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(+)-Jaborol, a *B*-Secowithanolide from *Jaborosa magellanica*

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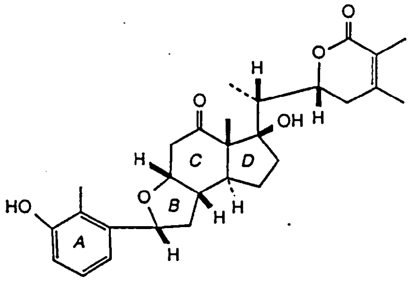
Abstract. $C_{28}H_{36}O_6$, $M_r = 468{\cdot}59$, monoclinic, $P2_1$, $a = 6{\cdot}919\,(3)$, $b = 17{\cdot}042$, $c = 10{\cdot}267\,(3)$ Å, $\beta = 93{\cdot}39\,(3)°$, $V = 1209\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}288$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}083$ mm^{-1}, $F(000) = 504$, $T = 293\,(1)$ K, $R = 0{\cdot}033$ for 2032 observed reflections with $I > 3\sigma(I)$. The average bond distances are $C(sp^3)$—$C(sp^3)$ 1·534 (3), $C(sp^3)$—$C(sp^2)$ 1·498 (3), $C(sp^2)$—$C(sp^2)$ 1·481 (3), C=C 1·336 (3), C—C (aromatic) 1·388 (3), $C(sp^3)$—O 1·445 (2), $C(sp^2)$—O 1·342 (3) and C=O 1·221 (2) Å. Ring *A* is essentially planar, the tetrahydrofuranoid ring *B* has a C(7)-envelope conformation while ring *C* has a twist-boat and ring *D* a C(13)-envelope conformation. The lactonic ring *E* is in a half-chair conformation. Atoms C(18) and O(4) are *β*, and the lactone moiety is α oriented. An hydroxy group is H-bonded to a ketonic O atom [$O(6^i)\cdots H(O1)$ 1·96 Å].

Introduction. Our continuing investigations on the withanolides found in *Jaborosa magellanica* (Griseb.) Drisen (Solanaceae) (Parvez, Fajardo & Shamma, 1988), has led to an usual withanolide, (+)-jaborol, in which the original steroidal ring *B* has suffered *in vivo* oxidative cleavage with formation of a phenolic ring *A*. Chemical and spectroscopic studies led to the proposal of structure (1) for jaborol (Fajardo, Freyer, Minard & Shamma, 1987). The crystal structure of (1) was determined in order to ascertain its conformation and molecular geometry. The absolute configuration was not established by the anomalous-dispersion method. However, the configuration indicated in (1) is derived 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. A colorless prismatic crystal of (1) of approximate size 0·50 × 0·45 × 0·35 mm was chosen for data collection. The density was measured by flotation. 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 0→8, k 0→20, and l ±12. The intensities of three reflections chosen as standards were monitored every 2 h of exposure time and showed no significant variation. Intensities of 2198 unique reflections were measured, of which 2032 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 deemed unnecessary.

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 at the difference-map positions with an overall isotropic temperature factor in the subsequent calculations, but not refined. Atomic scattering factors for C and O 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 $\Delta\rho = 0{\cdot}17$ e Å^{-3}. The final values of R and wR were 0·033 and 0·046, respectively, where $w = [\sigma^2(F_o) + (0{\cdot}050F_o)^2]^{-1}$ and goodness of fit $S = 1{\cdot}651$. 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.*

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* Lists of anisotropic temperature factors, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44554 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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

	x	y	z	B_{eq}
O(1)	0·3237 (3)	0·7780*	0·5033 (2)	5·17 (4)
O(2)	0·8020 (2)	0·9078 (1)	0·1995 (2)	3·20 (3)
O(3)	1·1229 (3)	1·1118 (1)	−0·0180 (2)	4·68 (4)
O(4)	1·4631 (2)	1·0362 (1)	−0·1957 (2)	3·48 (3)
O(5)	1·0715 (2)	1·1231 (1)	−0·4675 (2)	4·02 (3)
O(6)	0·9826 (3)	1·2090 (1)	−0·6138 (2)	5·18 (4)
C(1)	0·6264 (3)	0·7872 (1)	0·2282 (2)	2·80 (4)
C(2)	0·5234 (3)	0·7389 (1)	0·1393 (2)	2·94 (4)
C(3)	0·3534 (3)	0·7039 (1)	0·1726 (3)	3·41 (4)
C(4)	0·2848 (3)	0·7154 (1)	0·2943 (3)	3·58 (5)
C(5)	0·3850 (3)	0·7634 (1)	0·3823 (2)	3·41 (4)
C(6)	0·5589 (3)	0·7996 (1)	0·3521 (2)	3·11 (4)
C(7)	0·8164 (3)	0·8233 (1)	0·1961 (2)	2·80 (4)
C(8)	0·9788 (3)	0·9368 (1)	0·1499 (2)	2·92 (4)
C(9)	1·0553 (3)	0·8707 (1)	0·0625 (2)	2·77 (4)
C(10)	0·8956 (3)	0·8091 (1)	0·0637 (2)	3·04 (4)
C(11)	0·9346 (3)	1·0139 (1)	0·0797 (3)	3·76 (5)
C(12)	1·0942 (3)	1·0424 (1)	−0·0018 (2)	2·96 (4)
C(13)	1·2159 (3)	0·9795 (1)	−0·0587 (2)	2·55 (4)
C(14)	1·1036 (3)	0·9020 (1)	−0·0702 (2)	2·57 (4)
C(15)	1·2275 (4)	0·8504 (1)	−0·1553 (3)	3·69 (5)
C(16)	1·3391 (4)	0·9077 (2)	−0·2376 (2)	3·83 (5)
C(17)	1·2864 (3)	0·9924 (1)	−0·1994 (2)	2·75 (4)
C(18)	1·3941 (3)	0·9719 (2)	0·0386 (2)	3·81 (5)
C(19)	0·6665 (4)	0·8481 (2)	0·4531 (2)	3·98 (5)
C(20)	1·1333 (3)	1·0330 (2)	−0·2940 (2)	3·51 (5)
C(21)	0·9758 (5)	0·9793 (3)	−0·3547 (3)	7·60 (7)
C(22)	1·2307 (3)	1·0807 (1)	−0·3987 (2)	2·94 (4)
C(23)	1·3461 (4)	1·0374 (2)	−0·4955 (2)	3·64 (5)
C(24)	1·4028 (3)	1·0919 (2)	−0·6016 (2)	3·29 (4)
C(25)	1·2907 (3)	1·1529 (2)	−0·6374 (2)	3·27 (4)
C(26)	1·1069 (3)	1·1641 (2)	−0·5729 (2)	3·61 (5)
C(27)	1·3261 (4)	1·2091 (2)	−0·7441 (2)	4·50 (6)
C(28)	1·5891 (4)	1·0730 (2)	−0·6620 (3)	4·81 (6)

* Fixed to define the origin.

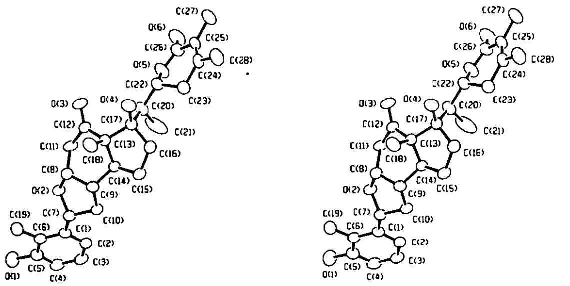

Fig. 1. Stereoview of the structure of the title compound with our numbering scheme.

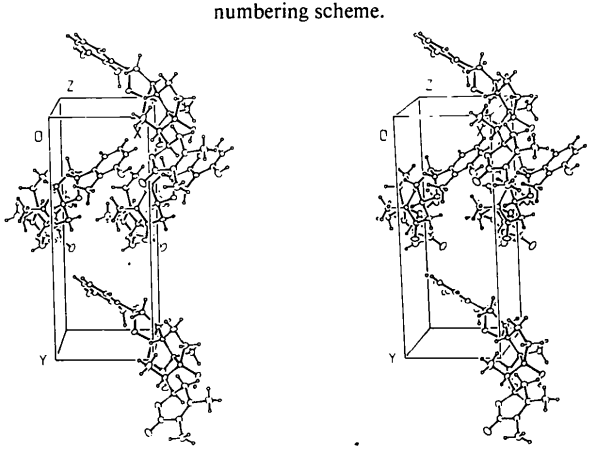

Fig. 2. Stereoview of the unit cell showing molecular packing.

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

O(1)–C(5)	1·359 (3)	C(14)–C(15)	1·536 (3)
O(2)–C(7)	1·443 (2)	C(15)–C(16)	1·529 (3)
O(2)–C(8)	1·441 (2)	C(16)–C(17)	1·546 (3)
O(3)–C(12)	1·213 (2)	C(17)–C(20)	1·557 (3)
O(4)–C(17)	1·430 (2)	C(20)–C(21)	1·527 (3)
O(5)–C(22)	1·464 (2)	C(20)–C(22)	1·535 (3)
O(5)–C(26)	1·324 (3)	C(22)–C(23)	1·504 (3)
O(6)–C(26)	1·208 (2)	C(23)–C(24)	1·501 (3)
C(1)–C(2)	1·393 (3)	C(24)–C(25)	1·336 (3)
C(1)–C(6)	1·397 (3)	C(24)–C(28)	1·498 (3)
C(1)–C(7)	1·506 (3)	C(25)–C(26)	1·481 (3)
C(2)–C(3)	1·380 (3)	C(25)–C(27)	1·487 (3)
C(3)–C(4)	1·377 (3)	C(9)–C(10)	1·525 (3)
C(4)–C(5)	1·376 (3)	C(9)–C(14)	1·518 (2)
C(5)–C(6)	1·403 (3)	C(11)–C(12)	1·505 (3)
C(6)–C(19)	1·490 (3)	C(12)–C(13)	1·502 (3)
C(7)–C(10)	1·515 (3)	C(13)–C(14)	1·534 (2)
C(8)–C(9)	1·553 (3)	C(13)–C(17)	1·567 (2)
C(8)–C(11)	1·521 (3)	C(13)–C(18)	1·546 (3)

C(7)–O(2)–C(8)	105·8 (1)	C(8)–C(9)–C(14)	111·4 (2)
C(22)–O(5)–C(26)	119·0 (2)	C(10)–C(9)–C(14)	116·6 (2)
C(2)–C(1)–C(6)	120·0 (2)	C(7)–C(10)–C(9)	101·4 (2)
C(2)–C(1)–C(7)	121·2 (2)	C(8)–C(11)–C(12)	114·1 (2)
C(6)–C(1)–C(7)	118·7 (2)	O(3)–C(12)–C(11)	121·5 (2)
C(1)–C(2)–C(3)	120·2 (2)	O(3)–C(12)–C(13)	122·8 (2)
C(2)–C(3)–C(4)	120·5 (2)	C(11)–C(12)–C(13)	115·6 (2)
C(3)–C(4)–C(5)	119·5 (2)	C(12)–C(13)–C(14)	110·6 (1)
O(1)–C(5)–C(4)	122·5 (2)	C(12)–C(13)–C(17)	118·1 (2)
O(1)–C(5)–C(6)	116·0 (2)	C(12)–C(13)–C(18)	104·6 (2)
C(4)–C(5)–C(6)	121·5 (2)	C(14)–C(13)–C(17)	103·5 (1)
C(1)–C(6)–C(5)	118·2 (2)	C(14)–C(13)–C(18)	111·0 (2)
C(1)–C(6)–C(19)	122·5 (2)	C(17)–C(13)–C(18)	109·1 (2)
C(5)–C(6)–C(19)	119·3 (2)	C(9)–C(11)–C(13)	111·8 (1)
O(2)–C(7)–C(1)	109·9 (2)	C(9)–C(14)–C(15)	118·0 (2)
O(2)–C(7)–C(10)	102·2 (1)	C(13)–C(14)–C(15)	103·8 (1)
C(1)–C(7)–C(10)	119·9 (2)	C(14)–C(15)–C(16)	105·5 (2)
O(2)–C(8)–C(9)	106·3 (1)	C(15)–C(16)–C(17)	108·7 (2)
O(2)–C(8)–C(11)	108·3 (2)	O(4)–C(17)–C(13)	111·1 (1)
C(9)–C(8)–C(11)	114·7 (2)	O(4)–C(17)–C(16)	106·3 (2)
C(8)–C(9)–C(10)	102·9 (1)	O(4)–C(17)–C(20)	109·5 (1)
C(13)–C(17)–C(16)	101·2 (2)	C(23)–C(24)–C(25)	120·6 (2)
C(13)–C(17)–C(20)	113·6 (1)	C(23)–C(24)–C(28)	115·8 (2)
C(16)–C(17)–C(20)	114·8 (2)	C(25)–C(24)–C(28)	123·6 (2)
C(17)–C(20)–C(21)	115·5 (2)	C(24)–C(25)–C(26)	118·5 (2)
C(17)–C(20)–C(22)	111·2 (1)	C(24)–C(25)–C(27)	125·9 (2)
C(21)–C(20)–C(22)	111·3 (2)	C(26)–C(25)–C(27)	115·4 (2)
O(5)–C(22)–C(20)	104·5 (1)	O(5)–C(26)–O(6)	117·1 (2)
O(5)–C(22)–C(23)	109·7 (2)	O(5)–C(26)–C(25)	120·2 (2)
C(20)–C(22)–C(23)	118·4 (2)	O(6)–C(26)–C(25)	122·7 (2)
C(22)–C(23)–C(24)	110·4 (2)		

C(8)O(2)–C(7)C(10)	−43·7 (3)	C(12)C(13)–C(14)C(9)	−63·5 (3)
C(7)O(2)–C(8)C(9)	24·4 (3)	C(17)C(13)–C(14)C(15)	40·7 (3)
C(26)O(5)–C(22)C(23)	−45·5 (3)	C(14)C(13)–C(17)C(16)	−38·8 (3)
C(22)O(5)–C(26)C(25)	13·8 (3)	C(13)C(14)–C(15)C(16)	26·0 (3)
C(6)C(1)–C(2)C(3)	0·7 (3)	C(14)C(15)–C(16)C(17)	1·4 (3)
C(2)C(1)–C(6)C(5)	−1·0 (3)	C(15)C(16)–C(17)C(13)	22·9 (3)
C(2)C(1)–C(7)C(10)	1·6 (3)	C(13)C(17)–C(20)C(22)	151·2 (3)
C(6)C(1)–C(7)O(2)	−63·8 (3)	C(16)C(17)–C(20)C(21)	35·0 (3)
C(1)C(2)–C(3)C(4)	−0·8 (3)	C(17)C(20)–C(22)O(5)	172·5 (3)
C(2)C(3)–C(4)C(5)	1·2 (3)	C(21)C(20)–C(22)C(23)	65·3 (3)
C(3)C(4)–C(5)C(6)	−1·6 (3)	O(5)C(22)–C(23)C(24)	51·3 (3)
O(1)C(5)–C(6)C(19)	2·3 (3)	C(22)C(23)–C(24)C(25)	−29·9 (3)
C(4)C(5)–C(6)C(1)	1·5 (3)	C(23)C(24)–C(25)C(26)	1·9 (3)
O(2)C(7)–C(10)C(9)	45·0 (3)	C(28)C(24)–C(25)C(27)	2·7 (3)
O(2)C(8)–C(9)C(10)	4·2 (3)	C(24)C(25)–C(26)O(5)	11·6 (3)
C(11)C(8)–C(9)C(14)	10·2 (3)	C(27)C(25)–C(26)O(6)	8·9 (3)
C(9)C(8)–C(11)C(12)	−48·9 (3)		
C(8)C(9)–C(10)C(7)	−29·4 (3)		
C(8)C(9)–C(14)C(13)	44·5 (3)		
C(8)C(11)–C(12)C(13)	30·4 (3)		
C(11)C(12)–C(13)C(14)	23·7 (3)		

$O(6^{i})\cdots H(O1)$ (Å)	1·96
$O(1)–H(O1)\cdots O(6^{i})$ (°)	159·6

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

Discussion. Our X-ray analysis has established the molecular structure and relative stereochemistry of (+)-jaborol. A stereoview of the molecule is given in Fig. 1 with our crystallographic numbering scheme. Fig. 2 is a stereoview of the crystal structure showing molecular packing. Bond distances, angles and important torsion angles are listed in Table 2. In the molecule of (+)-jaborol, the aromatic ring *A* is essentially planar to within 0·007 (2) Å. Ring *B*, a tetrahydrofuran ring, has a C(7)-envelope conformation with C(7) 0·654 (2) Å out of the plane of atoms O(2), C(8), C(9), C(10). This ring is *cis*-fused to ring *C*. Ring *C* itself has a twist-boat conformation with C(11) and C(14) 0·476 (2) and 0·637 (2) Å above the C(8), C(9), C(12), C(13) plane. Ring *D* is *trans*-fused with ring *C* and has a C(13)-envelope conformation with C(13) 0·626 (2) Å above the C(14)—C(17) plane. The six-membered ring *E* has a half-chair conformation with C(22) 0·611 (2) Å above the plane of atoms O(5), C(23), C(24), C(25) and C(26).

The molecular dimensions in (+)-jaborol are unexceptional, mean values being C(sp^3)—C(sp^3) 1·534 (3), C(sp^3)—C(sp^2) 1·498 (3), C(sp^2)—C(sp^2) 1·481 (3), aromatic C—C 1·388 (3), C=C 1·336 (2), C(sp^3)—O 1·445 (3), C(sp^2)—O 1·342 (3) and C=O 1·221 (2) Å.

One of the two hydroxy groups is involved in H bonding through its H atom with a ketonic O atom [O(6^i)···H(O1) 1·96 Å and O(1)—H(O1)···O(6^i) 159·6°].

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3,3′,5,5′-Tetrachloro-4,4′-dihydroxybiphenyl. A Coplanar Polychlorinated Biphenyl in the Solid State

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Abstract. $C_{12}H_6Cl_4O_2$, $M_r = 323·99$, monoclinic, $P2_1/c$, $a = 6·5696$ (7), $b = 4·7887$ (7), $c = 19·460$ (3) Å, $\beta = 95·10$ (1)°, $V = 609·8$ (2) Å^3, $Z = 2$, $D_x = 1·76$ g cm^{-3}, λ(Cu $K\bar{\alpha}$) = 1·54178 Å, $\mu = 87·5$ cm^{-1}, $F(000) = 324$, $T = 297$ K, $R = 0·050$ for 785 observed reflections. Non-*ortho*-substituted polychlorinated biphenyls (PCB's) have shown significantly higher binding affinities to certain receptor proteins when compared with their *ortho*-substituted counterparts. An important property of such PCB's is the accessibility of the more polarizable coplanar conformation that has been shown to be important in the crystalline form of certain biphenyl systems. 3,3′,5,5′-Tetrachloro-4,4′-dihydroxybiphenyl, which has shown strong receptor protein binding activity, crystallizes in the coplanar state. This compound is essentially isostructural with the related ‘coplanar-toxic’ PCB's. It is proposed that the dispersion-energy gain from a coplanar alignment of the phenyl rings stabilizes the interactions of these PCB compounds with important macromolecules some of which mediate their responses in biological systems, probably involving stacking interactions with aromatic (or conjugated) rings in amino acids or heme groups.

Introduction. The biological properties of PCB's vary considerably and are remarkably dependent on the number and positions of halogen atoms in the molecular structure (Goldstein, 1980). Non-*ortho*-sub-

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