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NEW GERMACRANE DERIVATIVES FROM GORGONIAN OCTOCORALS OF THE GENUS PSEUDOPTEROGORGIA

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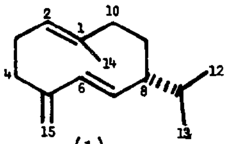
Abstract: Two new and five known germacrane derivatives were isolated from Pseudopterogorgia americana and a related species. Their structures were established by spectroscopic methods.

The Caribbean gorgonian octocoral Pseudopterogorgia americana (Gmellin), has been the subject of several chemical investigations.[1-4] We wish to report the isolation and characterisation of the germacrane derivatives (1 - 4) as the major metabolites of P. americana. Compounds (1) and (4) had spectroscopic data that were in agreement with those reported for (+)-germacrene-D,[5] and furanodiene,[6] respectively.

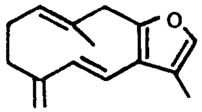
Compound (2) had identical ^1H and ^{13}C NMR chemical shifts with those reported for furanotriene.[4] However, long range coupling (J=1Hz) was observed between H-6 (δ 5.99) and an exo-methylene proton at δ 4.55. Thus, irradiation of the signal at δ 5.99 resulted in the collapse of the doublet of doublets at δ 4.55. This indicated that the exomethylene group was at C-5 as in (+)-germacrene-D (1).[5] Structure (2) is therefore proposed for furanotriene.

Compound (3), $C_{15}H_{18}O$ (M^+ 214) was isomeric with 2. The UV, IR and ^1H NMR spectra (Experimental) indicated that the two compounds had the same functional groups - including an extended conjugated system with a trans-disubstituted double bond and an exocyclic methylene. Significantly, compound 3 exhibited an AB system.

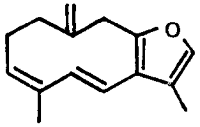
Further, decoupling experiments showed that none of the olefinic protons were coupled with the protons of the exocyclic methylene. Structure 3, previously assigned to furanotriene,



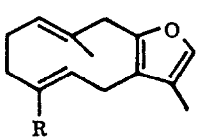
(1)



(2)

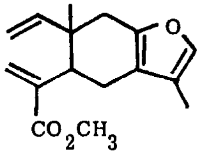


(3)

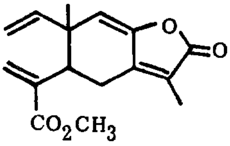


(4) R = CH_3

(5) R = CO_2CH_3



(6)



(7)

is consistent with the spectroscopic data for this new furanogermacrane derivative, designated isofuranotriene. Both 2 and 3 were quite unstable when exposed to air and rapidly decomposed.

A new elemanolide (7), along with the known derivatives (4 - 6),[4,6] were isolated from a Pseudopterogorgia sp. that is closely related to P. americana.[7] The elemanolide 7, $C_{16}H_{18}O_4$, $[\alpha]_D$ + 19 (C 0.05, $CHCl_3$) was isolated as a moderately stable gum and had IR absorptions for α,β-unsaturated γ-lactone (1765 cm^{-1}) and ester (1720 cm^{-1}) groups. The ^1H NMR spectrum had resonances for two methyl groups at δ 1.12 and δ 1.91 and the methoxy of a methyl ester at 3.75. An ABX spin system was evident from three one-proton doublet of doublets at δ 4.99, δ 5.17 and δ 5.85 respectively.

The presence of a ^{13}C NMR signal at δ 168.0 and the absence of an ^1H NMR resonance for an α-furan proton suggested that an α,β-unsaturated γ-lactone was present in 7 instead of a furan. Irradiation of the methyl resonance at δ 1.91 caused an olefinic proton at δ 5.50 and a broad doublet at δ 2.74 (2H) to sharpen. The doublet at δ 2.74 was further coupled to a proton at δ 3.32.

Two olefinic protons with resonances at δ 5.59 and δ 6.34 were attributed to a deshielded exomethylene group It was therefore conjugated to a methoxycarbonyl moiety. Structure 7 is consistent with the foregoing evidence. It should be noted in passing that the C-11 methyl group shows six-bond coupling to the C-10 proton.

In addition to the two gorgonians investigated, *P. rigida* and *P. blacquillenesis* are also known to contain sesquiterpenes as their major metabolites.[8-10] In contrast, all other members of the genus examined so far were shown to contain cembrane and pseudopterane diterpenoids.[11]

TABLE 1 - ^{1}H AND ^{13}C NMR DATA[a,b]

	2		3		7	
C#	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	-	134.2	-	148.4	-	42.3
2	5.02(1H,m)	136 2	2.50(2H,m)	38.6	4.99(1H,dd,18,10)	144.8
3	2.18(2H,m)	25.8	2.50(2H,m)	29.3	5.17(1H,dd,10,1.5) 5.85(1H,dd,18,1.5)	113.8
4	2.18(2H,m)	32.3	5.47(1H,t,7)	132.2	5.59(1H,bs) 6.34(1H,s)	126.2
5	-	148.3	-	136.4	-	140.8
6	5.99(1H,dd,12,1)	119.9	5.99(1H,d,15)	113.6	3.32(1H,t,8)	42.8
7	5 86(1H,d,12)	125.5	5.91(1H,d,15)	127.1	2.74(2H,bd,8)	25.4
8	-	118.2	-	120.4	-	121.4
9	-	144.8	-	150.2	-	148.8[c]
10	3.21(2H,bs)	39.5	3 34(1H,d,16) 3.55(1H,d,16)	40.3	5.50(1H,bs)	114.3
11	-	123.3	-	121.4	-	147.0[c]
12	7.03(1H,q,1)	139.0	7.05(1H,bs)	139.5	-	168.0
13	1.88(3H,d,1)	8.7	1 90(3H,d,1.5)	8.3	1.91(3H,d,1)	8.5
14	1.50(3H,d,1.5)	17.0	4.75(1H,bs) 5.05(1H,d,2)	107.9	1.12(3H,s)	20.1
15	4.55(1H,dd,2.5,1) 4.71(1H,d,2.5)	113.6	1 30(3H,s)	16.7	-	163.2
OMe					3.75(3H,s)	52.1

a. Proton NMR spectra were recorded at 80MHz in $CDCl_3$ solution with TMS as internal standard Chemical shifts are in δ units with *J* values in Hz.

b. Carbon-13 NMR spectra were recorded at 20MHz. Assignments were based on the J-Modulated Spin Echo ^{13}C NMR spectra and a comparison with model compounds

c. Assignments may be interchanged.

Experimental

General. UV spectra were obtained on a Perkin-Elmer 552A spectrophotometer. IR spectra were recorded on a Pye-Unicam spectrophotometer. ^{1}H and ^{13}C NMR spectra were determined in $CHCl_3$ on a Bruker WP80SY spectrometer with TMS as the internal standard.

Extraction and Isolation. Specimens of *Pseudopterogorgia* sp. and *P. americana* were collected at Man-O-War Bay, Tobago, in March 1984. Voucher specimens were kept at the Institute of Marine Affairs, Trinidad and Tobago. Air-dried specimens of *P. americana* (400g) were minced and allowed to stand in acetone (1.5L) for 24 hours. The acetone extract was partitioned between light petroleum (3 x 200 mL) and 90% aqueous methanol (500 mL). The light petroleum extract gave a dark green oil (24.9g) on evaporation of the solvent. The crude extract (1.0g) was separated by prep. TLC with light petroleum as eluant. This gave, in order of decreasing R_F, (+)-germacrene-D 1 (69 mg), furanotriene 2 (46 mg) and a mixture of isofuranotriene 3 and furanodiene 4. Isofuranotriene 3 (30 mg) and furanodiene 4 (15 mg) were separated after preparative TLC using silver nitrate (15%) impregnated silica with light petroleum-EtOAc (9:1) as eluant.

Furanotriene 2 was isolated as a yellow oil, UV (MeOH) 225 nm (ε 11300), 265 nm (ε 1100); IR (neat) 3080, 3020, 1640, 1630, 1550, 970, 890, 840 cm^{-1}; LREIMS m/z 214 (M$^+$, 18%), 199(19), 158(89), 145(100), 115(83), 105(22), 91(96), 79(25), 77(64).

Isofuranotriene 3 was also isolated as a yellow oil and had the following spectral properties: UV (MeOH) 215 nm (ε 8200), 260 nm (ε 3500); IR (neat) 3050, 1625, 1550, 890 cm^{-1}; LREIMS m/z 214 (M$^+$, 24%), 199(17), 158(89), 145(92), 115(78), 105(26), 91(100), 79(34), 77(68).

A CH_2Cl_2 extract of Pseudopterogorgia sp. (270g, dried wt.) was chromatographed on silica gel and eluted with light petroleum-CH_2Cl_2 (9:1), CH_2Cl_2 and finally with CH_2Cl_2-EtOAc to give four major fractions.

The elemanolide 7 (59 mg) was isolated from fraction #4 as a moderately stable gum after rechromatography on silica gel with CH_2Cl_2 elution and had the following spectral properties: UV (MeOH) 215 nm (ε 10000), 276 nm (ε 12000); IR (neat) 3080, 3020, 1765, 1720, 1670, 1655, 1625 cm^{-1}; LREIMS m/z 274 (M$^+$, 8%), 246(100), 231(12), 214(19), 186(22), 171(14), 159(33), 132(18), 122(20), 91(26).

Acknowledgements

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