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(4*R**,8*S**,11*R**,13*S**,14*R**)-8,11-Epoxy-14-hydroxy-11-methyl-4-(1-methylvinyl)-6,9-dioxocyclotetradec-1-ene-1,13-carbolactone

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Abstract. $C_{19}H_{24}O_6$, monoclinic, $P2_1$, $a = 12{\cdot}552$ (5), $b = 6{\cdot}098$ (3), $c = 11{\cdot}680$ (4) Å, $\beta = 98{\cdot}587$ (17)°, $Z = 2$, $V = 884$ Å^3, $D_x = 1{\cdot}30$, $D_c = 1{\cdot}31$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·104 mm^{-1}. The compound was isolated from a soft coral of the genus *Sinularia*. The structure was determined by direct methods and refined to a conventional R of 0·059 based on 1124 unique diffractometer data.

Introduction. Structural studies of the title compound (Fig. 1) by spectroscopic and chemical means did not yield an unambiguous solution (Bowden, Coll, Mitchell, Mulder & Stokie, 1978). The present crystallographic study was undertaken to provide an unambiguous structure.

A suitable single crystal (0·18 × 0·16 × 0·59 mm, recrystallized from dichloromethane) was mounted on the Australian Atomic Energy Commission's four-circle computer-controlled diffractometer. The diffractometer is fitted with a solid-state detector, the desired radiation being selected by pulse-height discrimination. 2991 intensities with $2\theta \leq 45°$ were collected using Mo $K\alpha$ radiation. The systematic absences ($0k0$, $k = 2n$) and the statistical distribution of the E's defined the space group as $P2_1$. After absorption correction (Elcombe, Cox, Pryor & Moore, 1971), crystallographically equivalent reflections were averaged and the Lp correction was applied to yield a set of 1363 unique reflections.

For data collected with a solid-state detector, Howard & Jones (1976) have shown that intensities may be affected by the incorporation of white radiation. Typical diffraction profiles are shown in Fig. 1 of Howard & Jones (1977). It can be seen from these that for larger values of 2θ the measured intensities should be unaffected, while for small angles of 2θ, where there is little dispersion of the white radiation, it seems inevitable that the measured intensity will incorporate a considerable contribution from the white radiation. At intermediate values of 2θ, where the diffraction profile resembles the 200 profile in the said Fig. 1, the scan can be set to include or exclude the white radiation as desired. Measurements of several reflections in this intermediate range establish a correction factor, which in the present experiment was 0·78. Data collected at $2\theta < 15°$ incorporated the white-radiation contribution, and the correction factor was subsequently applied to these data.

The structure was solved with the *MULTAN* 74 direct-method program package (Main, Woolfson, Lessinger, Germain & Declercq, 1974), using all 143 E's $\geq 1{\cdot}4$. Twenty of the twenty-five non-hydrogen atoms were visible in the E map calculated for the phase set having the second-highest combined figure of merit and the lowest PSIZERO. The remaining atoms were located by conventional structure factor/Fourier map techniques. The structure was refined using the Brookhaven full-matrix least-squares program *LINUS*, with anisotropic thermal parameters for all atoms. No extinction correction was applied. H atoms, although visible in a final difference Fourier map, were not included. Experimental weights of the form $w^{-1} = \sigma^2(F_o^2)$ were applied. The $\sigma^2(F_o^2)$ were estimated from an analysis of symmetry-equivalent reflections and

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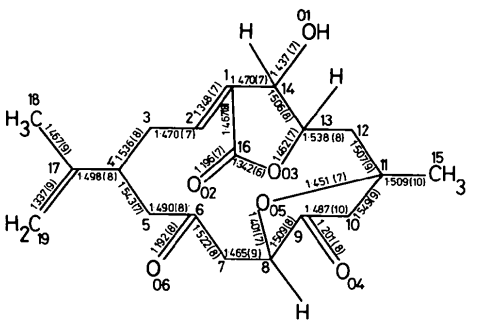

Fig. 1. Schematic structure and bond lengths (Å) of the title compound (IUPAC nomenclature has been adopted).

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Table 1. *Positional parameters* ($\times 10^4$)

	x	*y*	*z*
C(1)	6983 (2)	8094 (6)	4036 (2)
C(2)	5965 (2)	7343 (6)	3786 (2)
C(3)	4960 (2)	8611*	3551 (2)
C(4)	4201 (2)	8000 (6)	2442 (2)
C(5)	4826 (2)	7162 (7)	1487 (2)
C(6)	5670 (2)	8669 (7)	1169 (2)
C(7)	6573 (2)	7573 (7)	647 (3)
C(8)	7582 (2)	8824 (7)	840 (2)
C(9)	8517 (2)	7908 (7)	312 (3)
C(10)	9514 (2)	8113 (7)	1170 (3)
C(11)	9138 (2)	9318 (7)	2208 (3)
C(12)	9591 (2)	8353 (6)	3367 (2)
C(13)	8879 (2)	8377 (6)	4329 (2)
C(14)	7968 (2)	6759 (6)	4238 (2)
C(15)	9342 (3)	1753 (7)	2158 (3)
C(16)	7301 (2)	404 (6)	4215 (2)
C(17)	3338 (2)	6399 (6)	2631 (2)
C(18)	3643 (3)	4183 (7)	3046 (3)
C(19)	2306 (2)	7018 (9)	2447 (4)
O(1)	8079 (1)	5590 (5)	5321 (2)
O(2)	6779 (2)	2028 (5)	4254 (2)
O(3)	8380 (1)	530 (5)	4402 (2)
O(4)	8443 (2)	7099 (8)	−631 (2)
O(5)	7985 (1)	8938 (5)	2022 (1)
O(6)	5627 (1)	616 (6)	1276 (1)

* Origin defined by fixing *y* coordinate of C(3).

were constrained such that $\sigma^2(F_o^2) \geq$ counting statistics alone. The function minimized was $\sum w(|F_o^2| - |F_c^2|)^2$.

Refinement of the structure based on all unique reflections converged to a conventional R of 0·113 with an S (the estimated standard deviation of an observation of unit weight) of 12·7. An analysis of structure factor agreement indicated a bias in the low-angle data ($2\theta \leq 25°$). These data (242 reflections) were deleted from the data set and refinement converged at $R = 0{\cdot}059$, $S = 3{\cdot}9$. A final structure factor calculation based on the atomic parameters derived from the refinement using high-angle data, but using all data, gave a conventional R of 0·079. It is suggested that the poor agreement of the low-angle data is due to extinction and/or an overestimation of the white-radiation component.

Positional parameters are shown in Table 1, while bond lengths are shown in Fig. 1. The molecular geometry and unit-cell contents are shown in Fig. 2.*

* Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34233 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

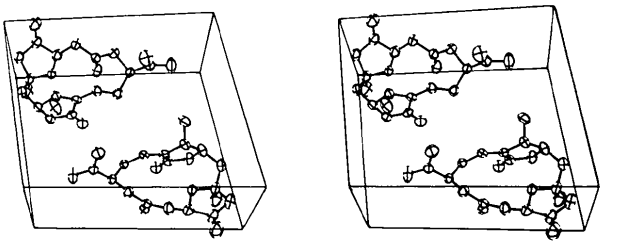

Fig. 2. Stereoview of the title compound showing the molecular geometry and unit-cell contents. Thermal ellipsoids are drawn at the 50% confidence limits.

Discussion. Bond lengths and angles are in agreement with those of similar cembranoid compounds (Bernstein, Shmueli, Zadock & Kashman, 1974). The molecule lies approximately parallel to the *ac* crystallographic plane. Intermolecular hydrogen bonding exists between the hydroxyl group and O(2) and O(3) of an adjacent molecule. The O(1)—O(2) distance of 2·886 (5) Å suggests a strong interaction, whereas the O(1)—O(3) interaction [3·308 (6) Å] is probably better described as a short van der Waals contact. Both five-membered rings are essentially planar. In agreement with spectroscopic measurements, bond lengths within the γ-lactone group indicate a high degree of conjugation.

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