

ular contact is 2.71 Å from O(20) to H(102) of a neighbouring molecule. The molecular dimensions are unexceptional.

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Riolozatrione

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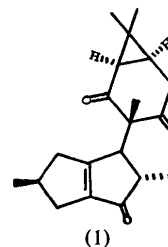
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Abstract. C₂₀H₂₆O₃, *M_r* = 314.42, orthorhombic, *P*2₁2₁2₁, *a* = 11.404 (3), *b* = 21.090 (8), *c* = 7.506 (3) Å, *V* = 1805 (1) Å³, *Z* = 4, *d_c* = 1.157 Mg m⁻³, λ(Cu Kα) = 1.54178 Å. A full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1586 reflexions led to a final *R* of 0.053. Riolozatrione represents a new diterpene structural type whose skeleton was named riolozane. The structure is composed of two five-membered rings sharing a common double bond. One five-membered ring exhibits a flattened envelope conformation while the other containing an α,β-unsaturated ketone moiety is more planar. The double bond deviates from planarity by 6.5°. A cyclohexanedione moiety containing a fused cyclopropane ring is attached to the five-membered ring containing the keto function. The six-membered ring exhibits a 1,2-diplanar conformation.

Introduction. *Jatropha dioica* var. *sessiliflora* (Hook) McVaugh (*J. spathulata*) (Standley, 1923; Vines, 1960) is a shrub found in the arid regions of Northeastern Mexico. It is known as 'Sangre-drago' or 'Sangre de Drago' and was called 'tlapelex patli' by the Aztecs. The red root juice is used in folk medicine and the roots are chewed to relieve toothache (Martinez, 1959). Root extracts exhibit antibiotic activity against *Staphylococcus aureus* and the new diterpene riolozatrione (1) was isolated from the active

fraction (Dominguez, Cano, Franco, Villarreal, Watson & Zabel, 1980). The structure was determined by X-ray diffraction techniques and represents a new diterpene structural type for which the name riolozane was proposed.



A crystal of dimensions 0.7 × 0.12 × 0.35 mm was used to collect intensity data on a Syntex P2₁ diffractometer system by the θ:2θ scanning technique using a variable scan speed and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 reflexions whose angles were measured by a centering routine associated with the diffractometer. Systematic absences were consistent with space group *P*2₁2₁2₁. A periodically monitored reflexion showed no significant change in intensity. Of the 1838 independent reflexions measured, 250 had intensities less than 2σ(*I*). Two additional reflexions showed significant secondary extinction and were dropped from the final refinement. Lorentz and polarization corrections were applied, but no absorption corrections were made.

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Table 1. *Positional parameters* ($\times 10^4$, for H $\times 10^3$) and *isotropic thermal parameters*

	x	y	z	U_{eq}/U^* ($\text{\AA}^2 \times 10^2$)
C(1)	6208 (7)	1355 (2)	6664 (5)	8.2 (3)
C(2)	6244 (7)	661 (2)	7233 (5)	9.0 (4)
C(3)	5574 (4)	284 (2)	5837 (6)	8.1 (2)
C(4)	5454 (3)	743 (1)	4342 (5)	6.4 (2)
C(5)	4951 (4)	735 (2)	2587 (5)	7.7 (2)
O(5)	4498 (5)	293 (2)	1800 (7)	13.5 (3)
C(6)	5035 (3)	1400 (2)	1817 (4)	6.3 (2)
C(7)	5534 (2)	1808 (1)	3374 (3)	4.9 (1)
C(8)	5793 (3)	1324 (1)	4790 (4)	5.4 (1)
C(9)	6593 (2)	2232 (1)	2791 (3)	5.0 (1)
C(10)	7027 (2)	2584 (1)	4453 (4)	5.3 (1)
O(10)	7972 (2)	2460 (1)	5097 (4)	8.2 (1)
C(11)	6238 (3)	3053 (1)	5260 (4)	5.5 (1)
C(12)	5345 (3)	3388 (2)	4136 (4)	6.1 (2)
C(13)	5232 (3)	3205 (2)	2203 (5)	6.8 (2)
C(14)	6071 (3)	2717 (2)	1479 (4)	5.9 (2)
O(14)	6309 (3)	2690 (1)	-81 (3)	8.2 (2)
C(15)	6387 (3)	3749 (1)	4781 (4)	6.0 (1)
C(16)	6181 (6)	4120 (2)	6306 (6)	8.6 (2)
C(17)	7341 (4)	3947 (2)	3523 (7)	7.9 (2)
C(18)	7587 (3)	1851 (2)	1956 (6)	7.0 (2)
C(19)	7602 (11)	465 (5)	7136 (21)	18.0 (9)
C(20)	3875 (4)	1613 (3)	1080 (7)	9.3 (3)
H(1a)	695 (5)	151 (3)	681 (7)	9 (1)
H(1b)	547 (6)	160 (3)	735 (10)	13 (2)
H(2)	599 (7)	60 (4)	863 (12)	15 (2)
H(3a)	477 (6)	17 (3)	600 (9)	11 (2)
H(3b)	606 (5)	-9 (3)	524 (9)	12 (2)
H(6)	560 (5)	129 (3)	75 (9)	12 (2)
H(7)	491 (3)	211 (1)	381 (4)	5 (1)
H(11)	612 (3)	301 (2)	658 (5)	6 (1)
H(12)	458 (4)	349 (2)	483 (6)	9 (1)
H(13a)	530 (4)	353 (2)	134 (7)	10 (1)
H(13b)	457 (4)	303 (2)	218 (6)	9 (1)
H(16a)	542 (5)	409 (3)	689 (9)	11 (2)
H(16b)	594 (6)	467 (3)	595 (10)	13 (2)
H(16c)	677 (9)	422 (5)	736 (4)	19 (3)
H(17a)	728 (4)	368 (2)	251 (6)	8 (1)
H(17b)	811 (6)	403 (3)	426 (10)	13 (2)
H(17c)	725 (5)	436 (3)	282 (9)	11 (2)
H(18a)	735 (5)	173 (3)	84 (10)	11 (2)
H(18b)	768 (5)	153 (3)	290 (9)	11 (2)
H(18c)	836 (5)	210 (2)	186 (7)	9 (1)
H(19a)	789 (11)	21 (6)	850 (21)	21 (5)
H(19b)	801 (8)	82 (5)	735 (12)	16 (3)
H(19c)	777 (12)	13 (6)	602 (21)	21 (5)
H(20a)	337 (7)	126 (4)	66 (12)	15 (2)
H(20b)	323 (10)	189 (5)	205 (15)	19 (3)
H(20c)	397 (6)	196 (3)	28 (9)	12 (2)

* For nonhydrogen atoms $U_{eq} = (U_1 U_2 U_3)^{1/3}$.

The direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971) was used to calculate phases for the 250 $|E|$ values greater than 1.46. The phase set with the largest combined figure of merit was selected, and the E map calculated with these phases revealed the positions of 22 atoms. After several cycles of refinement, the missing heavy atom and all H atoms were located by a difference Fourier calculation. Full-matrix least-squares refinement was terminated at

a final R of 0.053 where $R = \sum |F_o| - |F_c| / \sum |F_o|$. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(I)$ was determined from counting statistics. H-atom thermal parameters were refined isotropically.

Table 2. *Interatomic distances* (\AA)

C(1)—C(2)	1.526 (5)	C(9)—C(10)	1.534 (4)
C(1)—C(8)	1.485 (5)	C(9)—C(14)	1.539 (4)
C(2)—C(3)	1.522 (7)	C(9)—C(18)	1.524 (5)
C(2)—C(19)	1.609 (5)	C(10)—C(11)	1.467 (4)
C(3)—C(4)	1.489 (5)	C(10)—O(10)	1.211 (4)
C(4)—C(5)	1.437 (5)	C(11)—C(12)	1.500 (4)
C(4)—C(8)	1.329 (4)	C(11)—C(15)	1.522 (4)
C(5)—C(6)	1.520 (5)	C(12)—C(13)	1.508 (5)
C(5)—O(5)	1.219 (6)	C(12)—C(15)	1.492 (4)
C(6)—C(7)	1.559 (4)	C(13)—C(14)	1.507 (5)
C(6)—C(20)	1.502 (6)	C(14)—O(14)	1.204 (4)
C(7)—C(8)	1.503 (4)	C(15)—C(16)	1.520 (5)
C(7)—C(9)	1.565 (4)	C(15)—C(17)	1.500 (6)

Table 3. *Valence angles* ($^\circ$)

C(1)C(2)C(3)	107.2 (4)	C(10)C(9)C(14)	108.8 (2)
C(1)C(2)C(19)	105.8 (6)	C(10)C(19)C(18)	110.5 (2)
C(3)C(2)C(19)	108.1 (6)	C(14)C(9)C(18)	112.0 (2)
C(2)C(3)C(4)	103.0 (3)	C(9)C(10)O(10)	120.5 (3)
C(3)C(4)C(5)	136.1 (3)	C(9)C(10)C(11)	117.7 (2)
C(3)C(4)C(8)	112.5 (3)	C(11)C(10)O(10)	121.8 (3)
C(5)C(4)C(8)	111.0 (3)	C(10)C(11)C(12)	120.1 (2)
C(4)C(5)O(5)	128.5 (4)	C(12)C(11)C(15)	59.2 (2)
C(4)C(5)C(6)	108.3 (3)	C(11)C(12)C(13)	118.6 (3)
C(6)C(5)O(5)	123.2 (4)	C(11)C(12)C(15)	61.2 (2)
C(5)C(6)C(7)	104.3 (3)	C(13)C(12)C(15)	120.7 (3)
C(5)C(6)C(20)	111.1 (3)	C(12)C(13)C(14)	117.9 (3)
C(7)C(6)C(20)	115.7 (3)	C(13)C(14)O(14)	121.7 (3)
C(6)C(7)C(8)	103.1 (2)	C(13)C(14)C(9)	118.0 (2)
C(6)C(7)C(9)	112.8 (2)	C(9)C(14)O(14)	120.3 (3)
C(8)C(7)C(9)	115.7 (2)	C(11)C(15)C(12)	59.7 (2)
C(7)C(8)C(1)	134.6 (3)	C(11)C(15)C(16)	115.0 (3)
C(7)C(8)C(4)	113.0 (3)	C(11)C(15)C(17)	119.9 (3)
C(1)C(8)C(4)	111.9 (3)	C(12)C(15)C(16)	116.6 (3)
C(2)C(1)C(8)	103.4 (3)	C(12)C(15)C(17)	121.1 (3)
C(7)C(9)C(10)	107.4 (2)	C(16)C(15)C(17)	114.1 (3)
C(7)C(9)C(14)	105.1 (2)	C(10)C(11)C(15)	118.9 (2)
C(7)C(9)C(18)	112.8 (2)		

Table 4. *Torsion angles* ($^\circ$)

3-4-8-1	0.4 (4)	7-8-4-5	1.4 (4)
4-8-1-2	8.4 (3)	8-4-5-6	2.5 (4)
8-1-2-3	-13.6 (4)	4-5-6-7	-5.1 (4)
1-2-3-4	13.7 (4)	5-6-7-8	5.5 (3)
2-3-4-8	-9.0 (3)	6-7-8-4	-4.5 (3)
2-1-8-7	179.4 (4)	6-7-8-1	-175.3 (5)
2-3-4-5	179.1 (4)	3-4-5-6	174.5 (4)
1-8-4-5	174.4 (4)	3-4-8-7	-172.6 (4)
8-4-5-O(5)	-175.8 (4)		
9-10-11-12	-27.3 (4)		
10-11-12-13	3.6 (4)		
11-12-13-14	-3.2 (4)		
12-13-14-9	26.6 (4)		
13-14-9-10	-47.0 (3)		
14-9-10-11	47.2 (3)		

A final difference map showed no peak larger than $0.4 \text{ e } \text{\AA}^{-3}$ and an average shift/error of 0.19 during the final cycle of refinement. Atomic scattering factors and anomalous-dispersion corrections were calculated by XRAY 76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic positional parameters are presented in Table 1 while interatomic distances, valence angles and torsion angles are given in Tables 2, 3 and 4.*

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1965) of riolozatrione. The two five-membered rings exhibit flattened envelope conformations with ring C(4)C(5)C(6)C(7)C(8) approaching planarity due to the additional keto function. The planes defined by C(1)C(3)C(4)C(8) and C(4)C(5)C(7)C(8) make an interplanar angle of $173.5(4)^\circ$ indicating a π system which deviates from planarity by 6.5° . Such π -bond deformation has been reported recently for several sesquiorbornene derivatives (Watson, Galloy, Bartlett

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36360 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

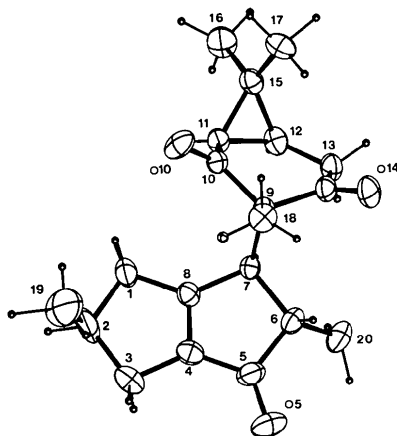


Fig. 1. *ORTEP* drawing of riolozatrione with thermal ellipsoids drawn at the 35% probability level. H atoms are shown as spheres of arbitrary size.

& Roof, 1981). The 18° deformation in the sesquiorbornene structures is attributed to relief of ring strain due to a slight rehybridization of the sp^2 C atoms (pyramidalization). The driving force is the unsymmetric substitution about the double bond which results in asymmetric interactions with the π -electron cloud. Such interactions are more difficult to rationalize in the present system.

The six-membered ring exhibits a 1,2-diplanar conformation with C(9) deviating from the ring plane. The C(2)–C(19) distance of $1.609(5) \text{ \AA}$ is unusually long; however, C(19) exhibits a large thermal motion which may be associated with flexing of the envelope conformation. Although the C(4)–C(8) double bond is highly strained and the π system deviates from planarity, the bond distance of $1.329(4) \text{ \AA}$ is normal.

Riolozatrione represents a new diterpene structural type which we have named riozane. The molecule is being screened for a variety of biological activities.

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