇, *M_r* = 535.08, orthorhombic, *P*2₁2₁2₁, *a* = 8.944 (4), *b* = 11.906 (4), *c* = 25.443 (6) Å, *V* = 2709 (3) Å³, *Z* = 4, *D_x* = 1.312 Mg m⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 0.182 mm⁻¹, *F*(000) = 1144, *T* = 293 (1) K, *R* = 0.0374 for 2337 observed reflections with *I* > 3σ(*I*). The crystal structure consists of discrete molecules of the title compound separated by normal van der Waals distances. Ring *A* is in a half-chair conformation, rings *B*, *C* and *E* are regular chairs, and ring *D* is a C(13) envelope; the lactone ring *F* has a nearly planar conformation. Atoms C(18) and C(19), both the hydroxyl groups, and the methoxyl group are all β, and Cl and the lactone moiety are α oriented. The bond lengths and angles are in accord with accepted values.

Introduction. The withanolides are a group of oxygenated steroidal lactones found among members of the Solanaceae (Tursunova, Maslennikova & Abubakirov, 1977; Kamernitskii, Reshetova & Krivoruchko, 1977; Vasina, Maslennikova & Abubakirov, 1986). Our continued investigations of *Jaborosa magellanica* (Griseb.) Dusen (Solanaceae) whole plants, collected along the Strait of Magellan, Chile, has yielded a new chlorowithanolide, (+)-

jaborochlorotriol, (1), containing a hemiacetal ring (Fajardo, Podesta & Shamma, 1990). During the isolation of (1), a new withanolide (2), was also isolated as a minor product and its crystal structure and absolute configuration were determined by the X-ray method.



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Experimental. Colorless prismatic crystals of (2) for X-ray study were grown by slow evaporation of a methanol solution at room temperature. A crystal of approximate dimensions 0.35 × 0.25 × 0.43 mm was used for data collection. Cell parameters and crystal orientation matrix were determined on an Enraf-Nonius CAD-4 diffractometer by a least-squares refinement of the setting angles of 25 reflections with 10 < θ < 15°. Intensity data were collected by the ω/2θ scan method using variable scan speed (1.10–

Table 1. Final fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

	x	y	z	B_{iso}^*
Cl	5779 (1)	-460 (1)	8925 (1)	56 (1)
O(1)	4025 (4)	3542 (2)	7426 (1)	57 (1)
O(2)	4783 (4)	665 (2)	7865 (1)	54 (1)
O(3)	6136 (2)	5379 (2)	9003 (1)	32 (1)
O(4)	3868 (3)	6320 (2)	9036 (1)	40 (1)
O(5)	4173 (3)	6368 (2)	10204 (1)	49 (1)
O(6)	8936 (3)	4778 (2)	9281 (1)	44 (1)
O(7)	9698 (4)	3462 (3)	8715 (1)	66 (2)
C(1)	4878 (5)	3053 (3)	7714 (1)	44 (2)
C(2)	6480 (5)	3077 (3)	7619 (2)	54 (2)
C(3)	7419 (5)	2396 (4)	7864 (2)	56 (2)
C(4)	6940 (4)	1553 (3)	8268 (2)	48 (2)
C(5)	5229 (4)	1364 (3)	8287 (1)	38 (2)
C(6)	4767 (4)	842 (3)	8817 (2)	42 (2)
C(7)	5015 (4)	1605 (3)	9287 (1)	38 (2)
C(8)	4297 (4)	2763 (2)	9220 (1)	33 (1)
C(9)	4729 (3)	3278 (3)	8686 (1)	31 (1)
C(10)	4350 (4)	2473 (3)	8215 (1)	35 (2)
C(11)	4103 (3)	4471 (3)	8612 (1)	33 (2)
C(12)	4564 (3)	5253 (2)	9055 (1)	30 (1)
C(13)	4169 (3)	4752 (2)	9589 (1)	32 (1)
C(14)	4846 (3)	3572 (3)	9640 (1)	32 (1)
C(15)	4641 (5)	3304 (3)	10229 (1)	44 (2)
C(16)	4751 (4)	4466 (3)	10498 (1)	43 (2)
C(17)	4919 (4)	5343 (3)	10059 (1)	38 (2)
C(18)	2459 (4)	4736 (3)	9664 (1)	42 (2)
C(19)	2656 (4)	2257 (3)	8173 (2)	43 (2)
C(20)	6583 (4)	5588 (3)	9957 (1)	39 (2)
C(21)	7208 (5)	6400 (4)	10368 (2)	57 (2)
C(22)	6870 (4)	6032 (3)	9398 (1)	36 (2)
C(23)	8507 (4)	5943 (3)	9249 (2)	44 (2)
C(24)	8877 (4)	6281 (3)	8698 (2)	46 (2)
C(25)	9384 (4)	5384 (3)	8440 (2)	48 (2)
C(26)	9375 (4)	4431 (3)	8795 (2)	47 (2)
C(27)	9853 (5)	5259 (4)	7874 (2)	70 (3)
C(28)	8663 (6)	7467 (4)	8516 (2)	68 (3)
C(29)	3895 (6)	6889 (3)	8548 (2)	59 (2)

$$* B_{\text{iso}} = [8\pi^2/3(U_{11} + U_{22} + U_{33})].$$

$3.30^\circ \text{ min}^{-1}$), scan width of $(0.70 + 0.35 \tan \theta)^\circ$, and monochromated radiation in the range $2 < \theta < 25^\circ$ with $h \leq 10$, $k \leq 14$ and $l \leq 30$. Three reflections were monitored every 2 h of exposure time and showed no significant intensity variations. The intensities of 2722 unique reflections were measured, of which 2337 had $I > 3\sigma(I)$, where $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$, $S = \text{scan count}$ and $B = \text{time-averaged background count}$ extended 25% on each side. Data were corrected for Lorentz and polarization effects; absorption was ignored.

The structure was solved by the direct methods using *MULTAN82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and refined by full-matrix least-squares calculations employing F^2 's with anisotropic temperature factors for the non-H atoms. A difference Fourier synthesis calculated at an intermediate stage of the refinement revealed all H atoms. These were included in the refinement with idealized geometry (C—H and O—H 0.95 Å) and overall isotropic temperature factors for different types of H atoms in subsequent refinement. Atomic scattering factors for non-H atoms were taken from Cromer & Mann (1968), and those for hydrogen were from Stewart, Davidson & Simpson (1965). At this point parallel and independent

refinement calculations were carried out on the two stereoisomers of the molecule, and anomalous-dispersion corrections for Cl (Cromer & Liberman, 1970) were applied to both.

After five cycles of full-matrix refinement, convergence was reached and one configuration gave $R = 0.0374$ and $wR = 0.0458$ [$w = 1/(\sigma^2 F + 0.0017 F^2)$], whereas the other gave $R = 0.0387$ and $wR = 0.0479$. A statistical test on the wR -factor ratio (Hamilton, 1965) indicated that the latter stereoisomer could be rejected at the 0.005 significance level. Accordingly, all coordinates reported here refer to the statistically favored configuration. At the conclusion of the refinement, $(\Delta/\sigma)_{\text{max}} < 0.10$, the difference electron density map was essentially featureless with $\Delta\rho = -0.19$ to 0.22 e \AA^{-3} .

The computer programs used in this study were from the Enraf-Nonius *Structure Determination*

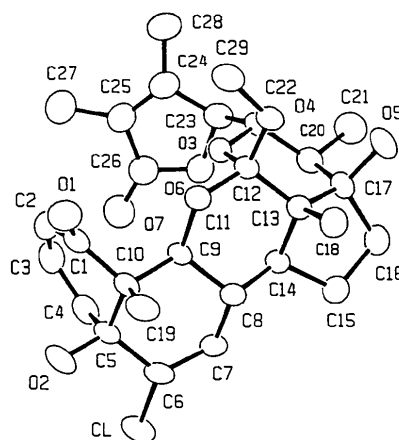


Fig. 1. A stereoview of the molecular structure of the title compound with the crystallographic numbering scheme.

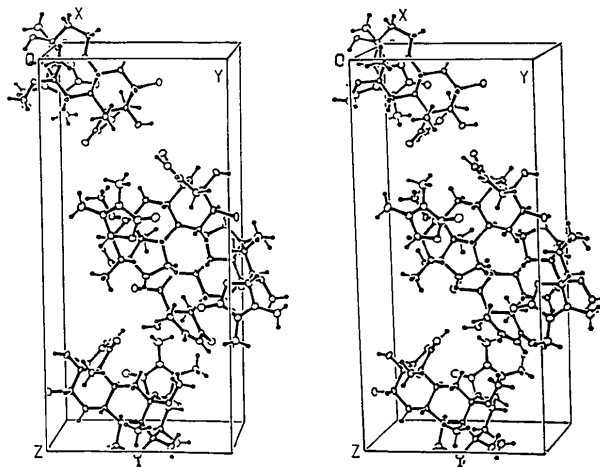


Fig. 2. A stereoview of the unit cell showing the molecular packing.

Package (B. A. Frenz & Associates, Inc., 1985), *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1976). Final fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s are given in Table 1.*

Discussion. Our X-ray analysis unequivocally establishes the molecular structure and absolute stereochemistry of the title compound. A view of the molecule is given in Fig. 1 with the crystallographic numbering scheme. The molecular dimensions are in accord with accepted values, mean bond lengths being C(sp³)—C(sp³) 1.537 (12) [range 1.516 (3)–1.573 (3) Å], C(sp³)—C(sp²) 1.505 (12), C(sp²)—C(sp²) 1.451 (3), C(sp²)=C(sp²) 1.328 (7), C(sp³)—O 1.425 (12), C(sp²)—O 1.362 (3) and C=O 1.208 (3) Å. Similar bond lengths have been reported in the structure of (+)-jaborosalactone M (Parvez, Fajardo & Shamma, 1988) which has an identical ring skeleton with different ring conformations of rings *A* and *B* than those observed in (2).

In the molecule of (2), ring *A* has a half-chair conformation; it is a twist boat in (+)-jaborosalactone M. Ring *B* is *cis* fused to ring *A* and has a chair conformation with an 8β,9α orientation while it is a half chair in (+)-jaborosalactone M. Rings *C* and *E* also have regular chair conformations. The five-membered ring *D*, which is *cis* fused to ring *C*, has a C(13) envelope conformation with C(13) 0.707 (3) Å above the plane C(14)–C(17). The lac-

tone moiety, ring *F*, is nearly planar, with maximum deviation of 0.021 (4) Å. The methyl groups, C(18) and C(19), the hydroxyl groups, O(2) and O(5) and the methoxyl group [O(4), C(22)] are all β oriented, while Cl and the lactone moiety exhibit α orientation. The crystal structure, Fig. 2, consists of a strong hydrogen bond O(1)⋯O(2)ⁱ 2.84 Å, where (i) = 1 - x, $\frac{1}{2}$ + y, $\frac{1}{2}$ - z + 1.

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* Lists of anisotropic temperature factors, hydrogen parameters, bond lengths, angles and torsion angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53234 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 6,7-Dihydro-2-phenyl-5*H*-2aλ⁴-thia-3-selena-1,2-diazacyclo[*cd*]indene

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Abstract. C₁₃H₁₂N₂SSe, *M_r* = 307.27, triclinic, *P*1̄, *a* = 7.698 (2), *b* = 7.818 (4), *c* = 11.685 (2) Å, α = 90.24 (2), β = 97.89 (2), γ = 117.60 (3)°, *V* = 615.4 Å³, *Z* = 2, *D_x* = 1.66 g cm⁻³, λ(Mo *K*α) =

0.71073 Å, μ = 59.7 cm⁻¹, *F*(000) = 376, *T* = 295 K, final *R* = 0.059 for 1865 unique observed [*F* ≥ 4.0σ(*F*)] diffractometer data. The tricyclic portion of the molecule is almost planar and possesses elon-