Tetrahedron Vol. 37, No. 16, pp. 2725 to 2733, 1981
Printed in Great Britain.

0040-4020/81/162725–09$02.00/0
Pergamon Press Ltd.

THE CORAXENIOLIDES, CONSTITUENTS OF PINK CORAL, *CORALLIUM* SP.[1a]

ROBERT E. SCHWARTZ and PAUL J. SCHEUER*
Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822, U.S.A.

and

VOLKER ZABEL and WILLIAM H. WATSON
Department of Chemistry, Texas Christian University, Fort Worth, TX 76129, U.S.A.

(*Received in USA* 26 *August* 1980)

Abstract—From a deep-sea (-350 m) gorgonian, *Corallium* sp., we have isolated five diterpenes, which are structurally related to the xenicins, previously known from soft corals and brown algae. The structure of the principal constituent, coraxeniolide-A (**1**) was determined by X-ray diffraction studies. Spectral analysis and chemical correlations elucidated the structures of coraxeniolides B(**3**), C(**7**), C′(**10**), and of corabohcin (**13**).

Man's fascination with ornaments fashioned from coral dates back at least 25,000 years, as judged by archeological evidence.[2] Until very recently coral was gathered in shallow caves by skin divers or in deep water by the use of *ingegno*, a device that is dragged over the ocean floor breaking and entangling corals—as well as everything else in its path.[2] In Hawaii, most black coral is collected by skin divers, but pink and other precious (gold, bamboo) corals are harvested by manned minisubmersible at depths of −300 to −350 m. This commercial operation has spearheaded scientific study of many previously inacessible animals.

Most corals suitable for fabrication of jewelry are gorgonians (order Gorgonacea, subclass Alcyonaria, class Anthozoa, phylum Cnidaria) with brightly colored and gracefully shaped endoskeletons, which are composed of calcium carbonate spicules that are embedded in a matrix of organic polymer. Shallow water (≤ -75 m) gorgonians are virtually absent in Hawaiian waters, but more than 90 deep-sea species have been described. The Hawaiian pink coral of commerce is pale pink ("angel skin") and is the endoskeleton of a *Corallium* sp.[3], which is harvested in the Molokai channel off Makapuu, Oahu, by the submersible *Star II*.

When the submarine returns to Makai Pier, Makapuu, from its daily dive the polyps of *Corallium* sp. were scraped off the skeleton and steeped in methanol. Cold methanol extraction was repeated twice. The combined extracts were filtered and concentrated. The concentrate was partitioned between methylene chloride and water. The organic residue ($\sim 0.3\%$ of whole wet animal) was purified by column chromatography on BioSil A, followed by hplc on Partisil.

The most abundant constituent, which we have named coraxeniolide-A (**1**) in recognition of its biological origin from *Corallium* sp. and its structural relationship to xenicin (**2**),[4] was isolated in about 650 mg/kg yield from the animal as a viscous colorless oil. Its composition of $C_{20}H_{30}O_2$, obtained by high resolution mass measurement, and salient spectral data (one each isopropyl, methyl, and exocyclic methylene group) pointed to the diterpenoid nature of the molecule. Furthermore, the presence of two additional carbon-carbon double bonds (four ^{13}C signals between δ153 and 124) and of a δ-lactone ring (1748 cm^{-1}) established the bicyclic nature of the molecule. However, neither extensive decoupling experiments nor transformations of **1** to a mixture of two epimeric hexahydro derivatives and to a diol, nor attempted double bond cleavage by ozone or by osmium tetroxide/periodate, provided unequivocal evidence of the size of the carbocyclic ring of **1**. Fortunately, coraxeniolide-A after prolonged standing in dichloromethane at −10° crystallized and its structure was determined by X-ray diffraction methods (Fig. 1). Coraxeniolide-A is an unrearranged diterpenoid. Its δ-lactone ring is *trans*-fused to a cyclononene. The lactone is in a boat conformation and the carbocyclic ring is approximately perpendicular to it. The shape of the ring system explains why only two and not four hexahydro-**1** were isolated after catalytic hydrogenation: the endocyclic double bond can be hydrogenated only from the outside of the ring, which makes the two hexahydro derivatives epimeric at C-11.

Prior to the isolation by Schmitz *et al.*[4] of xenicin (**2**, numbering according to Schmitz) from the soft coral *Xenia elongata* (order Alcyonacea, subclass Alcyonaria) in 1977 only a few cyclononane terpenoids had been described. Notable among these were the sesquiterpenoid caryophyllenes, constituents of many essential oils, and the diterpenoid jatrophatrione, isolated from a member of the Euphorbiaceae.[5] Since 1977, however, numerous xenicin derivatives have been reported from marine sources—by Kashman and Groweiss[6a,b] from *X. macrospiculata*, by Tursch and his group[7] from *X. novae-brittaniae*, by Fenical and coworkers[8] from the brown alga *Dictyota crenulata*, and by Finer *et al.*[9] from *D. flabellata* and from the sea hare *Aplysia depilans*.

The second most abundant constituent of *Corallium* sp. (325 mg/kg) was coraxeniolide-B (**3**), a colorless oil of composition $C_{20}H_{28}O_2$, thus possessing one more unsaturation than **1**. One additional carbon–carbon double bond was indicated by eight rather than six ^{13}C resonances in the olefinic region. Again, an exocyclic methylene (113.5 ppm, t) was present in **3**. Other parallel features included a δ-lactone (1729 cm^{-1}), in boat conformation and *trans*-fused to the carbocyclic ring, as evidenced by similar *vic* and *gem* *J*-values of the C-1 protons. The difference in chemical shifts of the C-1 protons

---

[a] Dedicated to the memory of Robert Burns Woodward, this paper will be included in the Book version of the special Woodward Memorial Supplement.

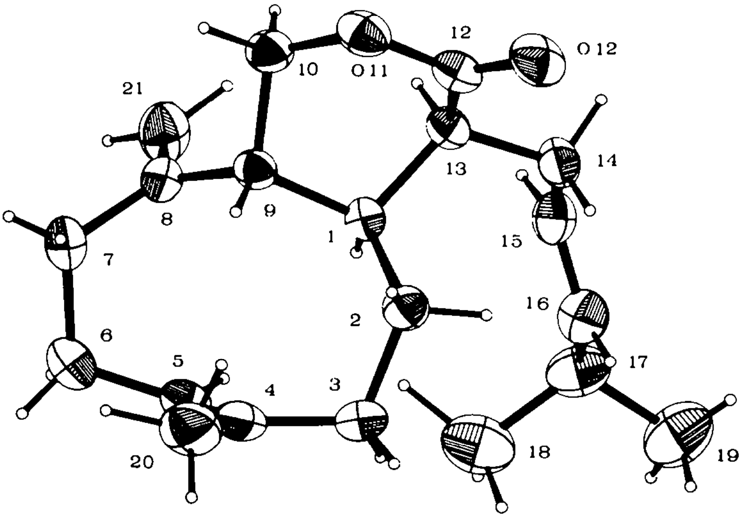


Fig. 1. Single crystal X-ray structure of coraxeniolide-A (1).

(4.05–3.54 = 0.51 ppm), however, is large when compared with the data for **1**, where $\Delta\delta = 4.19-3.93 = 0.26$ ppm. This difference is reflected in the multiplicity of the off-resonance C-1 carbon signal, which appears as a doublet of doublets in the spectrum of **3**, but as a triplet in the spectrum of **1**. This is consistent with Hagaman's[10] observation that the multiplicity of the carbon signal varies with the chemical shift difference of the geminal proton signals vs the geminal coupling constant, which is 12 Hz in our case. Whenever $\Delta\delta > 3x J_{gem}$, the carbon signal will change from a triplet to a doublet of doublets.

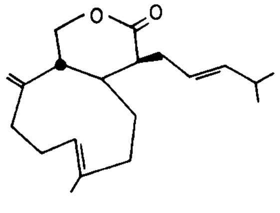
The ^{13}C spectrum of **3** also revealed *E*-geometry of the C-7 (8) double bond. The quartet signal for the C-18 methyl resonates at 16.73 ppm and not in the 22–25 ppm region anticipated for *Z*-configuration.[11] Entirely consistent with this assignment is the corresponding 16.73 ppm signal in **1**, where *E*-geometry is known from X-ray data.

The UV spectrum of **3**, λ_{max}^{MeOH} 270 nm (log ϵ 4.08), when compared with that of **1** (end absorption), proved that the additional carbon–carbon double bond of **3** is conjugated. Since NMR data had shown that size and shape of the rings in **1** and **3** were similar, the additional olefinic linkage had to be in the side chain, exocyclic and *alpha* to the lactone (ν_{max} 1729 cm^{-1}).

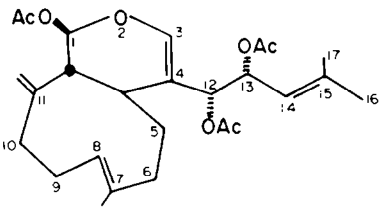
The remaining structural ambiguity, the configuration of the C-4 (12) double bond was resolved by comparison with appropriate models. In coraxeniolide-B (**3**) H-12 appears as a doublet ($J = 12$ Hz) at δ7.16, coupled to H-13, which resonates as a broad doublet of doublets ($J = 15$, 12 Hz) at δ6.38. H-13 in turn is *trans*-coupled to a doublet of doublets ($J = 15$, 8 Hz) at δ5.84, a signal assigned to H-14. In 13-*trans*-retinal (**4a**) H-12 (comparable to H-13 in **3**) resonates at δ6.27, while in 13-*cis*-retinal (**4b**) the signal appears downfield at δ7.28.[12] In both cases (**3** and **4a**) the upfield signal represents a γ-proton *trans* to the carbonyl. This is also the case in the synthetic intermediate **5**, where the comparable H-3 resonates at δ6.21.[13] Finally, the data for xeniolide-A (**6a**)[6b] and for isoxeniolide-A (**6b**)[7] (Table 1) agree with our assignment. The γ-proton (H-13) of **6a** resonates at δ6.53 vs δ6.85 in **6b**. In the UV spectra of **6a** and **6b** λ_{max}

Table 1. ^1H NMR spectral data of coraxeniolide-B (**3**), xeniolide-A (**6a**), and isoxeniolide-A (**6b**)

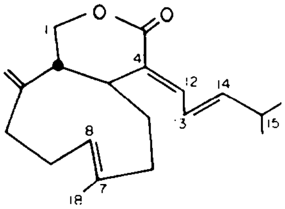
	3 (100 MHz, C_6D_6)	**3**, (100 MHz, $CDCl_3$)	**6a** (270 MHz, $CDCl_3$)	**6b** (100 MHz, $CDCl_3$)
HC-12	7.16 1H d (J=12 Hz)	6.86 1H d (J=12 Hz)	6.92 1H d (J=11 Hz)	6.39 1H d (J=10 Hz)
HC-13	6.38 1H bdd (J=15,12 Hz)	6.40-6.04 2H m	6.53 1H dd (J=15,11 Hz)	6.85 1H dd (J=15,10 Hz)
HC-14	5.84 1H dd (J=15,8 Hz)		6.26 1H d (J=15 Hz)	6.06 1H d (J=15 Hz)
H_3C-16,17	0.91 6H d (J= 6 Hz)	1.04 6H d (J=7 Hz)	1.38 6H s	1.33 6H s
HC-1β	3.88 1H dd (J=12,6 Hz)	4.05 1H dd (J=12,6 Hz)	4.08 1H dd (J=11,6 Hz)	4.07 1H dd (J=12,6 Hz)
HC-1α	3.46 1H dd (J=12,12 Hz)	3.54 1H dd (J=12,12 Hz)	3.61 1H dd (J=11,11 Hz)	3.61 1H dd (J=12,12 Hz)
H_2C-19	4.71 2H s	4.94 1H s 4.82 1H s	5.09 1H s 4.91 1H s	5.09 1H s 4.95 1H s
HC-8	5.37 1H m	5.38 1H m	5.32 1H d (J=8 Hz)	5.24 1H d (J=8 Hz)
H_3C-18	1.46 3H d (J=1.5 Hz)	1.69 3H d (J=1 Hz)	1.70 3H s	1.67 3H s



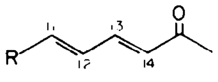
1(A)



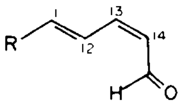
2



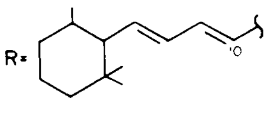
3(B)

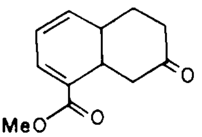


4a

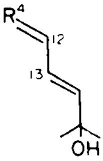


4b

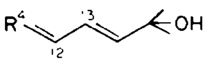




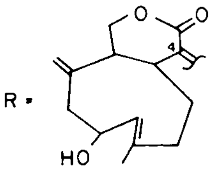
5



6a



6b



for **6a** [*E*-C-4(12)] is observed at 268 nm and at 263 nm in **6b** [*Z*-C-4(12)], consistent with the 270 nm maximum of coraxeniolide-B (**3**).

Coraxeniolide-C (**7**), $C_{20}H_{28}O_2$, which is isomeric with **3**, was isolated from pink coral (65 mg/kg) as a crystalline white solid, m.p. 68–69°. The spectral data (*see* Experimental Section) showed that the principal structural features of coraxeniolide-B (**3**) were also present in **7**. UV data (λ_{max}^{MeOH} 215 nm, log ϵ3.89) suggested an α,β-unsaturated-δ-lactone ($1737\,cm^{-1}$) and hence C-14 (15) as the site of the unassigned olefinic linkage. This point should be subject to proof by conversion of coraxeniolide-C (**7**) into coraxeniolide-B (**3**) *via* DBU-induced double bond migration: the C-14 (15) olefin was expected to move into conjugation with the C4 (12) olefin. The reaction, however, yielded two white solids, coraxeniolides-D (**8**) and -D′ (**9**), neither of them identical with coraxeniolide-B (**3**). Apparently, proton abstraction from doubly allylic C-13 by DBU preferentially generated an enolate anion, followed by ketonization and proton delivery to C-4. If this rationalization was correct, coraxeniolides-D (**8**) and D′ (**9**) should be epimeric at C-4.

The major crystalline product (26%), m.p. 127–129°, was designated coraxeniolide-D (**8**), and the minor amorphous compound (20%), m.p. 115–118°, coraxeniolide-D′ (**9**). In coraxeniolide-D (**8**) the UV maximum had shifted to 239 nm (log ϵ 4.11), thereby indicating formation of a conjugated dienic side chain in **8**. Loss of the side chain in the mass spectrum of **8** (*m*/*z* 219, 13%) from the molecular ion supports this assignment.

Although NMR data suggested persuasively that coraxeniolides-A (**1**), -B (**3**), and -C (**7**) shared *trans*-configuration of the ring juncture, independent proof appeared desirable. Attempts to hydrogenate coraxeniolide-C (**7**) to presumably the same epimeric pair of hexahydro derivatives that were obtained by hydrogenation of **1**, were unsuccessful and led only to an inseparable mixture of hexa- and octahydro compounds, presumably because of the difficultly reducible C-4 (12) double bond. However, hydrogenation of D (**8**) obtained from C (**7**) by double bond migration should be more amenable to hydrogenation and provide equally rigorous proof of ring fusion geometry. Indeed, hydrogenation of coraxeniolide-D (**8**) over palladium on carbon in methanol furnished a mixture of epimeric products identical with that obtained previously by hydrogenation of coraxeniolide-A (**1**). This reaction not only secured the *trans*-geometry of the ring juncture, but also proved that the side chain configuration of coraxeniolide-D (**8**) is identical with that of A (**1**), namely *beta*.

Coraxeniolide-D′ (**9**), the C-4 epimer of D (**8**), exhibits the ^1H NMR signals expected for the assigned structure (Table 2), except for the surprising difference of the signals for the C-1 hydrogens. At 360 MHz the C-1 protons absorb at δ4.15 and 4.01, both doublets of doublets, with $J_{gem} = 12$ Hz, and $J_{vic} = 4.5$, 3.5 Hz. The comparable signals in coraxeniolide-D (**8**) are doublets of doublets at δ4.21 and 3.96, with $J_{gem} = 12$ Hz, and $J_{vic} =$ 8, 12 Hz. This radical change in vicinal coupling must be caused by a change in conformation of the lactone ring. The C-1 proton coupling constants of D (**8**) parallel those of coraxeniolide-A (**1**), which was determined by X-ray diffraction. In these two compounds the lactone ring is in boat conformation with C-1 and C-4 pointing downward. In coraxeniolide-D′ (**9**), on the other hand, the δ-lactone boat is reversed, with C-1 and C-4 pointing up. In that conformation the dihedral angle between H-11a and both C-1 protons is approximately 45°, resulting in J_{vic} values of 3.5 and 4.5 Hz. The dihedral angle between H-4 and H-4a is approximately 170°, leading J_{vic} of 8 Hz.

Another constituent of pink coral, a colorless oil (200 mg/kg) of composition $C_{20}H_{28}O_2$ behaves chromatographically much like coraxeniolide-B (**3**), and could therefore not be rigorously purified. It was designated coraxeniolide-C′ (**10**) since all spectral data, including decoupling experiments, pointed to a close relationship with coraxeniolide-C (**7**), most likely one of C-12 epimers (Table 2).

Reaction of coraxeniolide-C′ (**10**) with DBU furnished a 29% yield of coraxeniolide-D (**8**) and 38% of D′ (**9**), as evidenced by full spectral comparison.

The only significant differences between the two compounds are the ^1H NMR data for protons at C-12 and C-13. In C′ (**10**) H 12 is a triplet ($J = 8$ Hz) resonating at δ6.57, coupled to a broad 2H doublet of doublets ($J =$ 8, 8 Hz) at δ2.72 (H_2-13). In turn, these protons are coupled to H-14, a triplet ($J = 8$ Hz) with additional fine coupling, absorbing at δ5.08. Conversely, in coraxeniolide-C (**7**) H-12 is a triplet ($J = 8$ Hz) observed at δ5.61. This proton is coupled ($J = 8,8$ Hz) to H_2-13, seen as a broad doublet of doublets at δ3.25. H-14 of coraxeniolide-C (**7**) was part of a 2H multiplet at δ5.28, which could not be resolved.

The large difference in chemical shifts of H-12 in C (**7**) and in C′ (**10**) is undoubtedly caused by anisotropy originating in the lactone carbonyl. But it is not immediately obvious whether the carbonyl causes an upfield or a downfield shift for the spatially proximate (*E* geometry) proton. Among the numerous α-methylene-δ-lactones for which ^1H NMR data are available the observed chemical shift differences were equally substantial, but we could find none, where the shift values had been assigned to specific protons. In compound **11** e.g. the pertinent protons resonate at δ6.47 and 5.78,[14] but the values are not assigned.

In many cases the situation-large shift differences, but no or contradictory assignments—was analogous for α-methylene-γ-lactones. However, for the isomeric cyclobuxines (**12a, b**) the proton or methyl that is closest to the carbonyl experiences the downfield shift.[15] On this basis, coraxeniolide-C (**7**) possesses *Z*, and C′ (**10**) *E*-geometry for the C-4 (12) olefin.

A trace constituent of pink coral (32 mg/kg) was isolated as a colorless oil of composition $C_{22}H_{34}O_2$. Spectral data indicated a normal diterpene biogenetically related to the coraxeniolides, for which we suggest the trivial name corabohcin (**13**).† Unlike the coraxeniolides, corabohcin (**13**) is a monocyclic acetate (ν_{max} 1732 cm^{-1},

Table 2. 100 MHz ^1H NMR spectral data of coraxeniolide-C (**7**), D (**8**), D′ (**9**), and C′ (**10**)

	7 (C_6D_6)	**8** ($CDCl_3$)^a	**9** ($CDCl_3$)^a	**10** (C_6D_6)	**8** ($CDCl_3$)^b	**9** ($CDCl_3$)^b
H-1	3.81 1H dd (J=12,7 Hz) 3.48 1H dd (J=12,12 Hz)	4.21 1H dd (J=12,8 Hz) 3.96 1H dd (J=12,12 Hz)	4.19 1H dd (J=12,4 Hz) 4.03 1H dd (J=12,4 Hz)	3.84 1H dd (J=12,6 Hz) 3.38 1H dd (J=12,12 Hz)	4.20 1H dd (J=12,8 Hz) 3.95 1H dd (J=12,12, Hz)	4.19 1H dd (J= 12,4 Hz) 4.03 1H dd (J=12,4 Hz)
H-4		3.58 1H bdd (J=7,7 Hz)	2.89 1H dd (J=8,8 Hz)		3.59 1H dd (J=7,7 Hz)	2.90 1H dd (J=8,8 Hz)
H-8	5.28 2H m	5.34 1H bt (J=7 Hz)	5.34 1H m	5.34 1H m	5.33 1H bt (J=7 Hz)	5.35 1H m
H-14		5.89 1H bd (J=10 Hz)	5.88 1H d (J=10 Hz)	5.08 1H mt (J=8 Hz)	5.89 1H bd (J=10 Hz)	5.89 1H bd (J=10 Hz)
H-13 H_2-13	3.25 2H bdd (J=8,8 Hz)	6.39 1H dd (J=15,10 Hz)	6.29 1H dd (J=15,10 Hz)	2.72 2H bdd (J=8,8 Hz)	6.39 1H dd (J=15,10 Hz)	6.30 1H dd (J=15,10 Hz)
H-12	5.61 1H t (J=8 Hz)	5.90 1H dd (J=15,7 Hz)	5.55 1H dd (J=15,8 Hz))	6.57 1H t (J=8 Hz)	5.90 1H dd (J=15,7 Hz)	5.56 1H dd (J=15,8 Hz)
H_3-16	1.66 3H bs	1.78 6H bs	1.79 3H bs	1.62 3H bs	1.77 6H bs	1.80 3H bs
H_3-17	1.62 3H bs	1.68 3H d (J=2 Hz)	1.76 3H bs	1.50 3H bs	1.67 3H d (J=2 Hz)	1.77 3H bs
H_3-18	1.40 3H d (J=1 Hz)		1.70 3H d (J=2 Hz)	1.42 3H d (J=1 Hz)		1.71 3H d (J=2 Hz)
H_2-19	4.73 1H s 4.69 1H s	5.04 1H s 5.01 1H s	4.92 1H s 4.82 1H s	4.72 1H s 4.67 1H s	5.04 1H s 5.00 1H s	4.90 1H s 4.81 1H s

[a] prepared from coraxeniolide-C (**7**)
[b] prepared from coraxeniolide-C′ (**10**)

---

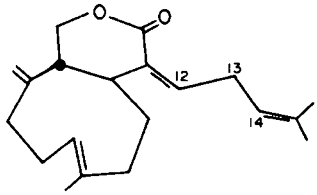
†*Cora* denotes the origin of the compound from *Corallium* sp., and *Boh* expresses our appreciation to Boh Bartko, the skipper of *Star II*.

M^+-60 mass peak) with four isolated double bonds, two of them terminal methylenes. The ^{1}H NMR spectrum of corabohcin (**13**) is characterized by four methyl singlets, resonating at δ1.94 (acetate) and at δ1.69, 1.63, and 1.57 (three vinylic methyls), and by two one-proton olefin signals at δ5.28 and 5.21. Irradiation of the signal at δ5.28 enhances the methyl singlet at δ1.57, while irradiation at δ5.21 enhances the remaining methyl signals at δ1.69 and 1.63. These experiments rule out a plausible alternate structure, which has the sidechain olefins placed at C-10 (17) and at C-14 (15). A quartet signal at δ26.33 in the ^{13}C off-resonance spectrum of **13** is compatible only with a methyl at C-15. Methyls attached to trisubstituted olefins do not absorb below 23 ppm.[11] The C-18 protons of corabohcin (**13**) are seen as doublets ($J = 12$, 6 Hz) of doublets ($J = 12$, 12 Hz) at δ4.01 and 3.81, indicating the rather hindered position of the methylene group.

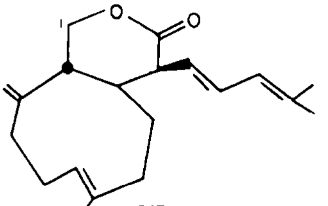
The mass spectrum of corabohcin (**13**) is in full accord with the proposed structure. The C-11 (12) bond is doubly allylic and should break readily. Indeed a peak at *m/z* 201 (M^+-60-69) displays 59% relative intensity. Another intense (77%) peak at *m/z* 227 represents a fragment of composition $C_{17}H_{23}$, corresponding to losses of acetic acid and of C_3H_7. Loss of isopropyl from **13** appears at first puzzling, but may be explained by analogy with the mass spectrum of $\Delta^{4(8)}$-menthene (**14**). Here, Weinberg and Djerassi[16] showed by deuterium labelling studies that the base peak corresponds to a loss of C_3H_7 and results from sidechain scission following double bond migration.

We have no firm evidence for the orientation of the side chains at C-2 and C-3. Because of the close structural relationship of corabohcin (**13**) to the coraxeniolides we would expect the C-2 (18) bond to have *alpha* and the C-3(10) bond to have *beta* orientation.

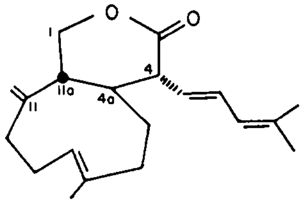
It is worth nothing that the gorgonian from which these metabolities have been isolated because of its deep-sea habitat must be devoid of symbiotic photosynthetic algae. These compounds, therefore, must be biosynthetic products of the animal or ingested with its diet.



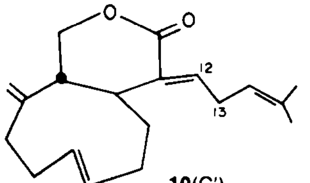
7(C)



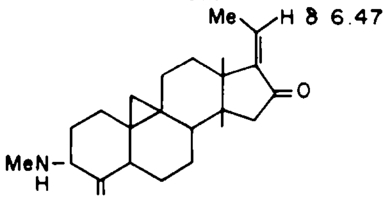
8(D)



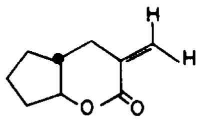
9(D')



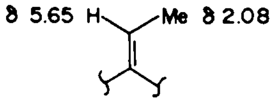
10(C')



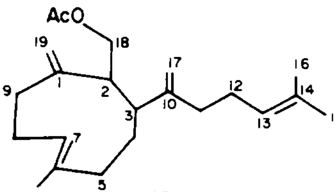
12a



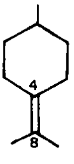
11



12b



13



14

EXPERIMENTAL

Apparatus, methods and materials. Natural abundance ^{13}C NMR spectra were recorded on a Varian XL-100 Fourier transform spectrometer at 25.2 MHz. The deuterium signal of $CDCl_3$ provided field/frequency locking. Proton NMR spectra were recorded on a Varian XL-100 NMR spectrometer at 100 MHz; field/frequency locking was provided by the deuterium signals of $CDCl_3$ and C_6D_6. Two hundred twenty MHz ^1H NMR spectra were obtained on a Varian HR220 NMR spectrometer; TMS was used as an internal reference. Three hundred sixty MHz ^1H NMR spectra were recorded on a Nicolet NTC 360 NMR spectrometer; field/frequency locking was provided by the deuterium signals of $CDCl_3$ and C_6D_6. The ^1H NMR spectra of many compounds contain signals which appear to be triplets but are due to coupling with two nonequivalent protons and, therefore, are referred to as doublets of doublets (dd).

Mass spectra were determined on a Varian MAT 311 high resolution mass spectrometer at an ionizing voltage of 70 eV. Field desorption mass spectra were obtained using a Varian MAT 731 high resolution mass spectrometer equipped with a field desorption ion source.

Infrared spectra were recorded on a Perkin–Elmer 467 grating infrared spectrophotometer. A Beckman ACTA III spectrophotometer was used for the UV spectra. Optical rotations were obtained on an ETL-NPL type 143A automatic polarimeter.

M.p. were taken on a Fisher–Johns apparatus. New England Nuclear silica gel of 250 μ plates were used for all tlc's.

Many separations were performed on a Waters Associates HLPC system consisting of an M-6000 solvent delivery system, a U6K injector, an R401 differential refractometer, a 440 absorbance detector, and a Varian 9176 recorder. A Whatman Partisil PXS 10 μ, 25 cm column or a Whatman Partisil M9 10 μ, 25 cm column was used for all separations requiring hplc. Waters Associates silica gel Sep-Paks were often used for preliminary clean-up of mixtures to be separated by hplc.

Isolation. Seven hundred and sixty grams of freshly collected pink coral (*Corallium* sp.) was steeped in MeOH 3X. This extract was filtered, concentrated, and partitioned between CH_2Cl_2 and water; the aqueous extract was discarded.

The CH_2Cl_2 layer (*ca* 2.2 g) was chromatographed on Bio-Sil A using CH_2Cl_2 as the eluent. Final purification of most compounds was accomplished by hplc with 10 μ Partisil as the absorbent and the eluents as indicated for each particular compound.

Coraxeniolide-A (**1**). Coraxeniolide-A (**1**) was purified by hplc with CH_2Cl_2 as the eluent; approximately 500 mg of **1** was present in the CH_2Cl_2 extract. Compound **1** forms white, plate-like crystals upon concentration, m.p. 88–91°C, R_f 0.38, CH_2Cl_2, and chars red with H_2SO_4/vanillin; $C_{20}H_{30}O_2$ (Calc. 302.224 586; Found 302.224 28), $C_{14}H_{20}O_2$ (Calc. 220.146 334; Found 220.142 98) *m/z* 302 (57%, M^+), 259 (13, M^+-C_3H_7), 220 (72, M^+-C_6H_{10}), 219 (57, M^+-C_6H_{11}). ^{13}C NMR: ($CDCl_3$) 175.16 (s), 153.06 (s), 140.73 (d), 139.97 (s), 124.00 (d), 123.47 (d), 112.20 (t), 70.80 (t), 49.93 (d), 44.39 (d), 42.98 (d), 39.89 (t), 35.84 (t), 31.35 (d), 30.03 (t), 25.28 (t), 22.90 (q), 22.90 (q), 16.73 (q) ppm. ^1H NMR: (220 MHz, $CDCl_3$) 5.50 1H dd (J = 15 Hz), 5.36 2H m, 4.98 2H s, 4.19 1H dd (J = 12 Hz, J = 7 Hz), 3.93 1H dd (J = 12 Hz, J = 12 Hz), 2.80 1H m, 1.70 3H bs, 1.00 6H d (J = 7 Hz) ppm; (100 MHz, C_6D_6) 5.58–5.12 3H m, 4.66 1H s, 3.82 1H dd (J = 12 Hz, J = 7 Hz), 3.48 1H dd (J = 12 Hz, J = 12 Hz), 1.41 (3H d (J = 1.5 Hz), 0.97 6H d (J = 7 Hz) ppm. Decoupling: (220 MHz, $CDCl_3$) irr 4.19 1H dd, 3.93 1H dd-d; irr 3.93 1H dd, 4.19 1H dd-d. UV: (MeOH) end absorption. IR: (CH_2Cl_2) 1748 (lactone C=O), 1640 (C=C), 1391 (CMe_2), 898 ($C=CH_2$) cm^{-1}. $[\alpha]_D^{25}$ +82° (*c*0.95, $CHCl_3$).

Hexahydro derivatives of coraxeniolide-A (**1**). Twenty-three milligram of **1** were dissolved in MeOH and stirred overnight with 10% Pd/C in an H_2 atmosphere. The reaction mixture was filtered, concentrated, and chromatographed by hplc (CH_2Cl_2) to give 19 mg of an inseparable mixture, as a colorless oil, R_f 0.42 (single spot), CH_2Cl_2, and chars red with H_2SO_4/vanillin; $C_{20}H_{36}O_2$ (Calc. 308.271 537; Found 308.270 16) *m/z* 308 (9%, M^+), 224 (100, M^+-C_6H_{12}). ^{13}C NMR: ($CDCl_3$) 176.22, 175.78, 69.57, 68.87 ppm and a large number of overlapping aliphatic carbons. ^1H NMR: (360 MHz, $CDCl_3$) 4.20–4.05 m, 2.50–2.37 m, 2.13–2.04 m, 0.95–0.82 8 3H d (J = 8 Hz) ppm. UV: (MeOH) end absorption. IR (CH_2Cl_2) 1741 cm^{-1} (lactone C=O), no C=C stretch in the region 1550–1650 cm^{-1}.

Diol derived from coraxeniolide-A (**1**). Eighteen milligram of **1** was reduced with $LiAlH_4$ in anhydrous Et_2O in an argon atmosphere. The reaction mixture was filtered, concentrated, and chromatographed by hplc with $EtOAc/CH_2Cl_2$ (7:3) as the eluent to give 4.5 mg of diol as a colorless oil, R_f 0.39, EtOAc, and chars red with H_2SO_4/vanillin; $C_{20}H_{34}O_2$, $C_{20}H_{32}O$ (Calcd. 288.245 321; Found 288.248 66) m/z 306 (1%, M^+), 288 (7, M^+-H_2O), 257 (33, M^+-H_2O, CH_2OH). ^1H NMR: (360 MHz, C_6D_6) 5.40 1H dd (J = 15 Hz, J = 6 Hz), 5.32–5.27 2H m, 4.73 1H ms, 4.72 1H ms, 3.65 1H dd (J = 11 Hz, J = 6 Hz), 3.50 1H dd (J = 11 Hz, J = 6 Hz), 3.29 1H dd (J = 11 Hz, J = 7 Hz), 3.24 (J = 11 Hz, J = 7 Hz), 1.51 3H s, 0.96 3H d (J = 7 Hz) ppm. UV: (MeOH) end absorption.

Coraxeniolide-B (**3**). Approximately 250 mg of **3** was isolated from the crude extract by hplc with CH_2Cl_2 as the eluent. Although coraxeniolide-B (**3**) is chromatographically similar to coraxeniolide-C′ (**10**), **3** was obtained with purity greater than 99%. Coraxeniolide-B (**3**) is a colorless oil, R_f 0.28, CH_2Cl_2, and chars blue with H_2SO_4/vanillin; $C_{20}H_{28}O_2$ (Calcd 300.208 936; Found 300.210 33) *m/z* 300 (20%, M^+), 257 (40, M^+-$C_{37}H_7$). ^{13}C NMR: ($CDCl_3$) 171.38 (s), 151.74 (s), 151.38 (d), 138.26 (d), 137.03 (s), 131.31 (s), 124.70 (d), 121.09 (d), 113.52 (t), 71.07 (dd), 49.76 (d), 43.59 (d), 40.69 (t), 38.31 (t), 34.70 (t), 32.14 (d), 25.28 (q), 22.28 (q), 16.73 (q) ppm. ^1H NMR data see Table 1.

Decoupling: (100 MHz, C_6D_6) irr 7.16 1H d, 6.38 1H dd-d; irr 6.38 1H bdd, 7.16 1H d-s, 5.84 1H dd-m; irr 5.84 1H dd, 6.38 1H dd-m; irr 3.88 1H dd, 3.46 1H dd-m; irr 3.46 1H dd, 3.88 1H dd-m; irr 0.91 6H d, 6.38 1H bdd-ddd (J = 15 Hz, J = 12 Hz, J = 1 Hz). UV λ_{max} (log ϵ): (MeOH) 270 nm (4.08). IR: (CH_2Cl_2) 1729 (lactone, C=O), 1640 (C=C), 890 (C–CH_2) cm^{-1}. $[\alpha]_D^{27}$ + 35° (*c* 1.38, CH_2Cl_2).

Coraxeniolide-C (**7**). Approximately 50 mg of **7** was isolated and purified from the CH_2Cl_2 extract by HPLC with CH_2Cl_2 as the eluent. Coraxeniolide-C (**7**) is a white, crystalline solid, m.p. 68–69°, R_f 0.44, CH_2Cl_2, and chars blue with H_2SO_4/ vanillin; $C_{20}H_{28}O_2$ (Calcd 300.208 936; Found 300.207 40) *m/z* 300 (100%, M^+), 257 (14, M^+-C_3H_7). ^{13}C NMR: ($CDCl_3$) 169.44 (s), 152.44 (s), 137.12 (d), 135.62 (s), 133.77 (s), 133.07 (s), 124.26 (d), 121.00 (d), 112.81 (t), 71.16 (dd) (Fig. 37), 51.77 (d), 50.02 (d), 40.16 (t), 38.04 (t), 35.23 (t), 28.27 (t), 25.89 (q), 25.01 (t), 18.05 (q), 16.56 (q), ppm. ^1H NMR: see Table 2. Decoupling: irr 5.79 1H t, 3.02 1H bdd-d; irr 5.22 1H bt, 3.02 1H bdd-d; irr 4.05 1H dd, 3.56 1H dd-d, 3.56 1H dd, 4.05 1H dd-d; irr 3.02 2H bdd, 5.79 1H t-s, 5.22 1H bt-d (J = 1.5 Hz); irr 1.68 6H bs, 5.22 1H bt-t, 3.02 2H bdd-dd. UV λ_{max} (log ϵ): (MeOH) 215 nm (3.89). IR: (CH_2Cl_2) 1737 (lactone C=O), 1643 (C=C), 1388 (CH_3), 900 ($C=CH_2$)^{cm} $^{-1}$. $[\alpha]_D^{25}$ + 113: (*c* 1.24, $CDCl_3$).

Twenty-eight milligram of coraxeniolide-C (**7**) was dissolved in toluene and stirred overnight with 24 μL of DBU. The reaction mixture was passed through a silica gel Sep-Pak, concentrated, and chromatographed by hplc (CH_2Cl_2) to give 7.2 mg of coraxeniolide-D (**8**) and 5.6 mg of coraxeniolide-D′ (**9**).

Coraxeniolide-D (**8**). Coraxeniolide-D (**8**) forms white, plate-like crystals upon purification and concentration, m.p. 127–129°, R_f 0.41, CH_2Cl_2, and chars red with H_2SO_4/vanillin; $C_{20}H_{28}O_2$ (Calc. 300.208 936; Found 300.207 40) *m/z* 300 (28%, M^+), 219 (13, M^+-C_6H_9). ^1HNMR data see Table 2. Decoupling: (100 MHz, $CDCl_3$) irr 6.39 1H dd, 5.90 1H dd-d, 5.89 1H d-s; irr 3.58 1H dd, 5.90 1H dd-d; irr 1.78 6H bs, 5.89 1H bd-d. UV λ_{max} (log ϵ): (MeOH) 239 nm (4.11). IR: (CH_2Cl_2) 1754 (lactone C=O), 1637 (C=C), 890 ($C=CH_2$)^{cm} $^{-1}$. $[\alpha]_D^{28}$ +31° (*c* 0.65, CH_2Cl_2).

Hexahydro derivatives of **1** *from coraxeniolide-D* (**8**). Four milligram of coraxeniolide-D (**8**) was hydrogenated by stirring overnight with 10% Pd/C in MeOH in a H_2 atmosphere. The reaction mixture was filtered and concentrated to give 2.9 mg of a mixture of two products identical to hexahydro compounds from **1**. The mixture is a colorless oil, R_f 0.44, CH_2Cl_2, and chars red with H_2SO_4/vanillin: $C_{20}H_{36}O_2$ (Calc. 308.271 537; Found 308.270 16) *m/z* 308 (12%, M^+), 224 (100, M^+-C_6H_{12}). ^1H NMR: (100 MHz, $CDCl_3$) 4.20–4.05 m 2.60–2.25 m, 0.85–0.92 (envelope of CH_3 doublets). UV: (MeOH) end absorption. IR: CH_2Cl_2) 1739 cm^{-1} (lactone C=O), no C=C stretch in the region 1550–1650 cm^{-1}.

Coraxeniolide-D′ (**9**). Compound **9** forms a white, amorphous solid upon isolation and concentration, m.p. 115–118°, R_f 0.35, CH_2Cl_2, and chars red with H_2SO_4/vanillin; $C_{20}H_{28}O_2$ (Calc. 300.208 936; Found 300.207 06) *m/z* 300 (100%, M^+), 219 (12, M^+-C_6H_9). ^1H NMR: (360 MHz, $CDcl_3$) 6.35 1H dd (J = 15 Hz, J = 10 Hz), 5.86 1H bd (J = 10 Hz), 5.51 1H dd (J = 15 Hz, J = 8 Hz), 5.32 1H bt (J = 8 Hz), 4.89 1H s, 4.78 1H s, 4.15 1H dd (J = 12 Hz, J = 4.5 Hz), 4.05 1H dd (J = 12 Hz, J = 3.5 Hz), 2.89 1H dd (J = 8 Hz, J = 8 Hz), 1.76 3H bs, 1.73 3H s, 1.67 3H bs ppm; 100 MHz data see Table 2. Decoupling: (100 MHz, $CDCl_3$) irr 6.26 1H dd, 5.85 1H bd-bs, 5.52 1H dd-m; irr 5.85 1H bd, 6.26 1H dd-m; irr 5.52 1H dd, 6.30 1H dd-m, 2.89 1H dd-d; irr 5.31 1H m, 1.67 3H d-s; irr 2.89 1H dd, 5.52 1H dd-bd. UV λ_{max} (log ϵ): (MeOH) 237 nm (4.00). IR: (CH_2Cl_2) 1735 (lactone C=O), 890 (C=CH_2). $[\alpha]_D^{27}$ −96° (*c* 0.56, CH_2Cl_2).

Coraxeniolide-C′ (**10**). Final purification of coraxeniolide-C′ (**10**) was accomplished by HPLC (CH_2Cl_2); the crude extract from pink coral contains approximately 150 mg of **10**. Due to its chromatographic similarity to coraxeniolide-B (3), coraxeniolide-C′ (**10**) was obtained in small quantities and its purity was somewhat greater than 90%. It is a colorless oil, R_f 0.36, CH_2Cl_2 and chars red with H_2SO_4/vanillin; $C_{20}H_{28}O_2$ (Calc. 300.208 936; Found 300.210 33) *m/z* 300 (11%, M^+), 257 (10, M^+-C_2H_7). ^{13}C NMR: ($CDCl_3$) 171.29, 152.44, 137.82, 135.53, 134.30, 133.77, 124.52, 119.86, 113.08, 71.07, 49.67, 43.68, 40.51, 38.04, 34.87, 27.04, 25.89, 25.10, 18.14, 16.64 ppm. ^1H data see Table 2. Decoupling: (100 MHz, C_6D_6) irr 6.57 1H t, 2.72 2H bdd-d; irr 5.34 1H m, 1.42 3H d-s; irr 5.08 1H mt, 2.72 2H bdd-d; irr 2.72 2H bdd, 6.57 1H t-s, 5.08 1H mt-bs; irr 1.62 bs, 5.08 1H mt-bt; irr 1.50 bs, 5.08 1H mt-bt. UV λ_{max} (log ϵ): (MeOH) 213 nm (3.81). IR (CH_2Cl_2) 1730 (lactone C=O), 1640 (C=C), 892 (C=CH_2)$^{cm^{-1}}$. α_D^{26} +85° (*c* 1.08, ÇHCl$_3$).

Thirteen milligram of coraxeniolide-C′ (**10**) was dissolved in toluene and stirred overnight with 30 μL of DBU. The reaction mixture was then passed through a silica gel Sep-Pak, concentrated, and chromatographed by hplc ($CHCl_2$) to give 3.7 mg of coraxeniolide-D (**8**) and 5.0 mg of coraxeniolide D′ (**9**).

Coraxeniolide-D (**8**). Coraxeniolide-D (**8**), from the reaction of coraxeniolide-C′ (**10**) with base, forms white, plate-like crystals upon concentration, m.p. 128-131°C, R_f 0.41, CH_2Cl_2, and chars red with H_2SO_4/vanillin; $C_{20}H_{28}O_2$ (Calcd. 300.208 936; Found 300.208 40) *m/z* 300 (45%, 219 (21, M^+-C_6H_9). All spectral data were identical with those of natural coraxeniolide-D (**8**).

Coraxeniolide-D′ (**9**). Coraxeniolide-D′ (**9**) is a white, amorphous solid, m.p. 116–118°, R_f 0.35, CH_2Cl_2, and chars red with H_2SO_4/vanillin; $C_{20}H_{28}O_2$ (calcd 300.208 936; found 300.210 33) *m/z* 300 (100%, M^+), 219 (17, M^+-C_6H_9). Spectral data were identical with those for **9** isolated from the DBU reaction on **7**.

Corabohcin (**13**). Approximately 25 mg of corabohcin (**13**) was isolated by HPLC with CH_2Cl_2/hexane (1 : 1) as the eluent. Corbohcin (**13**) is a colorless oil, R_f 0.55, CH_2Cl_2), and chars red with H_2SO_4/vanillin; $C_{22}H_{34}O_2$ (field desorption, Calcd. 330.255 67; Found 330.255 68), $C_{20}H_{30}$ (field desorption, calcd 270.234 59; found 270.234 65), $C_{17}H_{23}$ (70 eV, Calc. 227.179 980; found

Table 3. Anisotropic thermal parameters are of the form exp $[-2\pi^2\Sigma\Sigma U_{ij}h_ih_ja_i^*a_j^*]$ (x10^3) while thermal parameters for hydrogen atoms are given as isotropic U values (×10^2)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	46(1)	48(1)	49(1)	2(1)	-0(1)	-1(1)
C(2)	72(1)	66(1)	51(1)	11(1)	2(1)	2(1)
C(3)	79(2)	78(1)	62(1)	6(1)	26(1)	-0(1)
C(4)	73(1)	68(1)	74(1)	5(1)	26(1)	-16(1)
C(5)	67(1)	68(1)	84(1)	16(1)	16(1)	-5(1)
C(6)	99(2)	65(1)	107(2)	26(1)	21(2)	6(1)
C(7)	91(2)	47(1)	95(2)	2(1)	15(2)	7(1)
C(8)	67(1)	51(1)	62(1)	-3(1)	9(1)	4(1)
C(9)	50(1)	48(1)	50(1)	-2(1)	1(1)	-9(1)
C(10)	51(1)	59(1)	70(1)	-6(1)	12(1)	-7(1)
C(11)	43(1)	73(1)	84(1)	5(1)	1(1)	-13(1)
C(12)	52(1)	62(1)	62(1)	11(1)	0(1)	-9(1)
O(12)	65(1)	84(1)	86(1)	27(1)	-9(1)	3(1)
C(13)	50(1)	51(1)	51(1)	6(1)	-3(1)	-3(1)
C(14)	67(1)	49(1)	73(1)	3(1)	-0(1)	3(1)
C(15)	65(1)	54(1)	69(1)	-9(1)	-5(1)	3(1)
C(16)	72(1)	71(1)	71(1)	-7(1)	-7(1)	0(1)
C(17)	67(1)	113(2)	75(1)	-10(2)	3(1)	-7(2)
C(18)	77(2)	136(2)	124(3)	18(2)	0(2)	-5(2)
C(19)	87(2)	136(4)	131(4)	-35(3)	14(2)	7(3)
C(20)	111(3)	92(2)	88(2)	-14(2)	12(2)	-32(2)
C(21)	101(2)	78(1)	68(1)	3(1)	-17(1)	10(1)
H(1)	5.1(5)					
H(2a)	5.4(6)					
H(2b)	7.0(7)					
H(3a)	9.8(10)					
H(3b)	7.2(7)					
H(5)	9.7(9)					
H(6a)	11.9(13)					
H(6b)	9.0(9)					
H(7a)	9.6(9)					
H(7b)	9.3(10)					
H(9)	6.8(7)					
H(10a)	8.9(9)					
H(10b)	5.5(5)					
H(13)	5.7(6)					
H(14a)	10.0(10)					
H(14b)	7.6(8)					
H(15)	8.4(8)					
H(16)	7.0(7)					
H(17)	10.4(10)					
H(18a)	11.8(12)					
H(18b)	14.6(18)					
H(18c)	15.6(11)					
H(19a)	10.2(10)					
H(19b)	8.0(11)					
H(19c)	15.3(15)					
H(20a)	13.4(15)					
H(20b)	14.2(17)					
H(20c)	10.7(12)					
H(21a)	7.6(7)					
H(21b)	8.6(8)					

227.182 27) *m/z* (70 eV) 330 (4%, M^+), 270 (43, M^+-CH_3CO_2H), 227 (77, M^+-CH_3CO_2H, C_3H_7), 201 (59, M^+-CH_3CO_2H, C_5H_9) (Fig. 56). ^{13}C NMR: ($CDCl_3$) 170.85 (s), 152.71 (s), 147.33 (s), 136.15 (s), 131.83 (s), 124.60 (d), 124.50 (d), 117.58 (t), 109.03 (t), 65.62 (t), 52.31 (d), 47.73 (d), 40.25 (t), 33.91 (t), 32.23 (t), 31.26 (t), 28.71 (t), 26.68 (t), 26.33 (q), 21.22 (q), 18.14 (q), 17.97 (q) ppm. ^1H NMR: (220 MHz, $CDCl_3$) 5.28 1H bd (J = 8 Hz), 5.15 1H m, 4.91 2H s, 4.82 1H s, 4.71 1H s, 4.01 1H dd (J = 12 Hz, J = 6 Hz), 3.81 1H dd (J = 12 Hz, J = 12 Hz), 1.94 3H s, 1.69 3H s, 1.63 3H s, 1.57 3H s ppm. Decoupling: (220 MHz, $CDCl_3$) irr 5.28 1H bd, 1.57 3H s enhanced; irr 5.15 1H m, 1.63 3H s enhanced, 1.69 3H s enhanced. UV: (MeOH) end absorption. IR: (CH_2Cl_2) 1732 (lactone C=O), 1640 (C=C), 1386 (CH_3), 890 (C=CH_2)$^{\mathrm{cm}^{-1}}$. $[\alpha]^{27}_{D}$ −169° (*c* 0.71, $CHCl_3$).

X-ray Crystallography. Good crystals were obtained by the slow evaporation in a refrigerator of a CH_2Cl_2 solution of coraxeniolide-A (**1**). A crystal of dimensions 0.45 × 0.4 × 0.5 mm was cut from a larger crystal and was used in the collection of all data. Room-temperature (20°) lattice parameters were refined by a least-squares procedure utilizing 15 reflexions whose angles were measured by a centering routine associated with the Syntex $P2_1$ diffractometer.

Crystal data. $C_{20}H_{30}O_2$, M = 302.45, a = 11.037(2), b = 18.899(3), c = 0.050(1) Å, V = 1887.9(4) $Å^3$, Z = 4, d_c = 1.065 Mg m^{-3}. Systematic absences were consistent with space group $P2_12_12_1$.

All intensity data were collected by the θ: 2θ scanning technique ($2\theta < 140°$) using a variable scan speed and a graphite monochromator (CuK_α, λ = 1.54178 Å). A periodically monitored reference reflexion showed no significant change in intensity during data collection. Of the 1947 independent reflexions measured, 148 had intensities less than $2\sigma(I)$. These intensities were not used in least-squares refinements. Lorentz and polarization corrections were applied, but no absorption corrections were made.

The direct methods program MULTAN[17] was used to calculate phases for the 269 $|E|$ values greater than 1.4. After manual intervention in the phasing procedure, a subsequent E map revealed the positions of all nonhydrogen atoms. Isotropic and subsequent anisotropic full-matrix least-squares refinement yielded an R value of 0.089. Hydrogen atom positions were obtained from a difference Fourier map, and refinement with hydrogen thermal parameters isotropic led to a final R of 0.046 for 1795 reflexions (3 reflexions were given zero weight because of secondary extinction). $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ and the function minimized was $\Sigma\omega\,(|F_0|-F_c|)^2$ where $\omega = 1/\sigma(I)$ was determined from counting statistics.

All parameter shifts of nonhydrogen atoms during the final cycle were less than 0.3σ and a final difference map showed no peak larger than 0.2e/$Å^3$. Atomic scattering factors and anomalous dispersion corrections for carbon and oxygen atoms were taken from the International Tables for X-ray Crystallo-

Table 4. Atomic positional coordinates x 10^4 for carbon and oxygen atoms and x 10^3 for hydrogen atoms

atom	x/a	y/b	z/c
C(1)	6242(2)	5984(1)	4180(2)
C(2)	6252(2)	5966(1)	5883(2)
C(3)	5272(3)	6421(1)	6626(3)
C(4)	5355(2)	7182(1)	6146(3)
C(5)	4759(2)	7388(1)	4967(3)
C(6)	5025(3)	8031(1)	4039(4)
C(7)	6172(3)	7894(1)	3114(4)
C(8)	6274(2)	7138(1)	2578(2)
C(9)	6969(2)	6624(1)	3546(2)
C(10)	8061(2)	6359(1)	2665(3)
O(11)	8722(1)	5813(1)	3458(2)
C(12)	8063(2)	5251(1)	3896(2)
O(12)	8562(2)	4786(1)	4577(2)
C(13)	6744(2)	5287(1)	3526(2)
C(14)	6087(2)	4611(1)	3992(3)
C(15)	4779(2)	4622(1)	3618(3)
C(16)	3888(2)	4593(1)	4552(3)
C(17)	2578(3)	4607(2)	4164(3)
C(18)	2054(3)	5343(3)	4417(5)
C(19)	1869(4)	4063(4)	5024(6)
C(20)	6266(4)	7628(2)	6951(4)
C(21)	5784(3)	6934(2)	1305(3)
H(1)	542(2)	603(1)	390(2)
H(2a)	697(3)	611(1)	627(3)
H(2b)	612(3)	548(2)	628(3)
H(3a)	433(3)	628(2)	642(4)
H(3b)	549(2)	637(1)	767(4)
H(5)	426(3)	701(2)	431(4)
H(6a)	424(4)	810(3)	340(5)
H(6b)	499(3)	847(2)	457(4)
H(7a)	700(4)	801(2)	387(4)
H(7b)	621(3)	816(2)	242(4)
H(9)	730(2)	689(1)	448(3)
H(10a)	861(3)	675(2)	256(4)
H(10b)	774(2)	615(1)	167(3)
H(13)	664(2)	535(1)	251(3)
H(14a)	627(3)	455(2)	515(4)
H(14b)	644(3)	424(2)	339(3)
H(15)	464(3)	471(2)	261(4)
H(16)	393(3)	456(2)	548(4)
H(17)	240(4)	447(2)	305(5)
H(18a)	119(4)	527(2)	410(5)
H(18b)	251(5)	571(3)	368(6)
H(18c)	219(6)	538(3)	576(7)
H(19a)	208(4)	413(2)	620(5)
H(19b)	208(3)	367(3)	490(4)
H(19c)	083(5)	430(3)	473(6)
H(20a)	650(5)	808(3)	642(6)
H(20b)	604(5)	774(3)	808(7)
H(20c)	707(5)	746(2)	690(5)
H(21a)	520(3)	723(2)	062(3)
H(21b)	606(3)	645(2)	092(4)

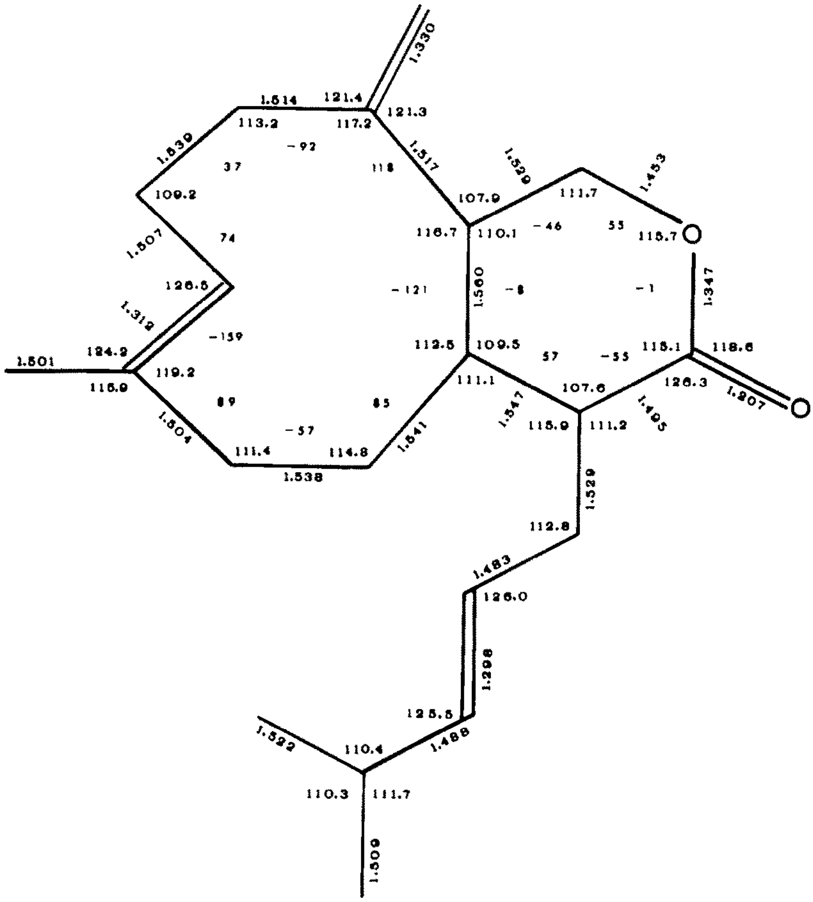


Fig. 2. Diagram of bond lengths, bond angles, and torsion angles.

graphy, Vol. IV[18] while those for hydrogen atoms were taken from Stewart *et al.*[19]

Tables 3 and 4 give the final atomic and thermal parameters. Figure 1 is an ORTEP drawing [20] of **1** with anisotropic thermal parameters drawn at the 35% probability level. The bond lengths 0.002 – .005 with an average of .003 Å, bond angles 0.1 – 0.3 with an average of 0.2°, and torsion angles 0.2–0.4 with an average of 0.3° are shown in Fig. 2.

The bond parameters lie within the expected ranges. The conformation of the nine-membered ring is similar to that found in xenicin by Vanderah *et al.*[4] The six-membered ring exhibits a boat conformation. The torsion angles associated with the ring jucture, 10-9-1-13 = – 8° and 8-9-1-2 = – 121°, may be compared with the –31° and –134° found in xenicin. Although the –8° value might normally be associated with a *cis* ring juncture, the function of the two rings is *trans*. This may be attributed to the high degree of flexibility of the cyclononene ring system.

Acknowledgments—We should like to thank Boh Bartko and Maui Divers, Inc. for procurement of the animals; Richard Grigg and Katherine Muzik for identification; and the National Science Foundation and the Robert A. Welch Foundation (P-074) for generous financial support.

REFERENCES

[1] From the Ph.D. Dissertation of R. E. Schwartz, University of Hawaii, 1980.

[2] R. W. Griggs, *Hawaii's Precious Corals.* Island Heritage, Ltd., Norfolk Island 2899, Australia.

[3] This and other deep-sea gorgonians from Hawaii are being studied by K. Muzik, U.S. National Museum, Washington, DC.

[4] D. Vanderah, P. Steudler, L. Ciereszko, F. Schmitz, J. Ekstrand and D. van der Helm, *J. Am. Chem. Soc.* **99**, 5780 (1977).

[5] S. J. Torrance, R. M. Wiedhopf, J. R. Cole, S. K. Arora, R. B. Bates, W. A. Beavers and R. S. Cutler, *J. Org. Chem.* **41**, 1855 (1976).

[6a] A. Groweiss and Y. Kashman, *Tetrahedron Letters* 2205 (1978); [b] Y. Kashman and A. Groweiss, *Ibid.* 4833 (1978).

[7] J. C. Braekman, D. Daloze, D. Tursch, J. P. Declercq, G. Germain, and M. van Meerssche, *Bull. Soc. Chim. Belg.* **88**, 71 (1979).

[8] F. McEnroe, K. Robertson, and W. Fenical, *Marine Natural Products Chemistry*, (Edited by Faulkner D. J. and Fenical W.) pp. 179–190. Plenum Press, New York (1977).

[9] J. Finer, J. Clardy, W. Fenical, L. Minale, R. Riccio, J. Battaile, M. Kirkup and R. E. Moore, *J. Org. Chem.* **44**, 2044 (1979).

[10] E. W. Hagaman, *Org. Magn. Res.* **8**, 389 (1976).

[11] P. A. Couperus, A. D. H. Clague and J. P. C. M. van Dongen, *Ibid.* **8**, 426 (1976).

[12] D. J. Patel, *Nature* (*London*) **221**, 825 (1969).

[13] D. S. Watt and E. J. Corey, *Tetrahedron Letters* 4651 (1972)

[14] H. Marschall, F. Vogel, and P. Weyerstahl, *Chem. Ber.* **107**, 2852 (1974).

[15] K. S. Brown, Jr. and S. M. Kupchan, *J. Am. Chem. Soc.* **84**, 4590 (1962).

[16] D. S. Weinberg and C. Djerassi, *J. Org. Chem.* **31**, 115 (1966).

[17] G. Germain, P. Main and M. M. Woolfson, *Acta Cryst.* **A27**, 368 (1971).

[18] *International Tables for X-ray Crystallography*, Vol. IV. Kynoch Press, Birmingham (1974).

[19] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.* **42**, 3175–3187 (1965).

[20] C. K. Johnson, *ORTEP*, Report ORNL 3794. Oak Ridge National Laboratory, Tennessee.