Five New Pseudopterane Diterpenes from the Caribbean Sea Plume *Pseudopterogorgia acerosa* PALLAS, Gorgonacea[1)]

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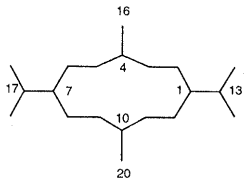
Five new pseudopteranoid diterpenes, pseudopteradiene (2), pseudopteradienoic acid (3), 11-pseudopteranol (4), pseudopteranoic acid (5), and diepoxygorgiacerodiol (7), along with five previously described analogues, have been isolated from Puerto Rican specimens of the gorgonian octocoral *Pseudopterogorgia acerosa*. Detailed analysis of the spectral data and chemical methods were used to establish their structures and to define the relative stereochemistry.

Key words pseudopterane diterpene; *Pseudopterogorgia acerosa*; Caribbean sea plume octocoral

Caribbean sea plumes (gorgonians) of the genus *Pseudopterogorgia* are abundant and chemically rich marine invertebrates responsible for the production of several classes of structurally complex metabolites valued for their cytotoxic and anti-inflammatory properties.[3)] In 1982, Fenical and Clardy reported the structure of pseudopterolide (**1**), a metabolite from *Pseudopterogorgia acerosa* now recognized as the prototype of a remarkable family of diterpenoids based on the 12-membered carbocyclic pseudopterane skeleton.[4)] Following the original characterization of **1**, other bioactive pseudopterane analogues were found in a specimen of *P. kallos* collected in the Bahamas Islands.[5)] Additional pseudopterane diterpenoids have been isolated also from Pacific Ocean specimens of the cold water soft coral *Gersemia rubiformis*.[6a,b)] More recently, nine additional pseudopteranoids, some of them containing nitrogen, have been reported from specimens of *P. acerosa* collected around the coast of Tobago.[7a–d)] We have recently investigated the extracts of Puerto Rican specimens of this organism and report here the isolation and structure determination of five additional metabolites which are structurally related to pseudopterolide (**1**).

A single collection of *P. acerosa* from La Parguera, Puerto Rico produced 6.7 kg of the wet gorgonian coral. Partitioning of an aqueous suspension of the crude extract against hexane and H_2O gave lipophilic solubles (368.0 g) which accounted for 58.0% of the total organic content of *P. acerosa*. Re-extraction of the lipid-free aqueous suspension with $CHCl_3$ followed by concentration yielded 39.3 g (6.2%) of organic solubles. A total of ten pseudopteranoids were obtained pure from the latter extract after routine application of adsorption and



Pseudopterane skeleton

Chart 1

Table 1. ^{1}H-NMR (300-MHz) Spectral Data of the New Pseudopteranes in $CDCl_3$

Proton No.	**2** δ, mult, *J* (Hz), intgr.	**3** δ, mult, *J* (Hz), intgr.	**4** δ, mult, *J* (Hz), intgr.	**5** δ, mult, *J* (Hz), intgr.	**7** δ, mult, *J* (Hz), intgr.
H_1	4.05, td, 3.9, 13.2, 1H	4.05, td, 3.0, 11.4, 1H	2.71, m, 1H	2.57, s, 1H	2.48, s, 1H
H_2	3.50, dd, 12.0, 15.3, 1H	3.52, dd, 12.9, 15.3, 1H	3.30, dd, 12.9, 14.7, 1H	3.21, t, 12.9, 1H	2.50, m, 1H
$H_{2'}$	2.79, dd, 3.9, 15.3, 1H	2.80, dd, 3.6, 15.3, 1H	2.62, dd, 4.2, 14.7, 1H	2.56, m, 1H	1.90, m, 1H
H_5	6.40, s, 1H	6.43, s, 1H	6.32, s, 1H	6.25, s, 1H	4.20, s, 1H
H_7	3.82, d, 4.8, 1H	3.85, d, 3.9, 1H	3.83, d, 4.2, 1H	3.79, brs, 1H	3.33, s, 1H
H_8	5.37, d, 4.5, 1H	5.38, d, 4.8, 1H	5.42, d, 4.2, 1H	5.32, brs, 1H	5.41, s, 1H
H_9	6.56, t, 1.5, 1H	6.58, t, 1.2, 1H	6.99, s, 1H	6.68, s, 1H	7.29, d, 1.2, 1H
H_{11}	5.94, dd, 0.9, 11.7, 1H	5.94, dd, 0.9, 11.7, 1H	4.51, dd, 3.3, 11.1, 1H	1.64, m, 1H	4.85, brd, 1H
$H_{11'}$	—	—	—	0.73, d, 10.2, 1H	—
H_{12}	5.46, t, 11.7, 1H	5.45, t, 11.1, 1H	1.89, m, 1H	2.24, m, 1H	3.63, brd, 9.0, 1H
$H_{12'}$	—	—	0.91, t, 12.3, 1H	2.15, m, 1H	—
H_{14}	4.96, brs, 1H	4.95, 1H, brs	4.95, brs, 1H	4.86, s, 1H	4.98, s, 1H
$H_{14'}$	4.89, brs, 1H	4.89, brs, 1H	4.75, brs, 1H	4.65, d, 10.5, 1H	4.85, s, 1H
H_{15}	1.89, s, 3H	1.89, s, 3H	1.75, s, 3H	1.64, s, 3H	1.79, s, 3H
H_{18}	5.03, brs, 1H	5.04, brs, 1H	4.98, brs, 1H	4.86, s, 1H	5.33, s, 1H
$H_{18'}$	4.85, brs, 1H	4.85, brs, 1H	4.75, brs, 1H	4.65, d, 10.5, 1H	5.07, s, 1H
H_{19}	1.97, s, 3H	1.98, s, 3H	1.92, s, 3H	1.83, s, 3H	1.84, s, 3H
H_{21}	3.79, s, 3H	—	3.75, s, 3H	—	3.81, s, 3H
11-OH	—	—	2.89, brs, 1H	—	4.10, brd, 8.7, 1H
12-OH	—	—	—	—	2.73, brd, 10.8, 1H

Assignments were aided by ^{1}H–^{1}H COSY, spin splitting patterns, selective decoupling experiments and comparison of *J* values. The δ values are in ppm and are referenced to the residual $CHCl_3$ signal (7.26 ppm).

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Table 2. ^{13}C-NMR Spectral Data (75 MHz; $CDCl_3$)[a] of the New Pseudopterane Diterpenoids **2**, **3**, **4**, **5**, and **7**

Carbon No.	**2** δ, (mult)	**3** δ, (mult)	**4** δ, (mult)	**5** δ, (mult)	**7** δ, (mult)
1	49.6 (d)	49.6 (d)	38.3 (d)	41.4 (d)	43.4 (d)
2	29.8 (t)	29.9 (t)	31.1 (t)	31.4 (t)	35.3 (t)
3	161.8 (s)	163.2 (s)	161.2 (s)	162.5 (s)	102.3 (s)
4	115.0 (s)	115.1 (s)	115.6 (s)	115.1 (s)	59.9 (s)
5	111.4 (d)	111.6 (d)	109.9 (d)	110.0 (d)	54.7 (d)
6	150.1 (s)	150.5 (s)	150.4 (s)	150.7 (s)	96.3 (s)
7	43.0 (d)	42.9 (d)	48.4 (d)	48.1 (d)	47.8 (d)
8	79.9 (d)	79.8 (d)	81.3 (d)	80.6 (d)	82.0 (d)
9	145.4 (d)	145.5 (d)	146.8 (d)	147.2 (d)	152.3 (d)
10	131.9 (s)	131.9 (s)	140.6 (s)	141.2 (s)	129.7 (s)
11	118.7 (d)	118.8 (d)	65.1 (d)	34.9 (t)	73.1 (d)
12	137.7 (d)	137.7 (d)	43.6 (t)	22.6 (t)	80.2 (d)
13	146.8 (s)	146.8 (s)	147.0 (s)	147.0 (s)	145.2 (s)
14	110.3 (t)	110.3 (t)	111.6 (t)	114.6 (t)	115.8 (t)
15	21.4 (q)	21.5 (q)	19.1 (q)	19.1 (q)	21.2 (q)
16	164.0 (s)	168.5 (s)	164.0 (s)	168.4 (s)	164.4 (s)
17	140.4 (s)	140.3 (s)	141.1 (s)	136.8 (s)	140.5 (s)
18	115.2 (t)	115.2 (t)	114.9 (t)	111.1 (t)	116.0 (t)
19	21.5 (q)	21.5 (q)	21.4 (q)	21.4 (q)	24.9 (q)
20	171.8 (s)	171.8 (s)	173.5 (s)	175.3 (s)	173.8 (s)
21	51.4 (q)	—	51.3 (q)	—	53.2 (q)

a) Multiplicities were obtained by an Attached Proton Test (APT) experiment. Assignments were made on the basis of heteronuclear chemical shift correlation methods, carbon atom multiplicities and chemical shift values. The δ values are in parts per million and are referenced to the $CDCl_3$ signal (77.0 ppm).

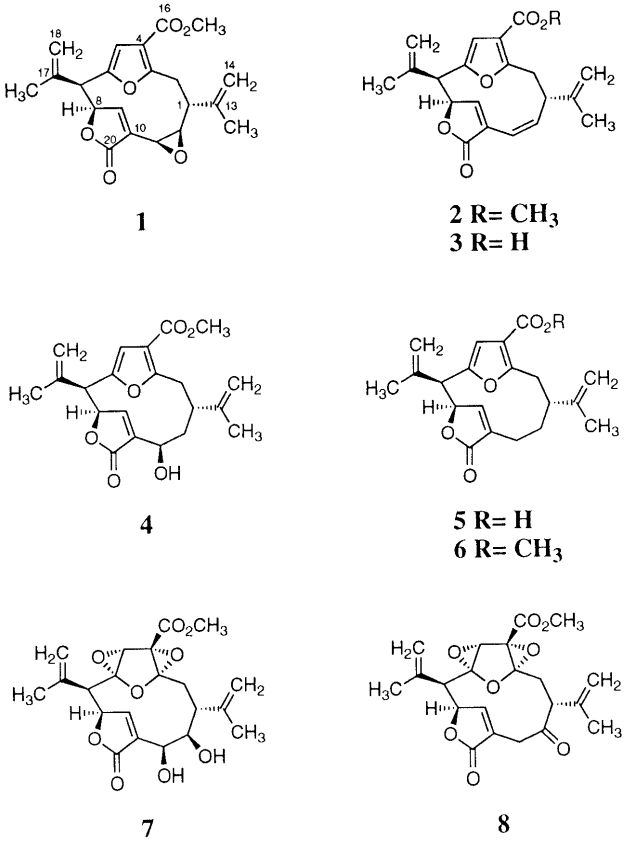

Chart 2

normal-phase chromatography. Five of these metabolites had been previously described, namely, pseudopterolide (**1**),[4] pseudopterolide methanol adduct,[4,7d] deoxypseudopterolide (**6**),[7b] gorgiacerodiol, and isogorgiacerodiol.[7d] These efforts provided all the ^{1}H- and ^{13}C-NMR chemical shift and coupling data shown in Tables 1 and 2 for five new pseudopteranoid analogues described here for the first time.

The high-resolution electron impact-mass spectra (HREIMS) of pseudopteradiene (**2**) established its molecular formula as $C_{21}H_{22}O_5$, signifying eleven sites of unsaturation. IR spectroscopy indicated the presence of olefin (3085 cm^{-1}) in addition to the unsaturated γ-lactone (1757 cm^{-1}) and β-carbomethoxyfuran (1717 cm^{-1}) groups common to many of these metabolites. The signals at δ 164.0 (s), 161.8 (s), 150.1 (s), 115.0 (s), 111.4 (d), and 51.4 (q) in the ^{13}C-NMR spectrum, coupled with the IR absorption at 1717 cm^{-1}, and two singlets in the ^{1}H-NMR spectrum at δ 6.40 (1H) and 3.79 (3H), indicated that **2** possessed the same α,α′-disubstituted β-carbomethoxyfuran constellation found in **1**. The second carbonyl absorption at 1757 cm^{-1}, along with a one-proton signal at δ 6.56 in the ^{1}H-NMR spectrum, and carbon resonances at δ 171.8 (s), 145.4 (d), 131.9 (s), and 79.9 (d) in the ^{13}C-NMR spectrum were ascribed to an α-substituted α,β-unsaturated γ-lactone functionality. The ^{13}C-NMR lines observed at δ 137.7 (d) and 118.7 (d) and ^{1}H-NMR peaks at δ 5.46 (1H, t, J = 11.7 Hz) and 5.94 (1H, dd, J = 0.9, 11.7 Hz) were confidently assigned to a *cis*-disubstituted olefin. Comparisons of the NMR spectral data for **2** with those of **1** together with the UV spectrum (λ_{max} = 248 nm, ε 10050), led to the conclusion that the α,β-unsaturated γ-lactone in **2** was in conjugation with the *cis*-disubstituted olefin moiety. This conclusion was confirmed by the presence of a weak four-bond cross-peak in the ^{1}H–^{1}H correlation spectroscopy (COSY) spectrum of **2** between the one-proton triplet at δ 6.56 (H-9) and the one-proton doublet of doublets centered at δ 5.94 ascribable to H-11.

The relative stereochemistry of **2** was deduced from vicinal ^{1}H–^{1}H coupling constants and from two dimensional nuclear Overhauser effect (2D NOE) measurements (Table 3). In the nuclear Overhauser effect spectroscopy (NOESY) spectrum, the δ 5.37 proton (H-8) gave a cross-peak with the methine proton at δ 3.82 (H-7), which in turn gave a cross-peak with the furanoid singlet located at δ 6.40 (H-5). These observations established the relative stereochemistry at C-7 and C-8 in conjunction with the vicinal ^{1}H–^{1}H couplings shown in **2**. The determination of the β-orientation of H-1 in the carbocyclic ring is consistent with the proposed stereochemistry on the basis of its lack of NOE with H-12. The C-11,12,1 constellation was correlated with the C-7,8 array through their NOEs to H-9. Thus the proton signals at δ 3.82 (H-7) and 5.37 (H-8) each gave NOE responses to the one-proton signal at δ 6.56 (H-9) which in turn showed a strong NOE with H-11 (δ 5.94). The *cis* stereochemistry at the C-11,12 double bond was confirmed by the $^3J_{11,12}$ coupling constant (11.7 Hz).

Pseudopteradienoic acid (**3**) shared many spectral features in common with compound **2**. High-resolution mass spectrometry established a molecular formula of $C_{20}H_{20}O_5$ for this compound. Except for an intense broad absorption near 3650—3100 cm^{-1} indicative of a carbohydroxyl functionality, the IR spectrum of **3** indi-

cated that this compound contained many of the same functional groups as **2**, *i.e.*, olefin, γ-lactone, and furan moieties. Because there were no significantly large differences in both ^{1}H and ^{13}C chemical shift values at most positions in **3** when compared to **2** (see Tables 1 and 2), it was quickly thought that **3** was merely the parent carboxylic acid of **2**. Methylation of **3** with diazomethane in ether at 25 °C yielded a product identical by ^{1}H-NMR, ^{13}C-NMR, IR, UV, and MS with pseudopteradiene (**2**), hence confirming that **2** and **3** are simple derivatives of each other.

A molecular formula of $C_{21}H_{24}O_6$ was established for 11-pseudopteranol (**4**) by HREIMS. Compound **4** showed IR absorptions that indicated the presence of olefin, α,β-unsaturated γ-lactone and β-carbomethoxyfuran functionalities. In addition, **4** showed a broad absorption at 3460 cm^{-1} that indicated the presence of a hydroxyl group. That several of the same structural features found in **1** and **2** were also present in **4** was supported by a UV absorption at λ_{max} 248 nm (ε 2880). Comparison of the ^{1}H- and ^{13}C-NMR spectra of **4** (see Tables 1 and 2) with those of **2** confirmed the structural similarity of these compounds. The α-substituted α,β-unsaturated γ-lactone and the α,α'-disubstituted β-carbomethoxyfuran functionalities were assumed to be intact in **4** on the basis of similar IR, UV, and NMR data (compare signals of related H's and C's in Tables 1 and 2). Compound **4**, however, had two oxygen-bearing methines as indicated by ^{1}H signals at δ 5.42 (1H, d, J=4.2 Hz), 4.51 (1H, dd, J=3.3, 11.1 Hz) and ^{13}C signals at δ 81.3 (d) and 65.1 (d). Unique to **4** was the proton signal at δ 4.51 which suggested the presence of an allylic secondary alcohol function. Allylic coupling between this proton signal and one of the olefinic proton signals (δ 6.99, H-9) was observed in the ^{1}H–^{1}H COSY spectrum. The signal at δ 4.51 (H-11) was likewise shown to be coupled to both of the diastereotopic methylene protons at δ 1.89 and 0.91 (H-12$\alpha\beta$). These data effectively established the site of attachment of the hydroxyl group at C-11. The OH signal assignment (δ 2.89) was confirmed by exchange with CD_3OD.

The NOEs observed for **4** (see Table 3) correlated with a Dreiding model representing the relative stereochemistry shown. This compound has also a logical structure from a biosynthetic viewpoint. Pseudopteradiene (**2**) could be envisioned as a precursor for 11-pseudopteranol (or *vice versa*) *via* hydration at C-11. Due to the extremely hindered "back" face of C-8 to C-12 in these molecules, hydration must involve substituents on the "front" face.

Pseudopteranoic acid (**5**) was shown by HREIMS to have a molecular formula of $C_{20}H_{22}O_5$. Resonances at δ 175.3 (s) and 168.4 (s) in the ^{13}C-NMR of **5** could be assigned to the carbonyls of one ester and one carboxylic acid, respectively. The ^{1}H- and ^{13}C-NMR data for **5** showed a strong resemblance to those displayed by deoxypseudopterolide (**6**), a previously reported metabolite from *P. acerosa*.[7b] The similarity in the spectral data of **5** and **6** suggested that they have the same relationship to each other as do **2** and **3**. In order to confirm this contention, **5** was treated with diazomethane in ether at 25 °C to give **6** quantitatively thus confirming the structure of the former metabolite.

Table 3. Selected NOE Correlations of the New Pseudopterane Diterpenoids **2**, **3**, **4**, **5**, and **7**[a]

Atom	2	3	4	5	7
1	—	—	—	—	H12
2	H14	H14	H11	—	H11, H12
5	H7	H7	H7	H7	H18
7	H5, H8, H9	H5, H8, H9	H5, H8	H5, H8, H9	H8, H18
8	H7, H9, H19	H7, H9, H19	H7, H9	H7, H9	H7, H19
9	H7, H8, H11	H7, H8, H11	H8	H7, H8	—
11	H9, H12	H9, H12	H2	—	H2, H12
12	H11	H11	—	—	H1, H2, H11
14	H2	H2	—	—	—
18	H19	H19	—	—	H5, H7
Me-19	H8, H18	H8, H18	—	—	H8

a) NOESY spectra were recorded at room temperature in $CDCl_3$ solutions.

Diepoxygorgiacerodiol (**7**) gave a parent ion at 420.1420 Da in the HREIMS appropriate for a molecular formula of $C_{21}H_{24}O_9$. After the ^{1}H- and ^{13}C-NMR spectra had been obtained, it became evident that the furan moiety present in other pseudopterane derivatives was absent from **7**. However, the isopropenyl side chains, the α,β-unsaturated γ-lactone and the 4-carbomethoxy group present in most of the pseudopteranoids described here, were still intact (Tables 1 and 2). The presence of two singly oxygenated ^{13}C-NMR signals at δ 59.9 (s) and 54.7 (d) were characteristic of epoxide carbons, and when these signals were combined with the presence of signals for two doubly oxygenated carbons at δ 102.3 (s) and 96.3 (s), we concluded that the furan ring had been modified by epoxidation.[8]

The gross structure of **7** was deduced from ^{1}H- and ^{13}C-NMR spectra data, ^{1}H-NMR spin decoupling and ^{1}H–^{1}H COSY experiments. The two oxygen-bearing methine protons at δ 4.85 (br d) and 3.63 (br d, J=9.0 Hz) were shown by a ^{1}H–^{13}C COSY experiment to be coupled to two carbons at δ 73.1 (d) and 80.2 (d), respectively. The signal at δ 4.85, however, seemed broader and taller compared to the other signal. Interestingly, these proton signals were strongly coupled to two exchangeable proton signals at δ 4.10 (1H, br d, J=8.7 Hz) and 2.73 (1H, br d, J=10.8 Hz), respectively. Upon addition of a few drops of CD_3OD, the latter signals disappeared and the broad doublet signals at δ 4.85 and 3.63 sharpened up. These data indicated the presence of two hydroxyl groups in **7** capable of hydrogen bonding with one another. One of these signals, δ 4.85, was assigned as the signal for H-11 from its chemical shift value and from its coupling with H-12 at δ 3.63. The latter proton signal in turn was coupled to the methine proton at δ 2.48 (H-1). These data established the connectivity as well as the *cis* stereochemistry of the vicinal diol functionality. The coupling constants between the C-11,12 and C-12,1 pairs of vicinal protons are noticeably small ($^3J_{HH}$ < 2.0 Hz) in **7**, and clearly, a Dreiding model with appropriate dihedral angles consistent with these couplings can be constructed if the hydroxyl functions have a *cis* relationship. The 3,4; 5,6-diepoxide function is shown as being on the α-face of **7** on the basis of a strong NOE between H-5 (δ 4.20)

and one of the C-18 exomethylene proton signals at δ 5.33. Moreover, the ^{13}C chemical shift values of carbons 3, 4, 5, and 6 in compound **7** were found to be almost identical with those reported for diepoxygorgiacerone (**8**), a related pseudopterane metabolite from *P. acerosa*.[7c,d] Other NOEs observed for **7** are given in Table 3.

Our examination of the chemistry of Puerto Rican specimens of *P. acerosa* has shown that this gorgonian elaborates interesting diterpenes that are structurally related to those found in specimens collected in other Caribbean locations. The isolation of diterpenes **2**, **3**, **4**, **5**, and **7** is of interest because of the structural complexity and biological importance of the pseudopterane metabolites. Further biotesting of these compounds is in progress.

Experimental

General Experimental Procedures IR were recorded on a Nicolet 600 FT-IR spectrophotometer. ^1H- and ^{13}C-NMR spectra were recorded on a General Electric Multinuclear QE-300. Optical rotations were determined on a Perkin-Elmer Polarimeter Model 243B. Column chromatography (CC) was performed on silica gel (35—75 mesh) and TLC analyses were carried out using glass packed precoated silica gel plates.

Collection and Extraction of *Pseudopterogorgia acerosa* The Caribbean sea plume *P. acerosa* was collected in December 1994 from La Parguera, Puerto Rico. The wet animal (6.7 kg) was blended with MeOH–$CHCl_3$ (1 : 1) (6 × 1 l), and after filtration, the crude extract was evaporated to yield a green residue (633.7 g). After partitioning the crude oil against hexane and H_2O, the lipid-free aqueous suspension was extracted with $CHCl_3$ (5 × 1 l). The resulting filtrate was concentrated *in vacuo* to yield 39.3 g of an oily residue which was chromatographed over silica gel (2.5 kg) using l—25% MeOH–$CHCl_3$. The pseudopterane rich mixture was fractionated into fractions I—XIII on the basis of TLC analyses. Purification of fraction IV (1.63 g) by CC with 15% EtOAc in hexane afforded fractions 1—8: fraction 6 (315 mg, 0.05%) was recognized as deoxypseudopterolide (**6**).[7b] Purification of fraction 7 (170 mg) by HPLC [Partisil 10 M9/50 silica gel with 5% 2-propanol in hexane] gave 32.0 mg (0.005%) of pseudopteradiene (**2**). Purification of fraction VII (1.17 g) by CC with 15% acetone in hexane afforded 150 mg (0.024%) and 200 mg (0.032%) of pseudopterolide (**1**) and pseudopterolide methanol adduct, respectively.[4,7d] Purification of fraction IX (2.27 g) by gradient CC (15—30% acetone in hexane) yielded fractions 1—9. Fraction 6 (183 mg) was purified by HPLC [Partisil 10 M9/50 silica gel with 30% 2-propanol in hexane] to afford 62.0 mg (0.009%) of 11-pseudopteranol (**4**). Purification of fraction 7 (397 mg) by HPLC [Partisil 10 M9/50 silica gel with 30% 2-propanol in hexane] gave 163 mg (0.026%) of gorgiacerodiol.[7d] Fraction XI (1.20 g) was passed over silica gel (75 g) to yield fractions 1—12: fraction 9 (225 mg, 0.036%) was identified as pseudopteranoic acid (**5**) and fraction 10 (236 mg), after purification by HPLC [Partisil 10 M9/50 silica gel with 15% 2-propanol in hexane], gave 57.0 mg (0.009%) of isogorgiacerodiol[7d] and 10.5 mg (0.002%) of pseudopteradienoic acid (**3**). Purification of fraction X (1.60 g) over silica gel (80 g) yielded fractions 1—6. Purification of fraction 5 (158 mg) by HPLC [Partisil 10 M9/50 silica gel with 40% 2-propanol in hexane] afforded 40.0 mg (0.006%) of diepoxygorgiacerodiol (**7**).

Pseudopteradiene (**2**): Pale yellow oil. $[\alpha]_D^{25}$ +17.5° (c=0.2, $CHCl_3$). IR (neat): 3085, 2951, 1757, 1717, 1647, 1613, 1574, 1440, 1221, 1076, 900 cm^{-1}. UV $\lambda_{max}^{CHCl_3}$ nm (ε): 248 (10050). EI-MS m/z: (rel. int. %) 354 (M^+, 2), 332 (4), 248 (3), 192 (base peak), 133 (38), 70 (15). HREI-MS, Calcd for $C_{21}H_{22}O_5$: 354.1467. Found: 354.1454. ^1H- and ^{13}C-NMR, see Tables 1 and 2.

Pseudopteradienoic Acid (**3**): Pale yellow oil. $[\alpha]_D^{25}$ +14.2° (c=0.2, $CHCl_3$). IR (neat): 3350—3160 (br), 3084, 2930, 2854, 1755, 1748, 1716, 1575, 1437, 1376, 1222, 1074 cm^{-1}. UV $\lambda_{max}^{CHCl_3}$ nm (ε): 250 (10200). EI-MS m/z: (rel. int. %) 340 (M^+, 5), 322 (9), 315 (4), 192 (8), 179 (16), 178 (base peak), 150 (14), 133 (39), 83 (45), 57 (29). HREI-MS, Calcd for $C_{20}H_{20}O_5$: 340.1311. Found: 340.1290. ^1H- and ^{13}C-NMR, see Tables 1 and 2.

11-Pseudopteranol (**4**): Pale yellow oil. $[\alpha]_D^{25}$ +5.0° (c=0.2, $CHCl_3$). IR (neat): 3460, 3084, 2925, 1753, 1745, 1725, 1711, 1692, 1649, 1446, 1223, 1080, 780 cm^{-1}. UV $\lambda_{max}^{CHCl_3}$ nm (ε): 248 (2880). EI-MS m/z: (rel. int. %) 372 (M^+, 0.5), 322 (1), 245 (2), 191 (7), 133 (5), 69 (base peak). HREI-MS, Calcd for $C_{21}H_{24}O_6$: 372.1574. Found: 372.1576. ^1H- and ^{13}C-NMR, see Tables 1 and 2.

Pseudopteranoic Acid (**5**): Pale yellow oil. $[\alpha]_D^{25}$ +5.0° (c=4.5, $CHCl_3$). IR (neat): 3650—3050 (br), 2927, 2657, 1753, 1725, 1687, 1679, 1578, 1444, 1227, 1074, 896 cm^{-1}. UV $\lambda_{max}^{CHCl_3}$ nm (ε): 252 (4000). EI-MS m/z: (rel. int. %) 342 (M^+, 9), 324 (4), 228 (11), 177 (base peak), 133 (22), 70 (28). HREI-MS, Calcd for $C_{20}H_{22}O_5$: 342.1467. Found: 342.1458. ^1H- and ^{13}C-NMR, see Tables 1 and 2.

Diepoxygorgiacerodiol (**7**): Stable white semi-solid. $[\alpha]_D^{25}$ −0.34° (c=7.8, $CHCl_3$). IR (neat): 3632—3100 (br), 2956, 2923, 2853, 1743, 1731, 1656, 1440, 1365, 1260, 1093, 1064, 905, 797 cm^{-1}. UV $\lambda_{max}^{CHCl_3}$ nm (ε): 246 (1200). EI-MS m/z: (rel. int. %) 420 (M^+, 7), 386 (5), 371 (9), 330 (9), 315 (21), 167 (39), 149 (51), 95 (67), 55 (base peak). HREI-MS, Calcd for $C_{21}H_{24}O_9$: 420.1420. Found: 420.1420. ^1H- and ^{13}C-NMR, see Tables 1 and 2.

Conversions with Diazomethane A solution of **5** (30 mg, 0.088 mmol) in ether (8 ml) was treated with excess diazomethane[9] at 25 °C for 30 min. The residue obtained after concentration was purified by CC (5% $CHCl_3$–MeOH) to give 31 mg of an oil whose TLC retention time, NMR, IR, UV and LREIMS spectra were identical to those obtained for **6**.[7b] **3** was transformed quantitatively into **2** under similar reaction conditions.

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References and Notes

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