

5-Deoxy-5-hydroperoxytelekin* *O*-Methyl Derivative and its Pyrazoline Adduct, C₁₆H₂₂O₄ and C₁₇H₂₄N₂O₄†

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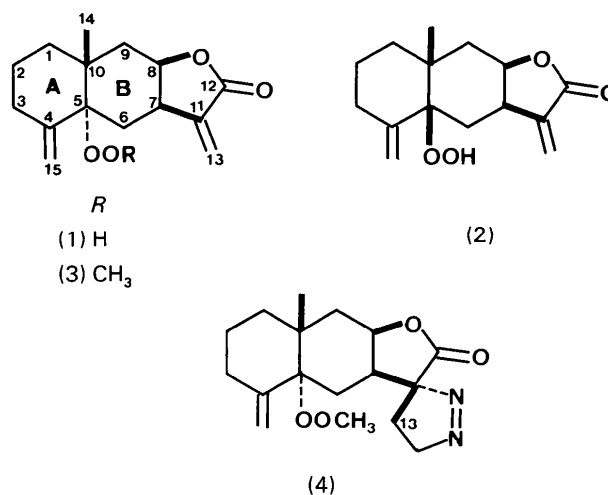
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Abstract. (3), C₁₆H₂₂O₄, $M_r = 278.3$, m.p. = 431–433 K, $[\alpha]_D^{25^\circ} = +231^\circ$ (CHCl₃, 0.5 g dm⁻³), orthorhombic, $P2_12_12_1$, $a = 6.953$ (3), $b = 10.108$ (3), $c = 21.211$ (5) Å, $U = 1490.8$ (7) Å³, $Z = 4$, $D_x = 1.23$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.09$ mm⁻¹, $F(000) = 600$, room temperature, $R = 0.040$ for 1327 independent reflexions. (4), C₁₇H₂₄N₂O₄, $M_r = 321.3$, m.p. = 428–429 K, $[\alpha]_D^{25^\circ} = +560^\circ$ (CHCl₃, 0.2 g dm⁻³), monoclinic, $P2_1$, $a = 6.278$ (2), $b = 12.522$ (6), $c = 10.885$ (4) Å, $\beta = 95.68$ (3)°, $U = 851.6$ (6) Å³, $Z = 2$, $D_x = 1.25$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.083$ mm⁻¹, $F(000) = 344$, room temperature, $R = 0.042$ for 1106 independent reflexions. In both compounds the *trans*-decalinic system shows the chair–chair conformation and the *cis*-fused γ -lactone ring is puckered. In (4) the peroxidic function shows positional disorder; the pyrazoline ring is almost orthogonal to the lactone moiety.

Introduction. 5-Deoxy-5-hydroperoxytelekin (1), an oil, is the major constituent of the alpine plant *Artemisia umbelliformis* Lam. This species also contains (2), the C(5) epimer of (1) and these compounds are the first hydroperoxyeudesmanolides encountered in nature (Appendino, Gariboldi & Nano, 1983). As part of an investigation on these naturally occurring hydroperoxides, we have undertaken the X-ray analysis of the pyrazoline adduct (4), which easily gave suitable crystals (Ricaldone, 1982). Since this compound showed evidence of disorder in the peroxidic function, we also carried out the analysis of (3) for which we

article we have illustrated the geometry of *trans*-decalin-type lactones leaving for a following article the illustration of *cis*-decalin-type lactones.



Experimental. Nicolet R3 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$, cell parameters from 19 reflexions for (3), $25 \leq 2\theta \leq 47^\circ$, from 24 reflexions for (4), $16 < 2\theta \leq 36^\circ$; ω scan at variable speed, backgrounds measured in stationary mode for 0.6 times the length of time of the peak scan; direct methods. (3): crystal 0.3 × 0.2 × 0.6 mm, 1549 independent reflexions, $2\theta \leq 50^\circ$, h 0–8, k 0–11, l 0–25, scan speed range 1.5° min⁻¹ for the weakest to 15° min⁻¹ for the strongest reflexions, scan range 1.4°; 1334 intensities with $I \geq 2\sigma(I)$ placed on absolute scale were able to obtain crystals only later, when enough purified material had become available. In the present

* Telekin is 9-hydroxy-1-methyl-6,10-dimethylene-4-oxatricyclo-[7.4.0.0^{3,7}]tridecan-5-one.

† Dedicated to the memory of Silvio Stefenelli.

by statistical methods using the Nicolet (1980) suite of programs; for all subsequent computations *SHELXTL* (Sheldrick, 1981) employed; structure solved by *RANT* (Yao Jia-Xing, 1981); 203 $|E|$'s > 1.57 and 2367 triple-phase relationships; best solution produced *E* map showing all non-hydrogen atoms; least-squares refinement on *F*; all H atoms found on difference Fourier map at advanced stage of anisotropic refinement and refined under initial constraint (Sheldrick, 1981) C—H = 0.96 (2) Å and three different thermal parameters for H atoms of $>CH_2$, $>CH$, and $-CH_3$ plus $=CH_2$ groups which converged to 0.064 (3), 0.036 (4) and 0.075 (3) Å²; $w = 1/[\sigma^2(F_o) + GF_o^2]$, σ is standard deviation of the observed amplitude based on counting statistics, $R = 0.040$, $wR = 0.044$, $G = 0.00117$, goodness of fit = 1.371, 1327 reflexions, 250 parameters; seven low-angle reflexions, measured with insertion of copper attenuator, discarded because of probable secondary-extinction effect; atomic scattering factors of *SHELXTL* used. (4): crystal 0.2 × 0.1 × 0.8 mm, 1255 independent reflexions, $2\theta \leq 45^\circ$, $h -7-6$, $k 0-13$, $l 0-11$, scan speed 1.50° min⁻¹ for the weakest to 10° min⁻¹ for the strongest reflexions, scan range 1.6°; 1106 intensities with $I \geq 2\sigma(I)$ treated as for (3); program *SOLV* (Sheldrick, 1981); 183 phases with $|E| > 1.45$ and 9 reflexions in the starting set yielded structure; refinement and weighting scheme as for (3); H atoms located on difference Fourier map; H atoms of the two methyl groups forced to ride on the bonded C(14) and C(16) atoms with thermal parameters set equal to 1.2 times the equivalent *U* of the carbon atoms; remaining hydrogens allowed to refine under initial (Sheldrick, 1981) constraint C—H = 1.02 (3) Å with two variable thermal parameters: one for the hydrogens at C(7) and C(8) and the other for remaining hydrogens; at convergence these parameters were 0.036 (5) and 0.063 (3) Å², respectively, with $R = 0.040$, $wR = 0.042$, $G = 0.0085$, goodness of fit = 1.370 for 1106 reflexions and 269 parameters. At this stage the C(16)—O(4) bond was abnormally short (1.30 Å) and the thermal motion of the two atoms was markedly anisotropic. We deemed this as due to positional disorder and completed the refinement assuming a 50% occupancy of the two dispositions of Fig. 3 and refining isotropically C(16) and O(4). The hydrogens at C(16) were then located on a difference Fourier map showing four peaks around C(16) and C(16'); two of them [H(161), H(162), Fig. 3], much higher, were considered shared by the two split carbons. Convergence yielded more sensible bond distances and angles for the peroxide group (Tables 4, 5) whilst the consistency values were of the same order as those for the unsplit model as expected, given the modest magnitude of the splitting: $R = 0.042$, $wR = 0.046$, $G = 0.00105$, goodness of fit = 1.375 for 1106 reflexions and 264 parameters; atomic scattering factors of *SHELX* used. Tables 1 and 2 give the final

coordinates and equivalent isotropic thermal parameters for (3) and (4), respectively.*

* Lists of structure factors, anisotropic temperature factors and hydrogen-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38832 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atom coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) for (3)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} *
O(1)	4470 (3)	7026 (2)	762 (1)	56 (1)
O(2)	5072 (3)	8194 (2)	-109 (1)	66 (1)
O(3)	5414 (3)	2746 (2)	1270 (1)	45 (1)
O(4)	5676 (3)	1730 (2)	776 (1)	62 (1)
C(1)	6580 (6)	4141 (3)	2342 (1)	70 (1)
C(2)	8512 (6)	3486 (4)	2468 (1)	79 (1)
C(3)	9021 (5)	2509 (3)	1959 (1)	65 (1)
C(4)	8851 (4)	3106 (2)	1302 (1)	47 (1)
C(5)	6906 (4)	3724 (2)	1171 (1)	37 (1)
C(6)	6702 (4)	4309 (2)	508 (1)	36 (1)
C(7)	4658 (4)	4826 (2)	373 (1)	39 (1)
C(8)	3825 (4)	5672 (2)	908 (1)	50 (1)
C(9)	4375 (5)	5298 (3)	1576 (1)	56 (1)
C(10)	6434 (4)	4796 (3)	1681 (1)	51 (1)
C(11)	4719 (4)	5811 (2)	-157 (1)	44 (1)
C(12)	4779 (4)	7145 (2)	134 (1)	49 (1)
C(13)	4746 (5)	5642 (3)	-772 (1)	61 (1)
C(14)	7867 (5)	5947 (3)	1634 (2)	63 (1)
C(15)	10294 (4)	3102 (3)	900 (1)	56 (1)
C(16)	4965 (5)	548 (3)	1033 (1)	61 (1)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

Table 2. Atom coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) for (4)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} *
O(1)	6690 (4)	5912	4470 (2)	53 (1)
O(2)	10076 (4)	6043 (3)	5342 (2)	63 (1)
O(3)	3054 (4)	8266 (2)	1912 (2)	51 (1)
O(4)	3865 (8)	9408 (5)	2061 (5)	56 (1)†
O(4')	3513 (8)	9389 (5)	1522 (5)	56 (1)†
N(1)	7132 (6)	7828 (3)	6293 (3)	64 (1)
N(2)	8498 (7)	8333 (4)	6975 (3)	76 (2)
C(1)	2299 (7)	6284 (3)	756 (4)	60 (1)
C(2)	2838 (7)	6560 (4)	-542 (4)	72 (2)
C(3)	3727 (7)	7692 (4)	-614 (4)	60 (1)
C(4)	5551 (5)	7888 (3)	406 (3)	45 (1)
C(5)	4964 (5)	7660 (3)	1700 (3)	41 (1)
C(6)	6713 (5)	7896 (3)	2738 (3)	40 (1)
C(7)	5963 (6)	7732 (3)	4030 (3)	45 (1)
C(8)	4870 (6)	6651 (3)	4158 (4)	51 (1)
C(9)	3445 (6)	6259 (3)	3030 (4)	54 (1)
C(10)	4195 (6)	6465 (3)	1759 (3)	44 (1)
C(11)	7878 (6)	7649 (3)	5011 (3)	41 (1)
C(12)	8404 (6)	6462 (3)	4976 (3)	44 (1)
C(13)	9814 (7)	8382 (4)	4996 (4)	52 (1)
C(14)	6023 (6)	5702 (3)	1539 (4)	55 (1)
C(15)	7457 (7)	8198 (4)	148 (3)	55 (1)
C(16)	2351 (14)	9993 (8)	2361 (8)	65 (2)†
C(16')	1955 (13)	10036 (8)	1802 (8)	59 (2)†
C(17)	10402 (10)	8595 (5)	6366 (4)	81 (2)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

† *U*_{iso}.

Table 3. Bond lengths (Å) and angles (°) for (3)

O(1)—C(8)	1.473 (3)	O(1)—C(12)	1.355 (3)
O(2)—C(12)	1.196 (3)	O(3)—O(4)	1.478 (2)
O(3)—C(5)	1.448 (3)	O(4)—C(16)	1.403 (3)
C(1)—C(2)	1.521 (6)	C(1)—C(10)	1.554 (4)
C(2)—C(3)	1.506 (5)	C(3)—C(4)	1.523 (4)
C(4)—C(5)	1.516 (3)	C(4)—C(15)	1.316 (4)
C(5)—C(6)	1.532 (3)	C(5)—C(10)	1.566 (3)
C(6)—C(7)	1.541 (3)	C(7)—C(8)	1.534 (3)
C(7)—C(11)	1.502 (3)	C(8)—C(9)	1.516 (4)
C(9)—C(10)	1.535 (4)	C(10)—C(14)	1.535 (4)
C(11)—C(12)	1.483 (3)	C(11)—C(13)	1.317 (3)
C(8)—O(1)—C(12)	109.7 (2)	O(4)—O(3)—C(5)	106.5 (2)
O(3)—O(4)—C(16)	105.9 (2)	C(2)—C(1)—C(10)	113.7 (3)
C(1)—C(2)—C(3)	111.5 (3)	C(2)—C(3)—C(4)	112.2 (3)
C(3)—C(4)—C(5)	113.6 (2)	C(3)—C(4)—C(15)	122.2 (3)
C(5)—C(4)—C(15)	124.2 (2)	O(3)—C(5)—C(6)	109.3 (2)
O(3)—C(5)—C(6)	109.3 (2)	C(4)—C(5)—C(6)	114.2 (2)
O(3)—C(5)—C(10)	102.8 (2)	C(4)—C(5)—C(10)	110.2 (2)
C(6)—C(5)—C(10)	110.4 (2)	C(5)—C(6)—C(7)	112.7 (2)
C(6)—C(7)—C(8)	113.6 (2)	C(6)—C(7)—C(11)	109.7 (2)
C(8)—C(7)—C(11)	101.2 (2)	O(1)—C(8)—C(7)	104.3 (2)
O(1)—C(8)—C(9)	110.6 (2)	C(7)—C(8)—C(9)	117.2 (2)
C(8)—C(9)—C(10)	117.0 (2)	C(1)—C(10)—C(5)	108.4 (2)
C(1)—C(10)—C(9)	109.4 (2)	C(5)—C(10)—C(9)	108.9 (2)
C(1)—C(10)—C(14)	109.8 (2)	C(5)—C(10)—C(14)	110.1 (2)
C(9)—C(10)—C(14)	110.2 (2)	C(7)—C(11)—C(12)	107.0 (2)
C(7)—C(11)—C(13)	131.0 (2)	C(12)—C(11)—C(13)	122.0 (2)
O(1)—C(12)—O(2)	121.9 (2)	O(1)—C(12)—C(11)	108.9 (2)
O(2)—C(12)—C(11)	129.2 (2)		

Table 4. Bond lengths (Å) and angles (°) for (4)

O(1)—C(8)	1.484 (4)	O(1)—C(12)	1.349 (4)
O(2)—C(12)	1.205 (5)	O(3)—O(4)	1.521 (6)
O(3)—O(4)	1.505 (6)	O(3)—C(5)	1.456 (4)
O(4)—O(4')	0.607 (7)	O(4')—C(16')	1.439 (11)
O(4)—C(16)	1.438 (10)	N(1)—N(2)	1.250 (5)
N(1)—C(11)	1.532 (5)	N(2)—C(17)	1.461 (7)
C(1)—C(2)	1.525 (7)	C(1)—C(10)	1.550 (5)
C(2)—C(3)	1.528 (7)	C(3)—C(4)	1.534 (5)
C(4)—C(5)	1.518 (5)	C(4)—C(15)	1.314 (5)
C(5)—C(6)	1.524 (5)	C(5)—C(10)	1.576 (5)
C(6)—C(7)	1.540 (5)	C(7)—C(8)	1.530 (5)
C(7)—C(11)	1.531 (5)	C(8)—C(9)	1.527 (5)
C(9)—C(10)	1.527 (6)	C(10)—C(14)	1.530 (5)
C(11)—C(12)	1.524 (5)	C(11)—C(13)	1.524 (6)
C(13)—C(17)	1.523 (6)	C(16')—C(16)	0.636 (12)
C(8)—O(1)—C(12)	109.9 (2)	N(1)—N(2)—C(17)	112.9 (4)
O(4)—O(3)—C(5)	103.6 (3)	C(1)—C(2)—C(3)	111.9 (4)
O(4')—O(3)—C(5)	105.0 (3)	C(3)—C(4)—C(5)	114.1 (3)
O(3)—O(4)—C(16)	103.2 (5)	C(5)—C(4)—C(15)	124.3 (3)
O(3)—O(4')—C(16')	100.9 (5)	O(3)—C(5)—C(6)	109.0 (3)
N(2)—N(1)—C(11)	111.2 (4)	O(3)—C(5)—C(10)	103.2 (3)
C(2)—C(1)—C(10)	113.2 (3)	C(6)—C(5)—C(10)	110.8 (3)
C(2)—C(3)—C(4)	111.2 (3)	C(6)—C(7)—C(8)	112.4 (3)
C(3)—C(4)—C(15)	121.5 (3)	C(8)—C(7)—C(11)	101.8 (3)
O(3)—C(5)—C(4)	109.2 (3)	O(1)—C(8)—C(9)	111.1 (3)
C(4)—C(5)—C(6)	115.3 (3)	C(8)—C(9)—C(10)	117.7 (3)
C(4)—C(5)—C(10)	108.6 (3)	C(1)—C(10)—C(9)	109.2 (3)
C(5)—C(6)—C(7)	112.8 (3)	C(1)—C(10)—C(14)	109.5 (3)
C(6)—C(7)—C(11)	110.8 (3)	C(9)—C(10)—C(14)	109.9 (3)
O(1)—C(8)—C(7)	103.3 (3)	N(1)—C(11)—C(12)	104.5 (3)
C(7)—C(8)—C(9)	116.3 (3)	N(1)—C(11)—C(13)	103.8 (3)
C(1)—C(10)—C(5)	109.1 (3)	C(12)—C(11)—C(13)	114.3 (3)
C(5)—C(10)—C(9)	108.7 (3)	O(1)—C(12)—C(11)	110.0 (3)
C(5)—C(10)—C(14)	110.4 (3)	C(11)—C(13)—C(17)	102.2 (4)
N(1)—C(11)—C(7)	109.6 (3)		
C(7)—C(11)—C(12)	101.9 (3)		
C(7)—C(11)—C(13)	121.6 (3)		
O(1)—C(12)—O(2)	123.1 (3)		
O(2)—C(12)—C(11)	126.9 (3)		
N(2)—C(17)—C(13)	106.0 (4)		

Table 5. Pertinent torsion angles (°); e.s.d.'s 0.2–0.4°

	(3)	(4)
(ω_1) C(8)O(1)C(12)C(11)	-10.8	-1.7
(ω_2) C(13)C(11)C(12)O(2)	-9.4	26.7
(ω_3) C(11)C(7)C(8)O(1)	-29.2	-34.7
(ω_4) C(9)C(8)C(7)C(6)	34.3	38.1
H(7)C(7)C(11)C(13)	-38 (2)	-80 (2)
C(15)C(4)C(5)O(3)	125.4	127.6
C(5)O(3)O(4)C(16)	151.7	159.0
C(5)O(3)O(4')C(16')		-147.8

Discussion. Tables 3 and 4 give the bond distances and angles and Figs. 1 and 2 the ORTEPII (Johnson, 1970) drawings of (3) and (4), respectively. In both molecules the *trans*-decalin system assumes a quasi-ideal chair-chair conformation as revealed by the relative positions of C(1) and C(4), and of C(6) and C(9), with respect to the mean planes through the remaining atoms of rings *A* and *B*. The angles at the C_{sp³} atoms of the six-membered rings (Tables 3, 4) range from 109 to 117°; the largest deviations from the ideal obtain at C(8) and C(9) in both compounds, indicating appreciable strain due to deviation from the axial position of O(1) (see below). The γ -lactone rings, *cis*-fused to ring *B*, show a puckered conformation, of the half-chair type, with C(7) above and C(8) below the plane through O(1), C(11) and C(12); $\sum |\omega_i|$ equals 83.7° for (3) and 101.2° for (4) (Table 5). The value of ω_3 (ring-junction torsion angle) is much narrower than 60° in both compounds, the value required by an ideal *cis* junction to a ring in the chair conformation, and closer to 20°, the value calculated for the minimum-energy conformation of an isolated α -methylene- γ -lactone (Guy, Sim & White, 1976). Besides, in this way O(1) moves away from C(14) minimizing the 1,3-diaxial interaction between these two functions. In (3) the sign of ω_2 (lactone-chromophore torsion angle) is paired to that of ω_3

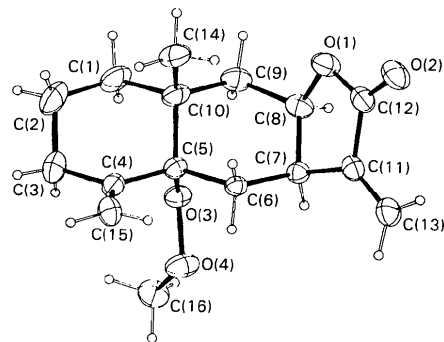


Fig. 1. ORTEPII drawing of one molecule of (3) with thermal ellipsoids at 20% probability level.

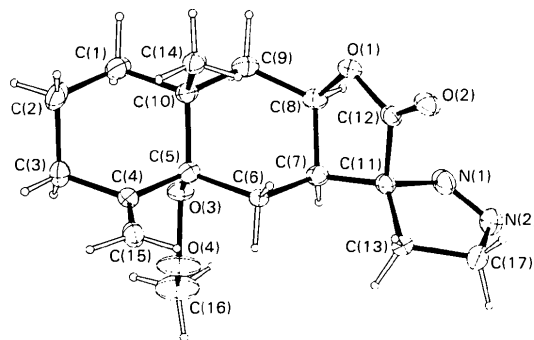


Fig. 2. ORTEPII drawing of one molecule of (4) with thermal ellipsoids at 20% probability level.

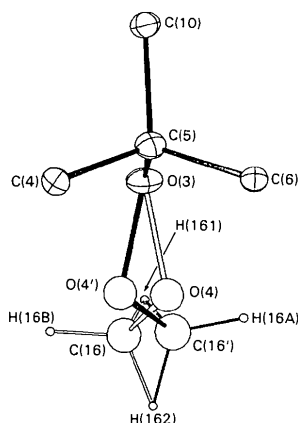


Fig. 3. ORTEP drawing, with thermal ellipsoids at 20% probability level, of a fragment of (4) showing the two alternative dispositions, with 50% occupancy factors, around the peroxidic function.

(Table 5), a result in agreement with the general relationship between the signs of these angles, for both the *cis*- and *trans*-fused lactones (Cox & Sim, 1977; McPhail & Sim, 1973). The chirality of ω_2 matches the sign of the experimental value of the circular dichroism (CD: $\theta_{260} = -1700^\circ$). The dihedral angle H(7)C(7)-C(11)C(13) is here $-38(2)^\circ$ corresponding to a conformation of the pseudo-rotational *A* type, after Samek (1979), for the exomethylene lactone; this is in keeping with the very small value of $J_{7,13}$ observed in the ¹H NMR spectrum of (3) (Appendino *et al.*, 1983).

The O(3)–O(4) length in the split model of (4) is longer than in (3) and several hydrogen peroxide complexes (1.46–1.47 Å; *e.g.* Fritchie & McMullan, 1981), but the O–C distances (Table 4) are normal and the torsion angles around the O–O bond (Table 5) approach the values of (3) whilst the torsion angle C(5)O(3)O(4)C(16) was $-174.7(4)^\circ$, refining the unsplit model.

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4 $\alpha\beta$,5,8,8 $\alpha\beta$ -Tetrahydronaphthoquin-1 α ,4 α -diol,* C₁₀H₁₄O₂

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Abstract. $M_r = 166.22$, orthorhombic, *Pbca*, $a = 20.479(4)$, $b = 8.101(1)$, $c = 21.375(3)$ Å, $V = 3546(1)$ Å³, $Z = 16$, $D_m(\text{floatation}) = 1.22(1)$, $D_x = 1.245$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.796$ cm⁻¹, $F(000) = 1440$, $T = 295$ K, $R = 0.048$ for

* IUPAC name: 1,4,4 $\alpha\beta$,5,8,8 $\alpha\beta$ -hexahydronaphthalene-1 α ,4 α -diol.

The pyrazoline ring of (4) is approximately planar [r.m.s.d. = 0.089 (2) Å] and it is almost orthogonal to the lactone ring. The torsion angle N(1)C(11)C(12)O(2) is negative, $-86.0(3)^\circ$, and this steric disposition gives rise to a strongly positive Cotton effect ($\theta_{327} = +22,000^\circ$; $\theta_{238} = +5640^\circ$) from the azochromophore. The sign of this effect complies with the empirical rule relating the junction type of an exomethylene- γ -lactone to the CD of the azochromophore of its corresponding pyrazoline adduct (Suchý, Doleiš, Herout, Šorm, Snatzke & Himmelreich, 1969).

We are indebted to Professor G. M. Nano for advice throughout this work. We warmly thank Rev. G. Culasso and the late Dr S. Stefenelli for providing the plant material.

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1953 observed data. Extensive hydrogen bonding links molecules in a three-dimensional network. The two crystallographically independent molecules adopt a similar conformation, half-chair cyclohexene ring *cis*-fused to a half-chair cyclohexenediol moiety. The OH configurations in each molecule are both *anti* with respect to the bridgehead H atoms; one is pseudo-equatorial, the other is pseudo-axial.