11-Gorgiacerol, a New Pseudopteranoid from Pseudopterogorgia acerosa

ARTICLE *in* JOURNAL OF NATURAL PRODUCTS · JUNE 2004

Impact Factor: 3.8 · DOI: 10.1021/np50126a032

Journal of Natural Products
Vol. 58, No. 12, pp. 1975-1977, December 1995

11-GORGIACEROL, A NEW PSEUDOPTERANOID FROM *PSEUDOPTEROGORGIA ACEROSA*

WINSTON F. TINTO,* RICHARD S. LAYDOO,

Institute of Marine Affairs, Hilltop Lane, Chaguaramas, P.O. Box 3160, Carenage Post Office, Carenage, Trinidad and Tobago

SAMUEL L. MILLER,

Department of Chemistry, University of the West Indies, Cave Hill Campus, Barbados

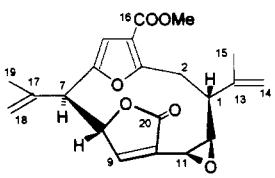
WILLIAM F. REYNOLDS,* and STEWART MCLEAN

Department of Chemistry, University of Toronto, Toronto M5S 1A1, Canada

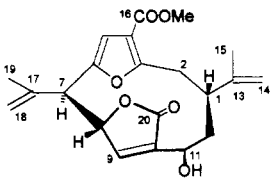
ABSTRACT.—A new pseudopteranoid, 11-gorgiacerol [**2**], has been isolated, along with previously described pseudopteranoids, from *Pseudopterogorgia acerosa*. The structure of **2** was established by 2D nmr spectroscopy.

The gorgonian coral *Pseudopterogorgia acerosa* Pallas (Gorgoniidae) provided the first pseudopteranoid, pseudopterolide, **1** (1), which stimulated considerable interest because of its chemical complexity and biological activity. When we subsequently studied collections of *P. acerosa* made at several locations off the coast of Tobago, we isolated and established the structures of a considerable number of novel diterpenoids. The array of metabolites isolated was found to vary markedly with season and location, but never included **1** (2,3). In order to study this variation further, we collected *P. acerosa* at a new location, Buccoo Reef, Tobago, in March 1994. The major diterpenoid isolated from this collection (86 g) was **1** (61 mg) along with smaller amounts of a new diterpene, **2** (2 mg), to which we have assigned the name 11-gorgiacerol, as well as gorgiacerodiol, **3** (4 mg), and isogorgiacerodiol (6 mg) (3).

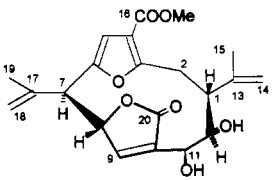
11-Gorgiacerol, **2**, was isolated as a pale yellow glass, $C_{21}H_{24}O_6$ (hrms), $[\alpha]_D$ +22°, ir ν max 3400, 1760, 1730 cm^{-1}, uv λ max 215 nm (ϵ 3900). These data suggested that this new diterpene was a hydroxylated pseudopteranoid with a C-9,C-10 double bond (butenolide) (3). This proposal was confirmed by nmr spectroscopy: the ^1H- and ^{13}C-nmr spectra showed a strong similarity to the data recorded for gorgiacerodiol (3), and the differences observed were associated with the C-11,C-12 diol component of **3**. The 2D nmr spectra showing ^{13}C-^1H one-bond (HMQC) and *n*-bond ($n=2$ or 3) (HMBC) shift correlations confirmed these proposals and unequivocally placed the single OH group at C-11. The ^1H-^1H coupling constants, derived from the multiplets observed in the standard ^1H-nmr spectrum, for the protons at C-11, C-12, C-1, and C-2, provided evidence that the stereochemistry at C-11 in **2** is the same as that in **3**. Molecular models showed that there is a conformation in which all of the dihedral angles are compatible with the coupling constants obtained,



1



2



3

but it was not possible to find a reasonable conformation having an acceptable set of dihedral angles when the configuration at C-11 was inverted.

The nmr characteristics of **2** are reported in condensed form in Table 1. Because **1** is a key reference compound, we have used the procedures described for **2** to assign unambiguously all ^{13}C- and ^{1}H-nmr chemical shifts for **1**, and these assignments are also shown in Table 1.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEUDRES.—A Cary 14 uv spectrometer (MeOH solution), a Nicolet 3DX Ft-ir spectrometer (thin film), a VG 70-250S mass spectrometer, a Perkin-Elmer 243B polarimeter, and a Varian Unity 500 nmr spectrometer equipped with a 5-mm inverse-detection probe were used. Solutions in $CDCl_3$ containing TMS as internal standard were used to obtain nmr measurements.

ANIMAL MATERIAL.—*Pseudopterogorgia acerosa* (86 g, dry wt) was collected at Buccoo Reef, Tobago, in March 1994 at a depth of 7 m. A voucher specimen is deposited at the Institute of Marine Affairs, Chaguaramas, Trinidad and Tobago.

EXTRACTION AND ISOLATION.—The ground material was extracted with Me_2CO (3 liters), and evaporation of the solvent provided a dark-red gum (4.9 g). The gum was dissolved in 100 ml of MeOH-H_2O (9:1) and extracted with hexane (3×40 ml). The aqueous layer was diluted with 50 ml H_2O and then extracted with CH_2Cl_2 (3×40 ml); evaporation of the CH_2Cl_2 left a dark-red gum (2.1 g), which was flash chromatographed on Si gel with elution by hexane-EtOAc (4:1), and five major fractions were collected. These fractions were subjected to prep. tlc with hexane/EtOAc elution: the third fraction provided **1** as a pale yellow gum (61 mg); the fourth fraction yielded **2**

TABLE 1. Nmr Characteristics of **1** and **2**.[a]

Position	**1**		**2**		
	δ_C	δ_H	δ_C	δ_H (J_{HH})	Observed connectivity
1	42.47	3.14	38.38	2.80 (12.8, 7.6, 4.2)	C-2, C-11, C-13
2	28.20	3.71	31.13	3.40 (15.2, 12.8)	C-1, C-3, C-13
		2.80		2.69 (15.2, 4.2)	C-1, C-3, C-4, C-12, C-13
3	160.63	—	161.25	—	—
4	114.67	—	115.73	—	—
5	111.32	6.42	110.00	6.38 (br s)	C-3, C-4, C-6
6	150.10	—	150.32	—	—
7	49.32	3.85	48.54	3.85 (4.7)	C-17, C-18
8	79.29	5.42	81.18	5.47 (4.4, 1.5, 1.5)	C-6
9	149.53	6.95	146.54	7.02 (1.6, 1.0)	C-8, C-11, C-20
10	129.97	—	140.56	—	—
11	52.05	3.62	65.42	4.64 (8.0, 1.0)	C-9, C-10
12	60.07	2.99	43.73	1.99 (11.6, 8.0)	
				1.01 (12.9, 11.6, 1.1)	C-1, C-2, C-10, C-11, C-13
13	145.01	—	146.81	—	—
14	112.71	5.05	111.82	5.04 (1.6, 0.8)	C-1, C-15
		5.01		4.82 (3.2, 1.5)	C-1
15	20.98	1.96 (3H)	19.16	1.81 (3H, 1.4, 0.8)	C-1, C-12, C-13
16	163.93	—	163.93	—	—
17	140.04	—	141.05	—	—
18	115.41	5.07	115.10	5.05 (2.5, 1.1)	C-7, C-19
		4.86		4.83 (1.6, 0.9)	C-7, C-19
19	21.52	1.98 (3H)	21.59	1.98 (3H, 0.7, 0.7)	C-7, C-17, C-18
20	170.50	—	174.14	—	—
-OCH_3	51.58	3.83 (3H)	51.42	3.81 (3H, s)	—

[a]The δ_C and δ_H (J_{HH}) data were provided by spectra obtained at 500 MHz and 125.8 MHz, respectively; δ_H values are for individual protons, except in the case of CH_3 groups. The connectivities between the ^{13}C identified in column 4 and the directly attached protons in column 5 were established by HMQC. Two- and three-bond connectivities between the protons in column 5 and the carbons identified in column 4 were established by HMBC. Connectivities observed for **1** are not listed, but were similar to those for **2**.

(2.0 mg) and **3** (4.2 mg); the fifth fraction gave isogorgiacerodiol (6.1 mg) (3).

11-Gorgiacerol [**2**].—Pale-yellow gum, $[\alpha]_D$ +22° (c=0.1, $CHCl_3$); ir ($CHCl_3$) ν max 3400, 1760, 1730 cm^{-1}; uv (MeOH) λ max 215 (ϵ 3900) nm; ms *m/z* 372 (15), 354 (5), 340 (16), 322 (24), 294 (12), 245 (240), 213 (25), 191 (100), 133 (93), 105 (49); hrms *m/z* 372.1590 (calcd for $C_{21}H_{24}O_6$, 372.1573).

ACKNOWLEDGMENTS

We thank Mr. Kurt Bonair of the Institute of Marine Affairs, Chaguaramas, Trinidad and Tobago, for the collection of *P. acerosa*. The Toronto authors gratefully acknowledge financial support through grants from the National Sciences and Engineering Research Council of Canada.

LITERATURE CITED

1. M.M. Bandurraga, W. Fenical, S.F. Donovan, and J. Clardy, *J. Am. Chem. Soc.*, **104**, 6463 (1982).
2. W.R. Chan, W.F. Tinto, R.S. Laydoo, P.S. Manchand, W.F. Reynolds, and S. McLean, *J. Org. Chem.*, **56**, 1773 (1991).
3. W.F. Tinto, L. John, W.F. Reynolds, and S. McLean, *Tetrahedron*, **47**, 8679 (1991).

Received 26 June 1995