

Fig. 1. A stereoscopic view of the unit cell with four morpholinium ions and two 4-morpholinecarboxylate ions. The c axis is horizontal, b vertical, and a into the paper.

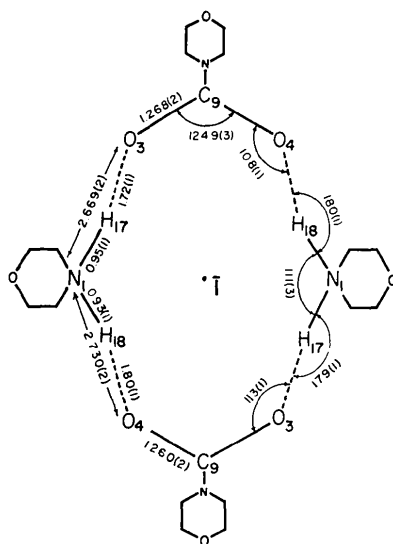


Fig. 2. A schematic view of the hydrogen-bonded ring of ions about the center of inversion at the origin.

and are in the chair conformation. The results of this analysis show both ions to be very symmetrical across the $O\cdots N$ line with identical distances and angles on both sides. This is more apparent here than in the values reported by Brown & Gray (1981). The C—N distances in the two different morpholine rings show the effects of different bonding to N. The sp^3 character of the cationic N has resulted in longer C—N bonds (1.487 Å) than for the partly sp^2 character of the anionic N (1.452 Å). Although the NC_3 group in the anion is not planar with the N atom 0.16 Å out of the plane of the three C atoms, the exterior CNC angles are both 120° ; the interior angle is constrained by the ring to be smaller (110°); and the N -carboxy group (NCO_2) is planar (r.m.s. deviations = 0.004 Å).

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Structure of Plaunolide, a New Furanoid Diterpene from *Croton sublyratus*, $C_{20}H_{20}O_5$

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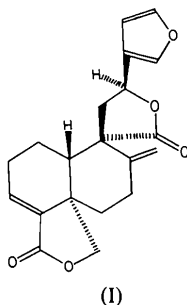
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Abstract. $M_r = 340.4$, orthorhombic, $P2_12_12_1$, $a = 1666.1 \text{ \AA}$, $Z = 4$, $D_x = 1.35 \text{ Mg m}^{-3}$, $\lambda(\text{Cu } K\alpha) = 11.745 (1)$, $b = 19.235 (1)$, $c = 7.375 (1) \text{ \AA}$, $V = 1.5418 \text{ \AA}^3$, $\mu = 0.811 \text{ mm}^{-1}$, $T = 300 \text{ K}$. Final $R =$

0.069 for 1476 observed reflections. Plaunolide is a novel *ent*-clerodane-type furanoditerpene. Its *trans*- $\Delta^{1,2}$ -octaline moiety has a distorted chair (*A* ring) and a skew-boat (*B* ring) conformation and both of the γ -lactones fused to the octaline ring are in envelope conformations.

Introduction. Throughout the course of screening for anti-peptic-ulcer activities of natural products in plants, we found six furanoditerpenes with anti-Shay-ulcer activity from *Croton sublyratus* Kurz (Euphorbiaceae) (Ogiso, Kitazawa, Mikuriya & Promdej, 1981) which have been named plaunol A, B, C, D and E, and plaunolide (I). Previously the absolute configuration of plaunol A was established by X-ray analysis of its mono-*p*-bromobenzoate (Kitazawa, Ogiso, Takahashi, Sato, Kurabayashi, Kuwano, Hata & Tamura, 1979) and the structure determinations of plaunol B, C, D and E could be made by spectroscopic and chemical correlations (Kitazawa, Sato, Takahashi, Kuwano & Ogiso, 1980). Since the spectroscopic study of plaunolide did not allow the chirality at C(12) to be assigned (Takahashi, Kurabayashi, Kitazawa, Haruyama & Ogiso, 1982, unpublished results), the X-ray analysis has been carried out.



Experimental. Colorless plate-like crystal, 0.5 × 0.5 × 0.1 mm, systematic absences showed space group $P2_12_12_1$, Rigaku automated four-circle diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, total of 1642 independent reflections up to $2\theta = 128^\circ$ measured in 2θ - ω scan mode, 1476 observed reflections with $I > 3\sigma(I)$, all intensities corrected for Lorentz and polarization factors but not absorption; structure determined by direct method (*MULTAN*, Germain, Main & Woolfson, 1971), all H atoms discernible on a difference map after block-diagonal least-squares refinement with anisotropic temperature factors for both C and O atoms, full-matrix least squares applied to final stage of refinement, converged to give $R = 0.069$ and $R_w = 0.068$, where $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ respectively, $w = 1/\sigma(F_o)$; atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974), $F(000) = 720$.

Discussion. The atomic parameters are given in Table 1,* and an *ORTEP* drawing (Johnson, 1965) of plaunolide is exhibited in Fig. 1.

This X-ray analysis confirmed the observation of a CD spectrum that plaunolide had a similar configuration to that of bacchotricuneatin B (Wagner, Seitz, Chari, Lotter & Herz, 1977; Wagner, Seitz, Lotter & Herz, 1978) except at C(12). The chiral center of C(12) was found to have the configuration *S*, despite it having *R* in bacchotricuneatin B, while the configuration of the other chiral centers corresponded to those of bacchotricuneatin B. Thus the absolute configuration was established as (I).

The bond lengths and angles are listed in Table 2. A deviation of bond angles from normal values was observed in rings *C* and *D* which may be caused by the

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38168 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$ for C and O, $\times 10^3$ for H) and equivalent isotropic temperature factors with e.s.d.'s in parentheses

For non-H atoms, $B_{eq} = \frac{4}{3} \sum_i \beta_{ij} a_i \cdot a_j$.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}/B_{iso}(\text{\AA}^2)$
C(1)	4302 (6)	3350 (3)	-15 (10)	2.4 (0.2)
C(2)	5116 (7)	3972 (4)	35 (12)	2.9 (0.2)
C(3)	4578 (6)	4541 (4)	1102 (11)	3.2 (0.2)
C(4)	2810 (6)	4419 (3)	2405 (11)	2.9 (0.2)
C(5)	3362 (6)	3720 (3)	2938 (10)	2.3 (0.2)
C(6)	3515 (8)	3566 (4)	4961 (12)	3.4 (0.2)
C(7)	3348 (8)	2794 (4)	5405 (12)	3.8 (0.2)
C(8)	2743 (6)	2411 (4)	3918 (11)	3.0 (0.2)
C(9)	3349 (5)	2419 (3)	2104 (9)	2.5 (0.2)
C(10)	3966 (6)	3139 (3)	1879 (11)	2.4 (0.2)
C(11)	4219 (6)	1813 (3)	1936 (12)	3.1 (0.2)
C(12)	4022 (7)	1472 (3)	136 (12)	3.2 (0.2)
C(13)	3826 (6)	704 (3)	226 (11)	3.0 (0.2)
C(14)	3010 (7)	338 (4)	1319 (11)	3.5 (0.2)
C(15)	3151 (7)	-339 (4)	927 (13)	4.2 (0.2)
C(16)	4402 (6)	217 (4)	-832 (12)	3.7 (0.2)
C(17)	1764 (8)	2074 (5)	4143 (15)	4.4 (0.3)
C(18)	2946 (7)	4943 (4)	2970 (13)	4.5 (0.2)
C(19)	2076 (6)	3862 (4)	2512 (12)	3.3 (0.2)
C(20)	2558 (6)	2300 (4)	506 (10)	2.9 (0.2)
O(1)	3036 (6)	5562 (3)	3248 (8)	4.9 (0.2)
O(2)	1933 (5)	4600 (3)	3108 (8)	4.4 (0.2)
O(3)	1711 (4)	2606 (2)	114 (8)	3.8 (0.1)
O(4)	2946 (4)	1784 (2)	-569 (7)	3.3 (0.1)
O(5)	4000 (4)	-435 (2)	-329 (8)	4.2 (0.2)
H(C1a)	468 (5)	296 (3)	-74 (8)	1.4 (1.2)
H(C1b)	371 (5)	348 (3)	-80 (9)	2.1 (1.5)
H(C2a)	528 (5)	412 (3)	-106 (9)	1.8 (1.4)
H(C2b)	585 (6)	382 (4)	34 (10)	3.9 (1.8)
H(C3)	473 (5)	498 (3)	52 (9)	2.4 (1.4)
H(C6a)	290 (5)	380 (3)	564 (9)	2.6 (1.4)
H(C6b)	420 (6)	370 (3)	551 (10)	2.8 (1.6)
H(C7a)	289 (8)	267 (4)	682 (13)	8.2 (2.4)
H(C7b)	406 (6)	258 (3)	585 (9)	3.0 (1.5)
H(C10)	489 (7)	308 (4)	266 (10)	4.3 (1.7)
H(C11a)	404 (5)	149 (3)	318 (8)	1.6 (1.2)
H(C11b)	522 (6)	200 (4)	211 (11)	4.6 (1.8)
H(C12)	485 (7)	163 (4)	-104 (12)	7.6 (2.5)
H(C14)	239 (4)	61 (3)	226 (7)	1.3 (1.1)
H(C15)	263 (6)	-83 (4)	179 (11)	5.8 (2.0)
H(C16)	497 (7)	26 (4)	-209 (11)	5.7 (2.0)
H(C17a)	128 (6)	225 (3)	499 (11)	4.2 (2.0)
H(C17b)	145 (6)	181 (3)	299 (11)	4.0 (1.8)
H(C19a)	154 (6)	354 (3)	351 (10)	4.4 (1.8)
H(C19b)	182 (6)	380 (3)	110 (10)	3.6 (1.7)

stereochemical strain of the fused-ring system. The value of the deformed tetrahedral angle C(4)–C(5)–C(19), 97.5°, is similar to that of molecules having the corresponding ring juncture, e.g. bacchotricuneatin B (Wagner, Seitz, Chari, Lotter & Herz, 1977; Wagner, Seitz, Lotter & Herz, 1978), 98.7°, and demethylmarrubiaketone (Kirfel, 1978), 97.9°.

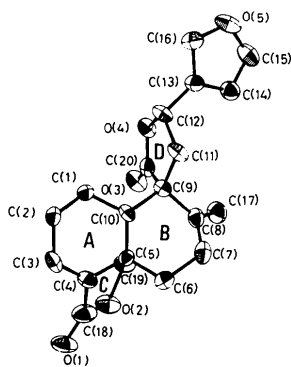


Fig. 1. An ORTEP drawing of the molecular structure with the atomic-numbering scheme.

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

C(1)–C(2)	1.531 (10)	C(9)–C(20)	1.518 (10)
C(1)–C(10)	1.508 (11)	C(11)–C(12)	1.498 (12)
C(2)–C(3)	1.489 (11)	C(12)–C(13)	1.498 (9)
C(3)–C(4)	1.338 (11)	C(12)–O(4)	1.493 (9)
C(4)–C(5)	1.497 (9)	C(13)–C(14)	1.436 (10)
C(4)–C(18)	1.489 (11)	C(13)–C(16)	1.394 (11)
C(5)–C(6)	1.531 (11)	C(14)–C(15)	1.347 (10)
C(5)–C(10)	1.538 (9)	C(15)–O(5)	1.374 (10)
C(5)–C(19)	1.567 (10)	C(16)–O(5)	1.392 (9)
C(6)–C(7)	1.534 (11)	C(18)–O(1)	1.212 (10)
C(7)–C(8)	1.500 (11)	C(18)–O(2)	1.364 (10)
C(8)–C(9)	1.515 (10)	C(19)–O(2)	1.495 (9)
C(8)–C(17)	1.330 (11)	C(20)–O(3)	1.192 (9)
C(9)–C(10)	1.572 (9)	C(20)–O(4)	1.349 (9)
C(9)–C(11)	1.555 (9)		
C(2)–C(1)–C(10)	110.6 (6)	C(5)–C(10)–C(9)	112.0 (5)
C(1)–C(2)–C(3)	108.8 (5)	C(1)–C(10)–C(9)	117.2 (7)
C(2)–C(3)–C(4)	122.5 (4)	C(1)–C(10)–C(5)	113.3 (4)
C(3)–C(4)–C(5)	125.6 (6)	C(9)–C(11)–C(12)	107.3 (6)
C(3)–C(4)–C(18)	122.9 (6)	C(11)–C(12)–O(4)	105.3 (5)
C(5)–C(4)–C(18)	107.1 (5)	C(11)–C(12)–C(13)	114.6 (8)
C(4)–C(5)–C(6)	112.8 (5)	C(13)–C(12)–O(4)	106.4 (4)
C(4)–C(5)–C(10)	111.0 (6)	C(12)–C(13)–C(16)	124.3 (8)
C(4)–C(5)–C(19)	97.5 (3)	C(12)–C(13)–C(14)	127.6 (8)
C(6)–C(5)–C(10)	107.5 (4)	C(14)–C(13)–C(16)	108.0 (3)
C(6)–C(5)–C(19)	110.0 (5)	C(13)–C(14)–C(15)	105.8 (7)
C(10)–C(5)–C(19)	118.0 (6)	C(14)–C(15)–O(5)	111.3 (6)
C(5)–C(6)–C(7)	112.3 (6)	C(13)–C(16)–O(5)	107.0 (7)
C(6)–C(7)–C(8)	112.3 (8)	C(4)–C(18)–O(1)	130.6 (10)
C(7)–C(8)–C(9)	123.9 (11)	C(4)–C(18)–O(2)	106.8 (4)
C(7)–C(8)–C(17)	114.7 (4)	O(1)–C(18)–O(2)	122.6 (9)
C(9)–C(8)–C(17)	121.3 (9)	C(5)–C(19)–O(2)	102.4 (4)
C(8)–C(9)–C(10)	108.5 (4)	C(9)–C(20)–O(3)	128.7 (10)
C(8)–C(9)–C(11)	111.8 (5)	C(9)–C(20)–O(4)	111.1 (5)
C(8)–C(9)–C(20)	113.4 (4)	O(3)–C(20)–O(4)	120.2 (11)
C(10)–C(9)–C(11)	110.4 (4)	C(18)–O(2)–C(19)	109.8 (4)
C(10)–C(9)–C(20)	109.4 (5)	C(12)–O(4)–C(20)	112.1 (5)
C(11)–C(9)–C(20)	103.1 (4)	C(15)–O(5)–C(16)	107.8 (3)

Table 3. Deviations (Å) from least-squares planes with e.s.d.'s in parentheses

Plane 1		Plane 2	
C(1)	0.62 (5)	C(5)	0.73 (3)
C(2)	–0.00 (5)*	C(6)	0.17 (3)*
C(3)	0.01 (5)*	C(7)	–0.17 (3)*
C(4)	–0.01 (5)*	C(8)	0.49 (3)
C(5)	0.00 (5)*	C(9)	0.09 (3)*
C(10)	–0.07 (5)	C(10)	–0.12 (3)*
Plane 3		Plane 4	
C(4)	–0.01 (5)*	C(9)	–0.00 (1)*
C(5)	–0.63 (5)	C(11)	0.16 (2)
C(18)	0.03 (5)*	C(12)	0.01 (2)*
C(19)	0.02 (5)*	C(20)	0.01 (2)*
O(1)	0.12 (5)	O(3)	–0.01 (1)
O(2)	–0.01 (5)*	O(4)	–0.00 (1)*

* Atoms defining the planes.

The ring junction between rings *A* and *B* is *trans*. Ring *A* has a distorted half-chair conformation, whereas ring *B* has a skew-boat conformation. Considering the least-squares planes in Table 3, C(1) lies 0.62 Å above and C(10) 0.07 Å below plane 1, and C(5) and C(8) lie 0.73 and 0.49 Å above plane 2 respectively. The skewness of ring *B* as well as the *sp*² character of C(8) may reduce the unfavorable bow-stern repulsion and 1,2-diaxial interaction in a boat conformation, while the bulky substituents at C(5) and C(9) may prevent ring *B* taking a chair conformation due to the strong 1,3-diaxial interaction. These conformational features are commonly observed in the triterpenes and trimethylsteroids (Hanack, 1965). As shown in Table 3, both γ -lactones (rings *C* and *D*) have the envelope conformation, where the flaps are at C(5) and C(11) respectively.

No significantly short intermolecular contacts can be observed, and therefore the molecular packing in the crystal can be thought of as governed by van der Waals interactions.

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