

**Arboxeniolide-1, a New,
Naturally Occurring Xeniolide Diterpenoid
from the Gorgonian *Paragorgia arborea*
of the Crozet Is. (S. Indian Ocean)**

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The gorgonian *Paragorgia arborea*, collected in the Crozet Is. waters at a depth of 280 m during the cruise MD.30/BIOMASS of M/S "Marion Dufresne", is shown, in what constitutes the first organic-chemical study of a Paragorgiidae, to possess three $C_{20}H_{28}O_2$ xeniolide diterpenoids, two of which are identical with those from a *Corallium* sp. of the Hawaii. The third xeniolide, arboxeniolide-1, is new as a naturally occurring compound.

Introduction

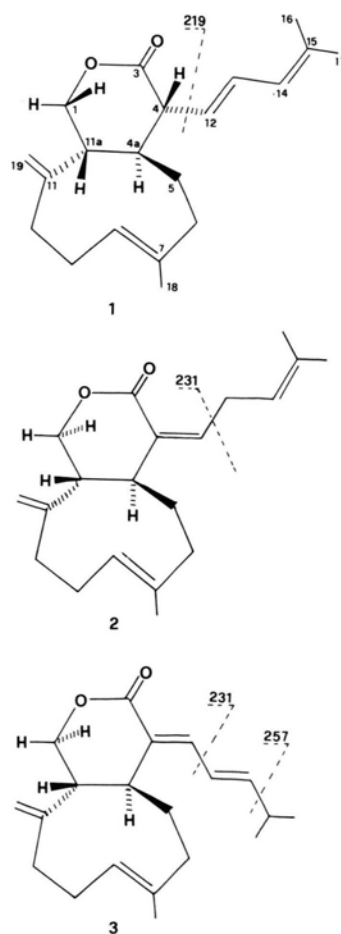
Paragorgia arborea is a marine colonial animal belonging to the phylum Cnidaria, class Anthozoa, subclass Alcyonaria, order Gorgonacea, suborder Scleraxonia, family Paragorgiidae. It is known from both the northern and the southern hemisphere, where it extends to the Subantarctic [1]. Whilst members belonging to the closely related families of the Briareidae [2] and the Coralliidae [3] have recently given interesting diterpenoids, the organic chemistry of the Paragorgiidae is unknown, to the best of our knowledge.

We report here that *P. arborea*, collected in the southern Indian Ocean, close to the Ile aux Cochons (Crozet Islands), has given two xeniolide diterpenoids already isolated from a *Corallium* sp. of the Hawaii [3], besides to a new – as a naturally occurring compound – xeniolide which had previously been obtained [3] by chemical transformation of one of the above *Corallium* xeniolides.

Results and Discussion

Three nicely crystalline compounds could be easily isolated from the gorgonian in relatively large amounts. The EIMS were closely similar when taken with heated ion source (see data for **2** and **3**)

whilst differences were revealed at lower temperatures. For example, the m/z 219 ion for **1**, indicating breaking at C-4–C-12, could only be revealed at low ion source temperature, suggesting easy migration of the double bonds. HRMS gave the composition $C_{20}H_{28}O_2$ for M^+ which, in combination with ^{13}C and 1H NMR spectra, indicates five double bonds and two rings, one of which is a lactone ring (IR). A high-field ^{13}C resonance at ca. 16 ppm (Table I) suggests a methyl at a *E*-double bond [4] which, in the hypothesis of a regular diterpenoid, could be in a nine-membered, caryophyllene-type ring, as the MS suggest the loss of isoprenoid side chains (C_6H_9 for **1** and C_5H_9 for both **2** and **3**). Also, as the NMR spectra only reveal three methyls and an exo-methylene, the fifth diterpenoid methyl must have been oxydized to the lactone carbonyl. These observations, and the classification of our colonial animal within the Alcyonaria, sug-



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Table I. ^{13}C NMR data for *P. arborea* xeniolides.

Carbon	Arboxeniolide-1 (1) (in C_6D_6)	2 (in CDCl_3)	3 (in C_6D_6)
C-1	67.1 t	71.0 t	70.6 t
C-3	173.1 s	169.4 s	169.8 s
C-4	47.2 d	135.5 s	135.3 s
C-4a	48.9 d	49.9 d ^a	43.7 d
C-5	35.4 t ^a	37.9 t	38.3 t
C-6	40.0 t	40.0 t	40.7 t
C-7	134.6 s	133.1 s ^b	132.5 s
C-8	124.6 d	124.2 d	124.8 d
C-9	25.0 t	24.8 t	25.4 t
C-10	35.0 t ^a	35.1 t	34.6 t
C-11	153.3 s	152.4 s	152.6 s
C-11a	50.0 d	51.6 d ^a	50.0 d
C-12	125.4 d	137.0 d	150.7 d
C-13	128.0 d	28.1 t	121.6 d
C-14	130.7 d	120.9 d	136.3 d
C-15	135.4 s	133.7 s ^b	32.0 d
C-16	18.2 q	17.8 q	22.2 q ^a
C-17	25.9 q	25.6 q	22.0 q ^a
C-18	16.1 q	16.3 q	16.5 q
C-19	113.4 t	112.7 t	113.2 t

^{a, b} These assignments may be interchanged.

gested xeniolide structures [5], such as those shown here by **1**, **2**, and **3**, which are fully supported by detailed, high-field ^1H NMR spectra, as well as by the off-resonance decoupled ^{13}C NMR spectra. Similar xeniolides have been isolated from various Alcyonacea of the genus *Xenia* [5], [6] and also from Gorgonacea of the family Coralliidae [3], which is close to the Paragorgiidae, to which *P. arborea* belongs. Actually, our spectral and chiroptical data suggest that **2** and **3** are identical with, respectively, coraxeniolide-C and coraxeniolide-B isolated from the Hawaiian Coralliidae *Corallium* sp. [3]. Our data also suggest that **1** is identical with a product, named coraxeniolide-D', of chemical transformation of either **2** or of another, naturally occurring xeniolide of *Corallium* sp. [3]. We have renamed **1** arboxeniolide-1, in order to indicate its natural source. No absolute configuration significance is to be attached to the structural formula. In fact, this is only known for the related xenicins [6].

It is to be remarked that both *P. arborea* and the *Corallium* sp. [3], from which these xeniolides come, have a profound habitat, which probably restricts the origin of the xeniolides to either the Scleraxonia themselves, or to non-photosynthetic organisms, or to dietary products [3]. It would be interesting to this concern, to examine *P. arborea* from deep-sea (it has been found at such depths as 1000 m [1]) where photosynthetic algae are certainly

not present. Also, due to the bipolar distribution of *P. arborea*, it would be interesting to examine *P. arborea* collections from boreal Atlantic.

Finally, it is worth noticing that besides to the xenicins and the xeniaphyllanes, which are related to the xeniolides [5], and have also been isolated from gorgonians of the genus *Xenia* [5–7], several other diterpenoids with the caryophyllene-type ring have been isolated from marine brown algae belonging to the Dictyotales. These include sea weeds of the genera *Dictyota* [8], *Dilophus* [9], and *Pachydictyon* [10].

Experimental Section

General

Mps: uncorrected from a Kofler hostage apparatus. — IR spectra: Perkin-Elmer 337. — UV spectra: Beckman DB-4. — Polarimetric data: JASCO DIP-181. — ^{13}C NMR SPECTRA: Varian CFT20 (20 MHz) equipped with a microprobe. — ^1H NMR spectra: Bruker CXP-300 (300 MHz) and Varian CFT20 modified for proton (80 MHz); in all cases δ values are relative to $(\text{CH}_3)_4\text{Si}$ and J values are in Hz. — MS spectra (EI, 70 eV, ion source 200°, if not otherwise stated): home-made spectrometer based on the ELFS 4-162-8 Extranuclear quadrupole and VG ZAB2F. Primary fragmentation (B/E) is indicated by stars and was determined for **2** and **3** only. Analytical HPLC: Perkin-Elmer Silica A-10 column, 9:1 hexane/ethyl acetate, 1 ml min⁻¹. — Preparative HPLC: Merck Hibar LiChrosorb Si 60, 7 μm , 9:1 hexane/ethyl acetate, 5 ml min⁻¹. Pink coloured *Paragorgia arborea* was collected on February 14, 1982, by beam trawl at a dept of 280 m, west of the Ile Aux Cochons, Crozet Is., S. Indian Ocean, 46° 13.6' S – 49° 32.0' E, Sta. 39, coll. CP113, during the cruise MD.30/BIOMASS of M/S "Marion Dufresne", and was immediately steeped in ethanol and stored in the cold.

Work-up of the Gorgonian

The colony, preserved as above and then held at room temperature for 2 weeks, was filtered, extracted again with fresh ethanol, and the combined ethanolic extracts were evaporated in vacuo. Dry weight of the colony after extraction 378 g. The aqueous residue was extracted with ethyl ether, which was then evaporated to leave a residue, 4.4 g, which was chromatographed on a 5 \times 60 Merck Kieselgel 60, 70–230 mesh, column. Gradient elu-

Table II. ^1H NMR data for *P. arborea* xeniolides (in CDCl_3).

Proton	Arboxeniolide-1 (1)	2	3
H α -1	4.03 dd ($J_{1\alpha,1\beta} = 11.4$; $J_{1\alpha,11a} = 3.3$)	3.58 dd ($J_{1\alpha,11a} = 12.2$; $J_{1\alpha,1\beta} = 11.2$)	3.57 dd ($J_{1\alpha,11a} = 12.0$; $J_{1\alpha,1\beta} = 11.2$)
H β -1	4.17 dd ($J_{1\beta,1\alpha} = 11.4$; $J_{1\beta,11a} = 4.0$)	4.05 dd ($J_{1\beta,1\alpha} = 11.2$; $J_{1\beta,11a} = 5.9$)	4.06 dd ($J_{1\beta,1\alpha} = 11.2$; $J_{1\beta,11a} = 5.7$)
H-4	2.91 br dd ($J_{4,4a} = J_{4,12} = 8.5$)	(b)	3.02 m
H-4a	1.8 m, superimposed (d)	1.3–1.6 m, superimposed (2 H)	1.5–1.7 m, superimposed (2 H)
H-5	1.3–1.6 m, superimposed (d)	a	c
H-6	5.3 m	b	c
H-8	a	b	c
H-9	a	b	c
H-10	a	b	c
H-11a	5.54 br dd ($J_{12,13} = 15.0$; $J_{12,4} = 8.5$)	5.79 td ($J_{12,13} = 7.5$; $J_{12,4a} = 0.9$)	2.15 m, superimposed ^c
H-12	6.28 ddd ($J_{13,12} = 15.0$; $J_{13,14} = 10.6$; $J_{13,4} = 0.8$)	3.04 br dd ($J_{13,12} = J_{13,14} = 7.5$)	6.88 dd ($J_{12,13} = 10.8$; $J_{12,4a} = 1.0$)
H-13	5.88 br d ($J_{14,13} = 10.6$)	5.13 tq ($J_{14,13} = 7.5$; $J_{14,16} = J_{14,17} = 1.4$)	6.24 ddd ($J_{13,12} = 10.8$; $J_{13,14} = 15.0$; $J_{13,15} = 1.0$)
H-14	1.78 br s	1.71 d ($J_{16,14} = 1.4$)	6.12 dd ($J_{14,13} = 15.0$; $J_{14,15} = 7.0$)
H-15	1.74 d ($J_{17,14} = 1.2$)	1.62 d ($J_{17,14} = 1.4$)	2.48 m, superimposed ^c
H-16	1.68 d ($J_{18,8} = 1.4$)	1.69 d ($J_{18,8} = 1.4$)	1.072 d ($J_{16,15} = 6.7$) ^d
H-17	4.91 br s and 4.81 br s	4.92 br s and 4.86 br s	1.068 d ($J_{17,15} = 6.7$) ^d
H-18			1.71 d ($J_{18,8} = 1.3$)
H-19			4.95 br s and 4.83 br s

^a Series of multiplets, for 8H, between 1.8 and 2.6.^b Series of multiplets, for 8H, between 2 and 2.6.^c Series of multiplets between 1.8 and 2.6, for 8H.^d These assignments may be interchanged.

tion from pet. ether to ethyl ether gave pure **2**, 0.14 g, 0.037% on dry animal w., followed by pure **3**, 1.2 g, 0.32% on dry animal w., and, finally, by the most polar **1** (the first eluted fractions of **1**, for a total of 0.10 g, proved to be pure, whilst the other fractions had to be further purified from contaminating sterols by HPLC, to give further 0.08 g of **1**). Total **1**: 0.048% on dry animal w.

1: colourless needles, mp 132–134 °C (from heptane). – $[\alpha]_D^{25} - 89^\circ$ ($c = 0.69$, ethyl ether). – UV (n -pentane): λ_{\max} 235 (log ϵ 4.10). – IR (nujol) 1730 (s), 1650 (w), 890 (m). – MS (ion source 130 °) m/z 300.2110 \pm 0.008 (M^+ , calcd. for $\text{C}_{20}\text{H}_{28}\text{O}_2$ 300.208917, 2%), 219 (2), 147 (9), 133 (17), 131 (19), 119 (20), 117 (11), 111 (12), 107 (10), 105 (38), 97 (25), 91 (45), 55 (100). – ^1H NMR: Table II. – ^{13}C NMR: Table I.

2: colourless needles, mp 74–75 °C (from pet. ether). – $[\alpha]_D^{25} + 209^\circ$ (c 0.17, pentane). – UV (n -pentane): λ_{\max} 208 (log ϵ 4.11). – IR (nujol) 1730 (s), 1650 (w), 912 (s). – MS: m/z 300.2117 \pm 0.008 (M^+ , calcd. for $\text{C}_{20}\text{H}_{28}\text{O}_2$ 300.208917, 32%), 285* (2), 282* (1), 271* (1), 267* (4), 257.1529 \pm 0.01*, calcd. for $\text{C}_{17}\text{H}_{21}\text{O}_2$ 257.154145 (6), 255* (6), 231.1357 \pm 0.01*, calcd. for $\text{C}_{15}\text{H}_{19}\text{O}_2$ 231.138496 (4), 185 (8), 161.1299 \pm 0.005*, calcd. for $\text{C}_{12}\text{H}_{17}$ 161.133018 (31), 105 (43), 91.0530 \pm 0.005, calcd. for C_7H_7 91.054772, 69 (35), 43 (35), 41 (100). ^1H NMR and ^{13}C NMR spectra: Tables II and I, respectively.

3: colourless needles, mp 48–49 °. – $[\alpha]_D^{25} + 57^\circ$ ($c = 0.07$, CH_2Cl_2). – UV (pentane): λ_{\max} (log ϵ) 255 (4.23), 208 (3.88). – IR (melt) 1730 (s), 1650 (m), 900 (m). – MS: 300.2002 \pm 0.008 (M^+ , calcd. for $\text{C}_{20}\text{H}_{28}\text{O}_2$ 300.208917, 2%), 285* (0.5), 271* (0.5), 257* (16), 255* (3), 244* (1), 231* (2), 91 (56), 69 (30), 43 (35), 41 (100). ^1H NMR and ^{13}C NMR spectra: Tables II and I, respectively.

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