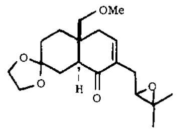
phenylseleninic acid and further oxidation with hydrogen peroxide to benzeneperoxyseleninic acid, which brings about epoxidation of the tri-



vi

substituted olefinic linkage. Details of this and other reactions will be reported shortly.[15]

(15) P. A. Grieco, Y. Yokoyama, S. Gilman, and M. Nishizawa, *J. Org. Chem.*, **42,** 2034 (1977).

(16) The use of *tert*-butyl hydroperoxide in *benzene* containing triton B has previously been employed for epoxidation of α,β-unsaturated enones [N. C. Yang and R. A. Finnegan, *J. Am. Chem. Soc.*, **80,** 5845 (1958)]. Our attempts to convert **22** → **23** in benzene solution resulted in complete recovery of starting enone.

(17) P. A. Grieco, K. Hiroi, J. J. Reap, and J. A. Noguez, *J. Org. Chem.*, **40,** 1450 (1975).

(18) K. B. Sharpless and M. W. Young, *J. Org. Chem.*, **40,** 947 (1975); P. A. Grieco, Y. Masaki, and D. Boxler, *J. Am. Chem. Soc.*, **97,** 1597 (1975).

(19) P. A. Grieco, S. Gilman, and M. Nishizawa, *J. Org. Chem.*, **41,** 1485 (1976).

(20) P. A. Grieco, J. A. Noguez, Y. Masaki, K. Hiroi, M. Nishizawa, A. Rosowsky, S. Oppenheim, and H. Lazarus, *J. Med. Chem.*, **20,** 71 (1977).

(21) The synthesis of lactone **31** and the conversion of its corresponding diol to bisnorvernolepin and bisnorvernomenin has been reported [S. Danishefsky, T. Kitahara, P. F. Schuda, and S. Etheredge, *J. Am. Chem. Soc.*, **98,** 3028 (1976)]. Recently the conversion of bisnorvernolepin to vernolepin has appeared [S. Danishefsky, T. Kitahara, R. McKee, and P. F. Schuda, *ibid.*, **98,** 67 15 (1976)].

(22) P. A. Grieco and K. Hiroi, *J. Chem. Soc., Commun.*, 1317 (1972).

(23) P. A. Grieco, N. Marinovic, and M. Miyashita, *J. Org. Chem.*, **40,** 1670 (1975).

(24) The products were isolated by extraction of the aqueous layer with several portions of the indicated solvent. The combined organic extracts were washed with water followed by saturated brine. The organic layer was usually dried with either anhydrous sodium sulfate or anhydrous magnesium sulfate. Filtration followed by removal of the solvent in vacuo (water aspirator) employing a rotary evaporator provided the products.

(25) H. Bauer, *Ber.*, **46,** 92 (1913). We have found that the crude crystalline material obtained from the procedure of Bauer can be sublimed at 100 °C (0.2 mmHg), providing yellow crystals of *o*-nitrophenyl selenocyanate, mp 144 °C.

Marine Natural Products. Xenicin: a Diterpenoid Possessing a Nine-Membered Ring from the Soft Coral, *Xenia elongata*[1]

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Abstract: The structure of a new diterpenoid, xenicin (**1**), isolated from a soft coral, *Xenia elongata*, has been determined by single crystal x-ray diffraction. Xenicin possesses a nine-membered carbocyclic ring trans-fused to a dihydropyran ring. The crystals are monoclinic, space group $C2$, four molecules per unit cell with dimensions $a = 17.704$ (3), $b = 9.061$ (2), $c = 18.656$ (4) Å; $\beta = 113.33$ (2)°. The intensity data (3015) were collected on an automatic diffractometer. The structure, determined by direct methods, was refined by least-squares methods. The final R was 0.046 for all the data.

In our continuing research on the chemistry of soft corals (alcyonaceans) we have isolated a diterpenoid, xenicin (**1**), having a new skeleton in which the only carbocyclic ring present is nine membered. The cyclononene ring itself occurs in only one diterpenoid isolated previously[2] and among sesquiterpenoids is restricted to a few compounds related to caryophyllene.[3] Other investigations of soft corals have resulted in the discovery of new sesquiterpenes,[4] diterpenes,[5] and sterols.[6] The diterpenes previously reported from alcyonaceans have a cembrene skeleton[5a–f] or one easily derived from it by cyclization.[5g]

Results and Discussion

Xenicin, mp 141.5–142.3 °C, $[\alpha]^{23.5}{}_{D}$ −36.7° (0.6, $CHCl_3$), was obtained by adsorption chromatography from the hexane soluble portion of an aqueous 2-propanol extract of *Xenia elongata* collected near Heron Island, Australia. Interestingly, specimens of *X. elongata* from Picnic Bay, Magnetic Island, Australia and from the Fiji Islands did not contain any of this new diterpenoid. High resolution mass spectral and elemental analysis established the formula $C_{28}H_{38}O_9$ for **1**. Its infrared spectrum lacked hydroxyl absorption, but displayed a strong, broad band centered at 1735 cm^{-1} (acetate) with a shoulder at 1700 cm^{-1}. The NMR spectrum contained signals for four acetates and three vinyl methyl groups in addition to downfield multiplets corresponding to nine protons from which some partial structural information could be gleaned, but from which it was not possible to deduce a complete structure. Preliminary hydrolytic and catalytic reduction experiments did not yield encouraging results. The complete structure of xenicin was elucidated by single crystal x-ray diffraction and is shown in **1**. This formula also connotes the absolute configuration derived from crystallographic data.

A stereoview[7] of xenicin is shown in Figure 1. Bond distances, bond angles, and torsion angles are given in Figures 2, 3, and 4. Xenicin possesses a dihydropyran ring trans-fused to a nine-membered carbocyclic ring and represents the first member of a hitherto unknown skeletal system.[8] The nine-membered ring contains a trans double bond with a torsion angle of −158° and an exocyclic double bond. Bond lengths and torsion angles indicate that the nine-membered ring is slightly strained. No short intermolecular distances were found in the crystal structure.

The NMR chemical shift assignments and proton couplings in **1**, confirmed by double irradiation experiments at 100 and 220 MHz, are shown in Table I. The enol ether proton H(3) exhibits allylic coupling to H(4a), but not to the conformationally mobile H(12). At 220 MHz (benzene-d_6) the H(9) signal is clearly visible as a broadened triplet, J = 7 Hz, indicating a coupling of nearly 7 Hz with one of the C(10) protons and only a very small coupling to the other as would be suggested by the conformation of crystalline **1**.

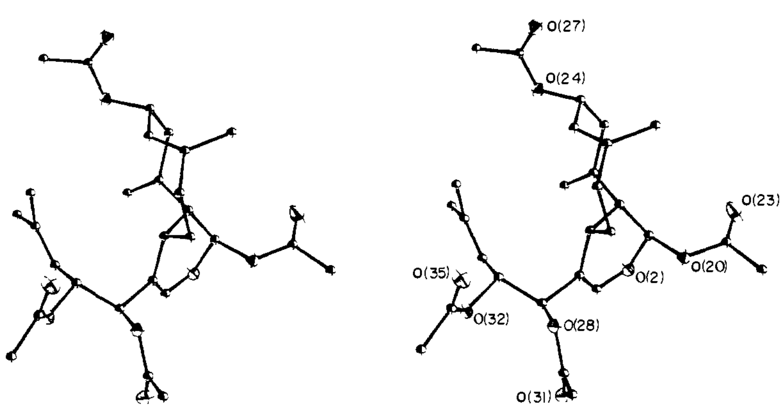


Figure 1. Stereoview of single molecule. The nine largest atoms are oxygen.

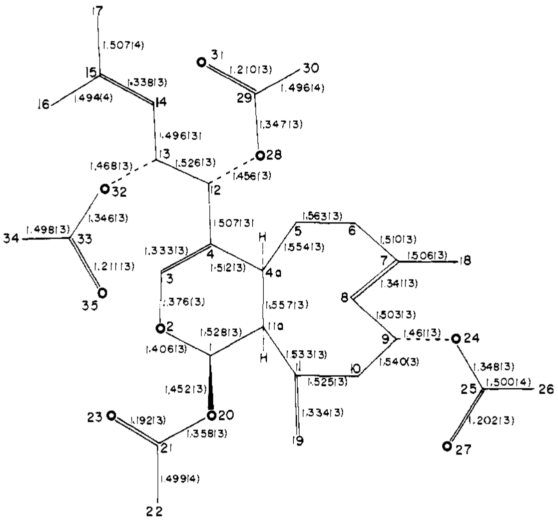


Figure 2. Bond distances with standard deviations for last digit in parentheses.

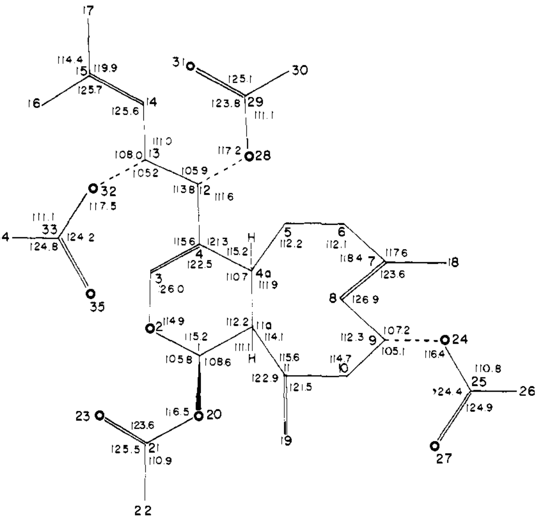


Figure 3. Bond angles. Standard deviations for the bond angles are between 0.18 and 0.25°.

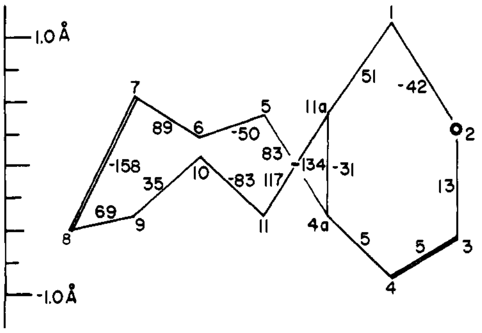
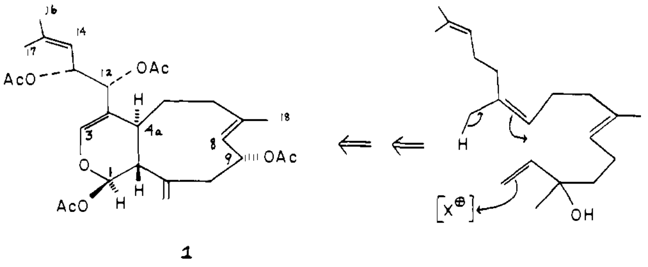


Figure 4. The torsion angles in the two rings. The vertical elevations describe the distances from the least-squares plane through both rings.

Table I. NMR Chemical Shift and Multiplicity Data for Xenicin (**1**)

Proton	Solvent C_6D_6	Solvent $CDCl_3$	Multiplicity, *J* [coupling proton(s)]
H(1)	6.10	5.87	d, 2 [H(11a)]
H(3)	6.65	6.58	d, 2 [H(4a)]
H(4a)	2.26	2.19	
H(8)	5.42	5.27	br d, 8-9 [H(9)]
H(9)	5.75	5.70	br t, 8-9 [H(8), one H(10)]
H(11a)	1.85	1.88	
H(12)	5.62	5.38	d, 9-10 [H(13)]
H(13)	6.10	5.82	t, 9-10 [H(12), H(14)]
H(14)	5.08	5.08	br d, ~10 [H(13); H(16,17)]
H(16); H(17)	(1.53, 1.84)	(1.74, 1.84)	
H(18)	1.48	1.74	
H(19)	4.91	4.82, 4.96	
OAc	1.60 (3) 1.74 (9)	2.04 (3) 2.06 (6) 2.08 (3)	

The biosynthesis of xenicin may involve cyclization of geranylgeraniol in a manner analogous to that proposed[9] for caryophyllene and related compounds, followed by oxidative cleavage of the resulting cyclobutane ring and eventual closure of the dihydropyran ring. However, a more direct formation of the nine-membered ring can be envisioned as occurring via oxidative cyclization of geranyllinalool as outlined below. We are searching for compounds related to xenicin which might provide some insight into this question.



1

Experimental Section

Melting points were taken on an A. H. Thomas Unimelt apparatus and are uncorrected. Infrared spectra were taken on a Beckman IR-8 spectrophotometer. NMR spectra were acquired on Varian T-60, XL-100, or HR-220 spectrometers in the solvents specified; signals are reported in parts per million (δ) downfield from internal tetramethylsilane. Low resolution mass spectra were obtained on a Hitachi RMU-7 spectrometer. Chromatographic supports were Florisil (Fisher Scientific, 100-200 mesh) and silica gel for thin layer chromatography (type 60; EM Reagents distributed by Brinkmann Instruments, Inc.). Elemental analyses were performed by Mr. E. Meier, Department of Chemistry, Stanford University, Stanford, Calif.

Isolation of Xenicin (1). To approximately 2 lb (wet weight) of *Xenia elongata* collected at Heron Island, Australia and preserved in 2-propanol was added water to give an approximately 1/1 water/alcohol mixture. The specimens were allowed to soak for a day after the dilution with water, then the solids were separated by filtration, the 2-propanol evaporated under reduced pressure, and the residual water removed by lyophilization.[10] The resulting light brown residue, 58.6 g, was extracted with distilled hexane in a Soxhlet extractor and the hexane solubles were chromatographed on Florisil using chloroform to give 1.2 g of a brown solid. Rechromatography of this material on 40 g of thin-layer mesh silica gel using ethyl acetate/benzene (1/9) as eluent (20-mL fractions) gave 357 mg of a white solid, homogeneous by TLC, in the 11-15th fractions. Recrystallization of this solid from benzene/hexane afforded 295 mg of xenicin (**1**): mp 141.5-142.3 °C; $[\alpha]^{23.5}{}_D$ −36.7° (0.61, $CHCl_3$); IR (KBr) 2980, 2940, 2860, 1735 (br), 1700 (sh), 1665, 1635, 1440, 1375, 1235 (vs), 1205, 1180, 1155, 1005, 930, 870; mass spectrum (70 eV) 518 (3) (M^+), 459 (6), 458 (2), 400 (3), 399 (5), 398 (5), 392 (52), 391 (21), 339 (5), 338 (4), 305 (8), 297 (3), 296 (4), 290 (5), 289 (29), 248 (8), 229 (37), 211 (5), 201 (9), 185 (5), 183 (7), 173 (8), 159 (7), 145 (7), 135 (8), 131 (7), 119 (8), 105 (11), 97 (15), 93 (11), 91 (11), 85 (35), 83 (20), 78 (23), 69 (17), 60 (11), 55 (17), 45 (12), 43 (100), and 41 (19). Anal. Calcd for $C_{28}H_{38}O_9$: C, 64.86; H, 7.38; M^+ 518.251 58. Found C, 64.90; H, 7.37; M^+ 518.248 88.

Crystallization and Crystal Data. Needle-like crystals were obtained from a benzene/hexane solution of the compound. The data crystal was cut from a needle and had the shape of a rectangular parallelepiped with an approximate volume of 0.26 mm³. A separate crystal having a similar shape and an approximate volume of 0.03 mm³ was used in the Friedel pair determination of the absolute configuration. The crystal data at −160 °C are: $C_{28}H_{38}O_9$; M = 518.6; monoclinic; $a = 17.704\ (3)$, $b = 9.061\ (2)$, $c = 18.656\ (4)$ Å; $\beta = 113.33\ (2)°$; $V = 2748.0$ Å³; $Z = 4$; ρ_{calcd} (−160 °C) = 1.254, ρ_{calcd} (room temp) = 1.207, ρ_{obsd} (room temp) = 1.197 g cm^{-3}; the unit cell dimensions at room temperature are $a = 18.073\ (2)$, $b = 9.183\ (1)$, $c = 18.855\ (3)$ Å, $\beta = 113.92\ (1)°$; F(000) = 1112; space group $C2$ as confirmed by structure determination; nickel filtered Cu Kα radiation; λ(Cu Kα_1) 1.540 51 Å for 2θ data and λ(Cu K$\bar{\alpha}$) 1.5418 Å for intensity data; μ(Cu K$\bar{\alpha}$) = 7.8 cm^{-1}. The cell parameters were determined by a least-squares fit to the $\pm 2\theta$ values of 32 reflections distributed throughout all of reciprocal space. The observed density was measured by the flotation method in a mixture of hexane and carbon tetrachloride.

The crystal was cooled in a stream of cold nitrogen gas. The temperature was measured as −160 °C, with maximum variations of 2 °C. The intensities of all 3015 unique reflections with $\theta < 75°$ were measured on a Nonius CAD-4 automatic diffractometer using a θ-2θ scan technique. The scan widths ($\Delta\theta$) were adjusted to the dispersion and calculated with the formula $\Delta\theta° = (1.2 + 0.12 \tan\theta)°$, for each reflection. A horizontal receiving aperture with a variable width [width (mm) = $4 + 0.86 \tan\theta$], and height of 6 mm was located 173 mm from the crystal. A reflection was scanned for a maximum of 60 s, with two-thirds of the time spent on scanning the peak (P) and one-sixth of the time spent on each the high θ and low θ backgrounds (LH and RH). The unscaled intensities (I) were calculated as $I = P - 2(RH + LH)$. A standard reflection was monitored after every 20 measurements. The orientation of three reflections was automatically checked after every 100 measurements. A new orientation matrix was automatically obtained if the 2θ, ω, ϕ, or χ angle of these reflections was changed by more than 0.1°.

There were 47 reflections which could not be distinguished from the background on the basis that the intensity (I) was less than $2(T)^{1/2}$ ($T = [P + 2(RH + LH)]$). These reflections were assigned intensities equal to $1.41T^{1/2}$ for the purpose of least-squares refinement. Lorentz and polarization corrections were applied to the data. Each amplitude

Table III. Final Fractional Coordinates (×10⁴) and Isotropic Thermal Parameters for Carbon Atoms[a]

	x	y	z	B, Å²
C(1)	9643 (1)	−6098 (3)	7060 (1)	1.31 (3)
C(3)	8859 (1)	−7721 (3)	7468 (1)	1.33 (3)
C(4)	8654 (1)	−6684 (2)	7866 (1)	1.18 (3)
C(5)	9330 (1)	−4257 (3)	8555 (1)	1.32 (3)
C(6)	9087 (1)	−2597 (3)	8548 (1)	1.35 (3)
C(7)	9043 (1)	−1813 (3)	7818 (1)	1.30 (3)
C(8)	8328 (1)	−1827 (3)	7191 (1)	1.31 (3)
C(9)	8207 (1)	−1582 (3)	6356 (1)	1.33 (3)
C(10)	8549 (1)	−2865 (3)	6032 (1)	1.43 (3)
C(11)	8459 (1)	−4385 (3)	6339 (1)	1.28 (3)
C(12)	8163 (1)	−7210 (2)	8316 (1)	1.24 (3)
C(13)	7347 (1)	−6399 (2)	8108 (1)	1.30 (3)
C(14)	6793 (1)	−6640 (3)	7271 (1)	1.48 (3)
C(15)	6315 (1)	−5615 (3)	6787 (1)	1.67 (3)
C(16)	6245 (2)	−4042 (3)	6993 (2)	2.36 (4)
C(17)	5789 (2)	−6011 (3)	5953 (2)	2.45 (4)
C(18)	9832 (1)	−1212 (3)	7809 (1)	1.60 (3)
C(19)	7835 (1)	−5277 (3)	5938 (1)	1.59 (3)
C(21)	11092 (1)	−5695 (3)	7695 (1)	1.73 (4)
C(22)	11824 (2)	−5889 (3)	8449 (2)	2.04 (4)
C(25)	6939 (1)	−266 (3)	5785 (1)	1.51 (3)
C(26)	6030 (2)	−439 (3)	5334 (2)	1.98 (4)
C(29)	8896 (1)	−8240 (3)	9585 (1)	1.54 (3)
C(30)	9264 (2)	−7882 (3)	10438 (1)	1.85 (4)
C(33)	6923 (1)	−6275 (3)	9183 (1)	1.40 (3)
C(34)	6599 (1)	−7174 (3)	9673 (1)	1.68 (4)
C(40)	8796 (1)	−5059 (2)	7784 (1)	1.13 (3)
C(41)	9125 (1)	−4802 (2)	7134 (1)	1.22 (3)

[a] Standard deviation for last digit is in parentheses.

Table II. Final Fractional Coordinates and Anisotropic Thermal Parameters for Oxygen Atoms[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(2)	9272 (1)	−7493 (2)	6989 (1)	232 (8)	171 (8)	241 (7)	4 (7)	133 (6)	−28 (7)
O(20)	10394 (1)	−6166 (2)	7762 (1)	163 (7)	269 (8)	210 (7)	38 (7)	85 (6)	45 (7)
O(23)	11107 (1)	−5206 (3)	7107 (1)	360 (11)	497 (14)	317 (10)	−180 (10)	169 (8)	28 (10)
O(24)	7322 (1)	−1583 (2)	5889 (1)	166 (7)	187 (8)	224 (7)	3 (6)	34 (6)	16 (7)
O(27)	7282 (1)	885 (2)	6026 (1)	234 (8)	213 (9)	324 (9)	30 (7)	89 (7)	−18 (7)
O(28)	8612 (1)	−7014 (2)	9153 (1)	185 (8)	162 (7)	168 (7)	−9 (6)	51 (6)	8 (6)
O(31)	8841 (1)	−9466 (2)	9312 (1)	303 (9)	196 (8)	253 (9)	30 (7)	81 (7)	40 (7)
O(32)	6963 (1)	−7083 (2)	8594 (1)	190 (7)	185 (8)	204 (7)	−26 (6)	97 (6)	−22 (6)
O(35)	7127 (1)	−4992 (2)	9301 (1)	349 (9)	233 (9)	335 (10)	−57 (8)	198 (8)	−73 (8)

[a] The x, y, and z (all ×10⁴) are fractional coordinates. The anisotropic parameters (Å², all ×10³) are used in the expression: $\exp(-[2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)])$. Standard deviation for the last digit is in parentheses.

Table IV. Final Fractional Coordinates ($\times 10^3$) and Isotropic Thermal Parameters for Hydrogen Atoms[a]

	x	y	z	β, Å^2
H(11)	975 (2)	−596 (4)	659 (2)	2.0 (6)
H(31)	872 (2)	−875 (4)	747 (2)	1.5 (6)
H(51)	929 (2)	−476 (4)	903 (2)	1.9 (6)
H(52)	989 (2)	−437 (4)	860 (2)	1.5 (6)
H(61)	942 (2)	−214 (4)	905 (2)	1.3 (5)
H(62)	858 (2)	−258 (5)	860 (2)	2.9 (8)
H(81)	784 (2)	−219 (4)	728 (2)	1.4 (5)
H(91)	842 (2)	−66 (4)	623 (2)	1.3 (5)
H(101)	828 (2)	−290 (4)	547 (2)	1.8 (6)
H(102)	914 (2)	−276 (4)	616 (2)	2.4 (7)
H(121)	805 (2)	−830 (4)	823 (2)	1.4 (6)
H(131)	743 (2)	−543 (4)	825 (2)	1.0 (5)
H(141)	681 (2)	−758 (4)	709 (2)	1.3 (5)
H(161)	640 (3)	−348 (6)	668 (2)	4.0 (9)
H(162)	567 (3)	−385 (5)	685 (3)	4.0 (9)
H(163)	650 (3)	−385 (6)	749 (3)	4.4 (10)
H(171)	519 (2)	−583 (4)	584 (2)	2.7 (7)
H(172)	584 (2)	−681 (4)	584 (2)	1.6 (6)
H(173)	594 (3)	−542 (6)	559 (3)	4.2 (9)
H(181)	1009 (2)	−49 (5)	824 (2)	3.0 (8)
H(182)	1024 (2)	−197 (5)	790 (2)	3.4 (8)
H(183)	976 (2)	−67 (4)	733 (2)	1.6 (6)
H(191)	776 (2)	−619 (4)	613 (2)	1.5 (6)
H(192)	740 (2)	−510 (4)	545 (2)	1.8 (6)
H(221)	1177 (4)	−541 (8)	881 (3)	6.0 (3)
H(222)	1186 (2)	−696 (4)	865 (2)	1.5 (6)
H(223)	1233 (2)	−543 (5)	841 (2)	3.0 (8)
H(261)	595 (2)	−119 (4)	507 (2)	2.6 (7)
H(262)	582 (3)	40 (5)	499 (2)	3.8 (9)
H(263)	579 (3)	−96 (5)	562 (2)	4.4 (10)
H(301)	949 (3)	−687 (6)	1057 (2)	4.3 (10)
H(302)	967 (3)	−859 (6)	1067 (3)	5.0 (11)
H(303)	883 (2)	−798 (5)	1065 (2)	3.0 (8)
H(341)	643 (3)	−648 (5)	998 (3)	4.2 (10)
H(342)	703 (2)	−778 (5)	1001 (2)	3.2 (8)
H(343)	611 (3)	−767 (7)	935 (3)	5.9 (13)
H(401)	822 (2)	−453 (4)	761 (2)	1.4 (6)
H(411)	953 (2)	−402 (3)	729 (2)	0.9 (5)

[a] Standard deviation for last digit is in parentheses.

was assigned an experimental weight based on counting statistics.[11]

Structure Determination and Refinement. Phase determination was carried out with the program MULTAN[12] using the 300 E values >1.5. The reflections 16 2 $\bar{9}$ and 3 1 $\bar{5}$ were used to define the origin. Three general reflections and one special reflection were permitted to generate 128 phase sets. As expected for a space group having no translational symmetry elements, the absolute figure of merit of the phase set yielding the solution was one of the lower values.[12] The coordinates of all nonhydrogen atoms were generated by MULTAN and refined isotropically with block-diagonal (9×9) least-squares[13] methods using isotropic temperature factors. All hydrogen atom positions were either determined from geometrical considerations or located in a difference Fourier and were included in the refinement. The oxygen atoms were given anisotropic temperature factors, and after the absolute configuration was assigned (vide infra) the observed structure factors were corrected[14] for the anomalous scattering of Cu radiation by the oxygen atoms. None of the carbon atoms showed anisotropic motion in the difference Fourier synthesis. Atomic and anomalous scattering factors for carbon and oxygen were taken from the "International Tables for X-ray Crystallography"[15] and those for hydrogen from Stewart, Davidson, and Simpson.[16]

The refinement was terminated when all shifts were <60% of the corresponding standard deviation. The final R value $R = \sum \| kF_o| - |F_c\| / \sum |kF_o|$ is 0.046 for all 3015 reflections. The final parameters are in Tables II, III, and IV. The least-squares calculations minimized the quantity $\sum w_F(|kF_o| - |F_c|)^2$. The mean values of $w_F \Delta F^2$ calculated for various ranges of $|F_o|$ were quite constant, validating the weighting scheme used. The final difference Fourier showed a peak (0.49 eÅ^{-3}) lying on the bond between C(8) and C(9), a negative peak (−0.40 eÅ^{-3}) near C(26), and a peak (0.46 eÅ^{-3}) located centrally in an apparent hole in the crystal structure with closest nonhydrogen distances of O(2), 2.893; O(24), 3.141; and C(26), 3.168 Å. It appears possible that this hole is large enough to accommodate partial occupancy by a water molecule. If this is the case the occupation is less than 10%. All other peaks were <0.35 eÅ^{-3}.

The absolute configuration was determined by measuring differences in I_+ and I_-,[17] first using Cu radiation and again using Cr radiation. Sensitive reflections were chosen based on the largest values of the quantity $(F_{c+}^2 - F_{c-}^2)/\sigma F_o^2$. For the Cu determination the anomalous scattering of the oxygen atoms was considered and for the Cr determination the anomalous scattering for both the oxygen and the carbon was considered. For each reflection intensities for hkl, $\bar{h}\bar{k}\bar{l}$, $\bar{h}k\bar{l}$, and $h\bar{k}l$ were measured ten times and averaged. The sign of the average difference between Friedel pairs was then compared to the calculated sign for the trial structure. Fifteen of the twenty reflections

Table V. Comparison of the Observed Bijoet Differences and Those Calculated for the Trial Structure[a]

Cu Radiation							Cr Radiation						
h	k	l	$\frac{I_{hkl} - I_{\bar{h}\bar{k}\bar{l}}}{I_{hkl}}$	$\frac{I_{\bar{h}k\bar{l}} - I_{h\bar{k}l}}{I_{\bar{h}k\bar{l}}}$	$\frac{\Delta I_{av}}{I}$[b]	$\frac{F_{c+}^2 - F_{c-}^2}{F_{c+}^2}$	h	k	l	$\frac{I_{hkl} - I_{\bar{h}\bar{k}\bar{l}}}{I_{hkl}}$	$\frac{I_{\bar{h}k\bar{l}} - I_{h\bar{k}l}}{I_{\bar{h}k\bar{l}}}$	$\frac{\Delta I_{av}}{I}$	$\frac{F_{c+}^2 - F_{c-}^2}{F_{c+}^2}$
−10	4	10	0.06	0.07	0.06	−0.05	−10	4	10	0.23	0.16	0.19	−0.06
−6	4	3	−0.02	−0.01	−0.01	0.06	−6	4	3	−0.11	−0.04	−0.07	0.07
−2	4	4	0.05	0.02	0.03	−0.04	−2	4	4	0.17	0.14	0.16	−0.05
−1	5	9	0.03	−0.05	−0.01	0.05	−1	5	9*	−0.01	0.08	0.03	0.07
−4	2	13	0.11	0.13	0.12	−0.07	−4	2	13	0.05	0.13	0.09	−0.07
4	2	5	−0.03	0.12	0.04	−0.05	4	2	5	0.23	−0.14	0.04	−0.05
−4	4	10	−0.06	−0.01	−0.03	0.04	−4	4	10*	0.01	0.04	0.02	0.05
5	1	7	0.05	0.06	0.05	−0.05	5	1	7	0.09	[c]	0.09	−0.05
3	3	9*	−0.53	0.00	−0.26	−0.04	3	3	9	0.02	0.13	0.07	−0.06
−6	4	16	0.07	0.06	0.06	−0.04	−3	1	10	−0.03	−0.02	−0.02	0.05
−12	4	5	0.08	0.01	0.04	−0.04	9	1	4	−0.09	0.00	−0.04	0.07
2	6	13*	−0.02	0.08	0.03	0.06	−11	1	1	−0.01	0.15	0.07	−0.10
9	1	10	−0.08	0.11	0.01	−0.07	−10	2	11	0.02	−0.08	−0.03	0.07
−21	3	10*	0.02	0.02	0.02	0.04	−3	3	6	0.17	0.20	0.18	−0.08
−2	4	20	0.06	0.14	0.10	−0.04	4	4	5	0.16	0.17	0.16	−0.07
−9	3	21	−0.11	0.00	−0.05	0.04	8	6	1*	0.28	0.40	0.34	0.14
13	1	9	−0.02	0.07	0.02	−0.04	5	5	1	−0.13	0.05	−0.04	0.15
4	2	19*	−0.01	0.15	0.07	0.04	−1	1	14	0.02	0.09	0.05	−0.04
1	3	20	0.01	0.13	0.07	−0.04							
−19	3	16*	0.04	0.06	0.05	0.04							

[a] Fifteen out of twenty reflections in the Cu radiation study and fifteen out of eighteen reflections in the Cr radiation study indicate an opposite absolute configuration than that of the trial structure. All positional coordinates and figures apply to the correct absolute configuration. Reflections not in agreement are starred (*). [b] $\Delta I_{av}/I$ is equal to the average of $(I_{hkl} - I_{\bar{h}\bar{k}\bar{l}})/I_{hkl}$ and $(I_{\bar{h}k\bar{l}} - I_{h\bar{k}l})/I_{\bar{h}k\bar{l}}$. [c] This value could not be calculated because of collision difficulties on the Nonius CAD-4 automatic diffractometer.

in the Cu radiation study and fifteen of the eighteen reflections in the Cr radiation study indicated that the correct absolute configuration was opposite to that of the trial structure. The partial occupancy by a water molecule does not affect the absolute configuration determination because its contribution to the anomalous part of the structure factor is <0.5% and will not change the sign of ΔF^2. Table V summarizes these results. Positional parameters and all drawings apply to the correct absolute configuration. The observed and calculated structure factors are available.[18]

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Supplementary Material Available: Listings of the structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Abstracted in part from the Ph.D. thesis of D. J. Vanderah, University of Oklahoma, Norman, Oklahoma, June, 1975.

(2) No diterpenoids having a nine-membered carbocyclic ring are listed in ref 3, and only one example was found in the literature since 1970: S. J. Torrance, R. M. Weidhopf, J. R. Cole, S. K. Arora, R. B. Bates, W. A. Beavers, and R. S. Cutler, *J. Org. Chem.*, **41**, 1855 (1976).

(3) T. K. Devon and A. I. Scott, "Handbook of Naturally Occurring Compounds", Vol. II, Academic Press, New York, N.Y., 1972, p 128.

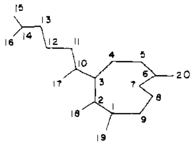
(4) Y. M. Sheikh, G. Singy, M. Kaisin, H. Eggert, C. Djerassi, B. Tursch, D. Daloze, and J. C. Braekman, *Tetrahedron*, **32**, 1171 (1976); B. Tursch, J. C. Braekman, D. Daloze, P. Fritz, A. Kelecom, R. Karlsson, and D. Losman, *Tetrahedron Lett.* 747 (1974); B. Tursch, M. Colin, D. Daloze, D. Losman, and R. Karlsson, *Bull. Soc. Chim. Belg.*, **84**, 81 (1975); M. Kaisin, Y. M. Sheikh, L. J. Durham, C. Djerassi, B. Tursch, D. Daloze, J. C. Braekman, D. Losman, and R. Karlsson, *Tetrahedron Lett.*, 2239 (1974).

(5) (a) F. J. Schmitz, D. J. Vanderah, and L. S. Ciereszko, *J. Chem. Soc., Chem. Commun.*, 407 (1974); (b) J. Bernstein, U. Shmeuli, E. Zadock, Y. Kashman, and I. Neeman, *Tetrahedron*, **30**, 2817 (1974); (c) B. Tursch, J. C. Braekman, D. Daloze, M. Herin, R. Karlsson, and D. Losman, *ibid.*, **31**, 129 (1975); (d) B. Tursch, M. Colin, D. Daloze, D. Losman, and R. Karlsson, *Bull. Soc. Chim. Belg.*, **84**, 81 (1975); (e) B. Tursch, J. C. Braekman, and D. Daloze, *ibid.*, **84**, 767 (1975); (f) M. G. Missakian, B. J. Burreson, and P. J. Scheuer, *Tetrahedron*, **31**, 2513 (1975); (g) J. E. Burks, D. van der Helm, C. Y. Chang, and L. S. Ciereszko, *Acta Crystallogr., Sect. B*, **33**, 704 (1977).

(6) For recent examples see: B. Tursch, C. Hootelé, M. Kaisin, D. Losman, and R. Karlsson, *Steroids*, **27**, 137 (1976); M. Bortolotto, J. C. Braekman, D. Daloze, and B. Tursch, *Bull. Soc. Chim. Belg.*, **85**, 27 (1976); J. M. Moldowan, W. L. Tan, and C. Djerassi, *Steroids*, **26**, 107 (1975); J. M. Moldowan, B. Tursch, and C. Djerassi, *ibid.*, **24**, 387 (1974).

(7) C. K. Johnson, ORTEP, Oak Ridge National Laboratory Report ORNL-3794 (1965).

(8) We recommend the name xeniane for the new carbon skeleton present in xenicin and suggest the numbering shown in **1**.



1

(9) J. B. Hendrickson, *Tetrahedron*, 7, 82 (1959).

(10) A procedure used to obtain a standard sample for surveying for various types of biological activity.

(11) D. van der Helm, S. E. Ealick, and J. E. Burks, *Acta Crystallogr., Sect. B*, **31**, 1013 (1975).

(12) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, **27**, 368 (1971).

(13) F. R. Ahmed, SFIS program, NCR-10, National Research Council, Ottawa (1966).

(14) A. L. Patterson, *Acta Crystallogr.*, **16**, 1255 (1963).

(15) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, 1974, pp 73, 149.

(16) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175-3187 (1965).

(17) J. M. Bijvoet, A/ F. Peerdeman, and A. J. van Bommel, *Nature (London)*, **168**, 271 (1951).

(18) See paragraph at end of paper regarding supplementary material.