The benzene ring of compound (I) deviates statistically significantly from planarity with a maximum departure from the plane of 0·015 (2) Å (C9). The benzene ring in compound (II) is planar. The molecules in both structures are dimerized through a pair of hydrogen bonds with the opposite enantiomer; see Table 2 for bond data.

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(+)-Jaborosalactone M, a Hemiketal Withanolide from *Jaborosa magellanica*

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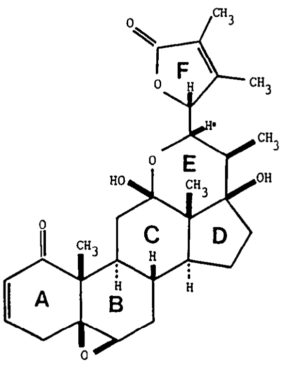
Abstract. $C_{28}H_{36}O_7$, $M_r = 484{\cdot}59$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}444\,(4)$, $b = 11{\cdot}920\,(4)$, $c = 18{\cdot}556\,(6)$ Å, $V = 2531\,(3)$ Å^3, $Z = 4$, $D_m = 1{\cdot}26$, $D_x = 1{\cdot}27$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}084$ mm^{-1}, $F(000) = 1040$, $T = 293\,(1)$ K, $R = 0{\cdot}037$ for 2201 observed reflections with $I > 3\sigma(I)$. The crystal structure consists of discrete molecules of (+)-jaborosalactone M separated by normal van der Waals distances. The mean bond lengths are C(sp^3)—C(sp^3) 1·532 (3), C(sp^3)—C(sp^2) 1·501 (3), C(sp^2)—C(sp^2) 1·464 (4), C=C 1·312 (4), C(sp^3)—O 1·448 (3), C(sp^2)—O 1·360 (3) and C=O 1·211 (3) Å. Ring *A* is in a twist-boat conformation, ring *B* is a half-chair, ring *C* a regular chair, and ring *D* is a C(13)-envelope. The hemiketal ring *E* is a chair while the lactonic ring *F* is essentially planar. Atoms C(18), C(19), O(3) and O(4) are β and O(5) and the lactone moiety are α oriented. Both the hydroxy groups are involved in hydrogen bonding [O(1)···H(O3$^{\rm i}$) 2·18 and O(3$^{\rm i}$)···H(O4) 2·10 Å].

Introduction. The withanolides are C_{28} steroids found among members of the Solanaceae (Tursunova, Maslennikova & Abubakirov, 1977; Kamernitskii, Reshetova & Krivoruchko, 1977; Vasina, Maslennikova & Abubakirov, 1986). An investigation of *Jaborosa magellanica* (Griseb.) Dusen (Solanaceae), collected along the Strait of Magellan, Chile, has yielded a wide variety of new withanolides. We now describe the first of these novel withanolides, (+)-jaborosalactone M, whose most unusual feature is the presence of a six-membered hemiketal ring *E*. We did not establish the absolute configuration by anomalous scattering. Rather, the configuration indicated in (1) derives from the fact that naturally occurring steroidal derivatives generally incorporate a C(18) methyl group which lies above the mean plane of the molecule.



(1)

Experimental. Colorless prismatic crystals of (+)-jaborosalactone M for X-ray crystallographic study were grown by slow evaporation of an ethanol:ethyl acetate

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(4:1) solution at room temperature. The density was measured by flotation. A crystal of approximate size 0·37 x 0·40 x 0·35 mm was used for the data collection. Accurate cell parameters and a 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 $10 < \theta < 15°$. Intensity data were collected by the $\omega/2\theta$ scan method using monochromatized radiation in the range $2 < \theta < 25°$ with $h \leq 13$, $k \leq 14$, and $l \leq 22$. The intensities of three reflections, chosen as standards, were monitored every 2 h of exposure time and showed no significant variations. The intensities of 2527 unique reflections were measured, of which 2201 had $I > 3\sigma(I)$, where $\sigma^2(I) = S + 2B + [0{\cdot}04(S-B)]^2$, S = scan count, and B = time-averaged background count. Data were corrected for Lorentz and polarization effects; an absorption correction was not considered necessary.

The structure was solved by direct methods using *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). The structure was refined by full-matrix least-squares calculations employing F's with anisotropic thermal parameters for the non-hydrogen atoms. A difference Fourier synthesis calculated at this 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 fixed isotropic temperature factors in subsequent refinement. Atomic scattering factors for carbon and oxygen were taken from Cromer & Mann (1968), and for H from Stewart, Davidson & Simpson (1965). At the conclusion of the refinement, $(\Delta/\sigma)_{\max} < 0{\cdot}01$, the difference electron density map was essentially featureless with $\Delta\rho = 0{\cdot}28$ e Å^{-3}. The final values of R and wR were 0·037 and 0·052, respectively, where $w = [\sigma^2(F_o) + (0{\cdot}060F_o)^2]^{-1}$ and goodness of fit $S = 1{\cdot}554$. The computer programs used in this study were from the Enraf–Nonius *Structure Determination Package* (B. A. Frenz & Associates, Inc., 1985) and *ORTEP* (Johnson, 1976). Final fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s are given in Table 1.*

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å^2), *with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	$B_{\rm eq}$
O(1)	−0·1573 (2)	0·9291 (2)	0·9501 (2)	6·45 (5)
O(2)	0·0302 (2)	1·1781 (2)	0·7784 (1)	3·83 (4)
O(3)	0·2205 (1)	0·7464 (1)	0·9696 (1)	2·99 (3)
O(4)	0·4853 (1)	0·8170 (1)	0·9754 (1)	3·35 (3)
O(5)	0·1996 (1)	0·9042 (1)	1·0417 (1)	2·55 (3)
O(6)	0·2271 (2)	1·0398 (1)	1·1615 (1)	3·60 (3)
O(7)	0·0641 (2)	1·1413 (2)	1·1759 (1)	5·61 (5)
C(1)	−0·1340 (2)	1·0219 (2)	0·9272 (2)	3·86 (5)
C(2)	−0·2017 (3)	1·1205 (3)	0·9512 (2)	4·76 (6)
C(3)	−0·2215 (3)	1·2035 (3)	0·9068 (2)	4·80 (7)
C(4)	−0·1638 (2)	1·2064 (2)	0·8343 (2)	4·17 (6)
C(5)	−0·0425 (2)	1·1578 (2)	0·8410 (1)	3·09 (5)
C(6)	0·0555 (2)	1·2356 (2)	0·8449 (1)	3·29 (5)
C(7)	0·1678 (2)	1·2047 (2)	0·8805 (1)	3·39 (5)
C(8)	0·1876 (2)	1·0775 (2)	0·8827 (1)	2·69 (4)
C(9)	0·0804 (2)	1·0193 (2)	0·9159 (1)	2·38 (4)
C(10)	−0·0361 (2)	1·0387 (2)	0·8721 (1)	2·88 (4)
C(11)	0·1014 (2)	0·8936 (2)	0·9301 (1)	2·63 (4)
C(12)	0·2136 (2)	0·8658 (2)	0·9698 (1)	2·43 (4)
C(13)	0·3197 (2)	0·9230 (2)	0·9348 (1)	2·48 (4)
C(14)	0·2932 (2)	1·0501 (2)	0·9287 (1)	2·58 (4)
C(15)	0·4134 (2)	1·0999 (2)	0·9101 (2)	3·57 (5)
C(16)	0·5025 (2)	1·0208 (2)	0·9457 (1)	3·40 (5)
C(17)	0·4321 (2)	0·9248 (2)	0·9810 (1)	2·69 (4)
C(18)	0·3445 (2)	0·8705 (2)	0·8604 (1)	3·39 (5)
C(19)	−0·0519 (3)	0·9540 (2)	0·8101 (2)	4·33 (6)
C(20)	0·4055 (2)	0·9526 (2)	1·0609 (1)	2·60 (4)
C(21)	0·5116 (2)	0·9312 (2)	1·1093 (1)	3·44 (5)
C(22)	0·2986 (2)	0·8868 (2)	1·0874 (1)	2·55 (4)
C(23)	0·2568 (2)	0·9221 (2)	1·1626 (1)	2·89 (4)
C(24)	0·1475 (2)	0·8648 (2)	1·1866 (1)	3·06 (5)
C(25)	0·0637 (2)	0·9391 (2)	1·1953 (1)	3·44 (5)
C(26)	0·1115 (3)	1·0509 (2)	1·1772 (2)	3·83 (5)
C(27)	0·1443 (3)	0·7410 (2)	1·1960 (2)	4·27 (6)
C(28)	−0·0617 (3)	0·9256 (3)	1·2167 (2)	5·07 (7)

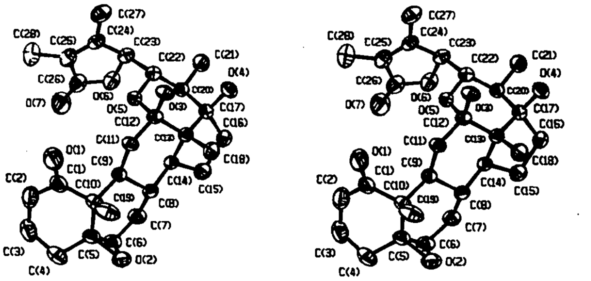

Fig. 1. Stereoview of the molecular structure of the title compound with the crystallographic numbering scheme.

Discussion. Our X-ray analysis unequivocally establishes the molecular structure and relative stereochemistry of the title compound. A view of the molecule is given in Fig. 1 with the crystallographic numbering scheme. Bond lengths, bond angles and important torsion angles are given in Table 2. Ring *A* has a 1α,4α-twist-boat conformation with C(1) and C(4) 0·213 (3) and 0·576 (3) Å, respectively, above the C(2), C(3), C(5), C(10) plane. Ring *B* is *cis*-fused to ring *A* and has a half-chair conformation with 8β,-9α-orientation. Rings *C* and *E* 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 (2) Å above the plane C(14)—C(17). The lactone moiety, ring *F*, is essentially planar, with maximum deviation 0·027 (2) Å. The methyl groups, C(18) and C(19), the hydroxy groups, O(3) and O(4), and the epoxide, O(2), are all β-oriented, while O(5) and the lactone moiety exhibit α-orientation.

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* Lists of anisotropic temperature factors, H-atom parameters, least-squares-planes data and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44553 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *bond angles* (°), *torsion angles* (°) *and details of intermolecular hydrogen bonding*

O(1)–C(1)	1·215 (3)	C(9)–C(10)	1·579 (3)
O(2)–C(5)	1·449 (3)	C(9)–C(11)	1·539 (3)
O(2)–C(6)	1·440 (3)	C(10)–C(19)	1·541 (3)
O(3)–C(12)	1·426 (2)	C(11)–C(12)	1·518 (3)
O(4)–C(17)	1·426 (3)	C(12)–C(13)	1·536 (3)
O(5)–C(12)	1·420 (2)	C(13)–C(14)	1·550 (3)
O(5)–C(22)	1·430 (2)	C(13)–C(17)	1·547 (3)
O(6)–C(23)	1·445 (3)	C(13)–C(18)	1·541 (3)
O(6)–C(26)	1·360 (3)	C(14)–C(15)	1·537 (3)
O(7)–C(26)	1·207 (3)	C(15)–C(16)	1·538 (3)
C(1)–C(2)	1·477 (4)	C(16)–C(17)	1·545 (3)
C(1)–C(10)	1·530 (3)	C(17)–C(20)	1·550 (3)
C(2)–C(3)	1·307 (4)	C(20)–C(21)	1·531 (3)
C(3)–C(4)	1·498 (4)	C(20)–C(22)	1·535 (3)
C(4)–C(5)	1·509 (3)	C(22)–C(23)	1·534 (3)
C(5)–C(6)	1·457 (3)	C(23)–C(24)	1·492 (3)
C(5)–C(10)	1·534 (3)	C(24)–C(25)	1·316 (4)
C(6)–C(7)	1·492 (3)	C(24)–C(27)	1·487 (3)
C(7)–C(8)	1·533 (3)	C(25)–C(26)	1·480 (3)
C(8)–C(9)	1·538 (3)	C(25)–C(28)	1·498 (4)
C(8)–C(14)	1·516 (3)		

C(5)–O(2)–C(6)	60·6 (1)	C(1)–C(10)–C(5)	109·7 (2)
C(12)–O(5)–C(22)	114·9 (1)	C(1)–C(10)–C(9)	104·8 (2)
C(23)–O(6)–C(26)	108·7 (2)	C(1)–C(10)–C(19)	109·1 (2)
O(1)–C(1)–C(2)	120·3 (2)	C(5)–C(10)–C(9)	111·7 (2)
O(1)–C(1)–C(10)	120·9 (2)	C(5)–C(10)–C(19)	108·6 (2)
C(2)–C(1)–C(10)	118·8 (2)	C(9)–C(10)–C(19)	112·8 (2)
C(1)–C(2)–C(3)	120·2 (3)	C(9)–C(11)–C(12)	115·3 (2)
C(2)–C(3)–C(4)	120·5 (2)	O(3)–C(12)–O(5)	109·3 (1)
C(3)–C(4)–C(5)	108·8 (2)	O(3)–C(12)–C(11)	105·3 (2)
O(2)–C(5)–C(4)	113·5 (2)	O(3)–C(12)–C(13)	113·4 (2)
O(2)–C(5)–C(6)	59·4 (1)	O(5)–C(12)–C(11)	106·9 (2)
O(2)–C(5)–C(10)	115·4 (2)	O(5)–C(12)–C(13)	110·2 (2)
C(4)–C(5)–C(6)	117·9 (2)	C(11)–C(12)–C(13)	111·5 (2)
C(4)–C(5)–C(10)	115·5 (2)	C(12)–C(13)–C(14)	108·0 (2)
C(6)–C(5)–C(10)	122·2 (2)	C(12)–C(13)–C(17)	115·4 (2)
O(2)–C(6)–C(5)	60·0 (1)	C(12)–C(13)–C(18)	110·2 (2)
O(2)–C(6)–C(7)	115·8 (2)	C(14)–C(13)–C(17)	100·9 (2)
C(5)–C(6)–C(7)	121·8 (2)	C(14)–C(13)–C(18)	111·6 (2)
C(6)–C(7)–C(8)	112·5 (2)	C(17)–C(13)–C(18)	110·4 (2)
C(7)–C(8)–C(9)	109·8 (2)	C(8)–C(14)–C(13)	114·0 (2)
C(7)–C(8)–C(14)	110·2 (2)	C(8)–C(14)–C(15)	120·3 (2)
C(9)–C(8)–C(14)	108·2 (2)	C(13)–C(14)–C(15)	102·6 (2)
C(8)–C(9)–C(10)	113·6 (2)	C(14)–C(15)–C(16)	105·1 (2)
C(8)–C(9)–C(11)	112·5 (2)	C(15)–C(16)–C(17)	106·9 (2)
C(10)–C(9)–C(11)	111·3 (2)	O(4)–C(17)–C(13)	107·6 (2)
O(4)–C(17)–C(16)	114·5 (2)	O(6)–C(23)–C(24)	104·6 (2)
O(4)–C(17)–C(20)	110·2 (2)	C(22)–C(23)–C(24)	114·0 (2)
C(13)–C(17)–C(16)	102·1 (2)	C(23)–C(24)–C(25)	109·9 (2)
C(13)–C(17)–C(20)	111·7 (2)	C(23)–C(24)–C(27)	120·7 (2)
C(16)–C(17)–C(20)	110·5 (2)	C(25)–C(24)–C(27)	129·4 (2)
C(17)–C(20)–C(21)	111·7 (2)	C(24)–C(25)–C(26)	107·9 (2)
C(17)–C(20)–C(22)	110·7 (2)	C(24)–C(25)–C(28)	131·3 (2)
C(21)–C(20)–C(22)	111·0 (2)	C(26)–C(25)–C(28)	120·8 (2)
O(5)–C(22)–C(20)	111·5 (2)	O(6)–C(26)–O(7)	121·3 (2)
O(5)–C(22)–C(23)	104·6 (2)	O(6)–C(26)–C(25)	108·7 (2)
C(20)–C(22)–C(23)	113·6 (2)	O(7)–C(26)–C(25)	129·9 (3)
O(6)–C(23)–C(22)	109·1 (2)		

Ring *A*	
C(10)C(1)–C(2)C(3)	32·9 (3)
C(2)C(1)–C(10)C(5)	−10·7 (3)
C(1)C(2)–C(3)C(4)	−7·6 (3)
C(2)C(3)–C(4)C(5)	−35·4 (3)
C(3)C(4)–C(5)C(10)	56·1 (3)
C(4)C(5)–C(10)C(1)	−32·9 (3)

Ring *B*	
C(10)C(5)–C(6)C(7)	−1·0 (3)
C(6)C(5)–C(10)C(9)	7·2 (3)
C(5)C(6)–C(7)C(8)	24·1 (3)
C(6)C(7)–C(8)C(9)	−52·7 (3)
C(7)C(8)–C(9)C(10)	60·9 (3)
C(8)C(9)–C(10)C(5)	−37·1 (3)

Ring *C*	
C(14)C(8)–C(9)C(11)	−51·2 (3)
C(9)C(8)–C(14)C(13)	59·4 (3)
C(8)C(9)–C(11)C(12)	49·2 (3)
C(9)C(11)–C(12)C(13)	−50·3 (3)
C(11)C(12)–C(13)C(14)	53·4 (3)
C(12)C(13)–C(14)C(8)	−60·9 (3)

Ring *D*	
C(17)C(13)–C(14)C(15)	45·9 (3)
C(14)C(13)–C(17)C(16)	−43·8 (3)
C(13)C(14)–C(15)C(16)	−29·9 (3)
C(14)C(15)–C(16)C(17)	2·5 (3)
C(15)C(16)–C(17)C(13)	25·9 (3)

Ring *E*	
C(22)O(5)–C(12)C(13)	−57·7 (3)
C(12)O(5)–C(22)C(20)	63·1 (3)
O(5)C(12)–C(13)C(17)	46·9 (3)
C(12)C(13)–C(17)C(20)	−41·9 (3)
C(13)C(17)–C(20)C(22)	44·1 (3)
C(17)C(20)–C(22)O(5)	−54·1 (3)

Ring *F*	
C(26)O(6)–C(23)C(24)	−4·4 (3)
C(23)O(6)–C(26)C(25)	4·7 (3)
O(6)C(23)–C(24)C(25)	2·4 (3)
C(23)C(24)–C(25)C(26)	0·3 (3)
C(24)C(25)–C(26)O(6)	−3·2 (3)

Table 2 (*cont.*)

O(1)···H(O3^{i}) (Å)	2·18
O(3^{i})···H(O4)	2·10
H(O3^{i})–O(3^{i})···H(O4^{ii}) (°)	122·6
O(3^{i})–H(O3^{i})···O(1)	134·7
O(4^{ii})–H(O4^{ii})···O(3^{i})	153·7

Symmetry codes: (i) $\frac{1}{2}+x-1, \frac{1}{2}-y+1, -z+2$; (ii) $x-1, y, z$.

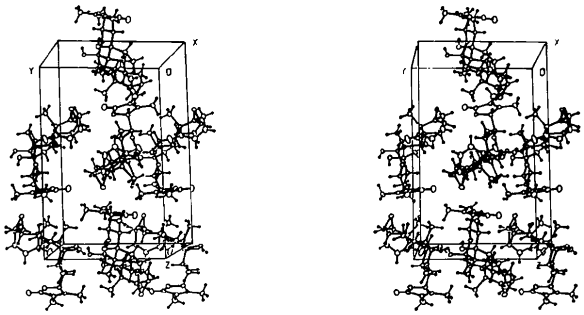

Fig. 2. Stereoview of the unit cell showing molecular packing.

The molecular dimensions are in accord with accepted values, mean bond lengths being C(sp^3)—C(sp^3) 1·532 (3) [the shortest, 1·457 (3), and the longest, 1·579 (3) Å, being in ring *B* to which the highly constrained epoxide is fused], C(sp^3)—C(sp^2) 1·501 (3), C(sp^2)—C(sp^2) 1·464 (4), C(sp^2)=C(sp^2) 1·312 (4), C(sp^3)—O 1·448 (3), C(sp^2)—O 1·360 (3), and C=O 1·211 (3) Å.

The crystal structure, Fig. 2, is stabilized by hydrogen bonding involving both the hydroxy groups with O(1)···H(O3^{i}) and O(3^{i})···H(O4) separations of 2·18 and 2·10 Å respectively (Table 2).

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