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CAROTENOIDS FROM THE SOFT CORAL *SARCOPHYTON ELEGANS*

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ABSTRACT

*By various chromatographic separations, three carotenoids were isolated from the soft coral Sarcophyton elegans. They were elucidated as peridinin (**1**), peridininol (**2**), and all-trans-peridininol-5,8-furanoxide (**3**) by spectroscopic methods and in comparison with reported data. This is the first report of **3** from soft corals.*

I - INTRODUCTION

Oceans and seas are the greatest biodiversity of life. This diversity has been the source of unique chemical compounds with potential for the benefit of human life. It is now believed that the chemical diversity found in marine organisms mirrors this biological diversity. The prospect of finding new drug in the sea may be 300 to 400 times more likely than isolating one from a terrestrial ecosystem. However, the bioactive compounds from terrestrial organism are still dominated today. It is estimated that the appearance of natural products and their derivatives is about one quarter of the drugs selling in the world; most of them are derived from the terrestrial plants and animals [1 - 3].

The interest in marine natural products emerged in the 1950s, since then a large number of interesting compounds has been isolated [4 - 6]. Some of them are in various clinical stages. Vietnam, with over 1 million km^2 coastal areas, has rich sources of marine organisms. According to preliminary statistic data, there are about 12,000 marine animals and plants. This rich biodiversity is an advantage in the development of the marine natural product researches in Vietnam. In the course of our researches on chemical constituents and biological activities of Vietnamese marine organisms, this paper reports the isolation and structure elucidation of three carotenoids (**1** - **3**) from the soft coral *Sarcophyton elegans*.

II - MATERIAL AND METHODS

General experimental procedures

All NMR spectra were recorded on a Bruker AM500 FT-NMR spectrometer (500 MHz for ^{1}H- and 125 MHz for ^{13}C-NMR), and chemical shifts (δ) are reported in ppm using TMS as an internal standard. Column chromatography (CC) was performed on silica gel 230 ÷ 400 mesh (0.040 ÷ 0.063 mm, Merck) or YMC RP-18 resins (30 ÷ 50 µm, Fujisilisa Chemical Ltd.). Thin layer chromatography was performed on

DC-Alufolien 60 F_{254} (Merck 1.05715) or RP_{18} F_{254s} (Merck) plates. Compounds were visualized by spraying with aqueous 10% H_2SO_4 and heating for 5 minutes.

Animal material

The specimens of *S. elegans* were collected in Hai Van - Son Cha, Da Nang, Vietnam during November, 2009 and deep frozen until used. The scientific name was identified by Dr. Do Cong Thung, Institute of Marine Resources and Environment, Vietnam Academy of Science and Technology. A voucher specimen (N^o HV-SC 22) is deposited at Institute of Marine Biochemistry and Institute of Marine Resources and Environment, VAST, Hanoi, Vietnam.

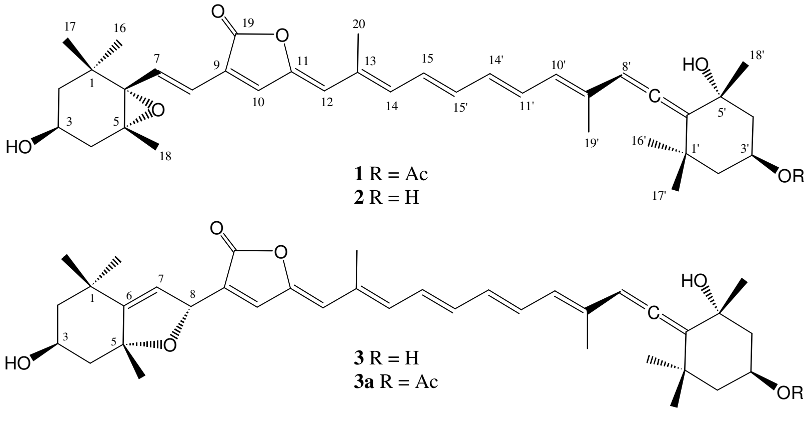
Extraction and Isolation

Fresh frozen samples of the soft coral (30 kg) were well grinded and extracted with hot MeOH three times (50 ^{o}C for 3 hours each time) and then concentrated under reduced pressure to give MeOH extract (250 g). This extract was suspended in water and partitioned with chloroform. The chloroform extract (180 g) was crudely separated on silica gel CC gradient concentration of acetone in *n*-hexane from 0 to 100% to give 10 fractions (C1-C10). Fraction C6 (8.5 g) was further separated on YMC RP-18 CC eluting with acetone/water 3/1, followed by silica gel CC with chloroform/acetone 7/1, to furnish compounds **2** (16 mg) and **3** (13 mg) as reddish solids. Compound **1** (Purple crystals, 150 mg) was purified from fraction C7 (12 g) by repeated silica gel CC eluting with chloroform/acetone 5/1.

Peridinin (1): Purple crystals; mp 128-132^o C; ESI-MS *m/z* 631 $[M+H]^+$ ($C_{39}H_{50}O_7$). ^{1}H-NMR ($CDCl_3$, 500 MHz) and ^{13}C-NMR ($CDCl_3$, 125 MHz) see Table 1.

Peridininol (2): Reddish solid; ESI-MS *m/z* 589 $[M+H]^+$ ($C_{37}H_{48}O_6$). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ (ppm): 3.90 (1H, m, H-3), 7.16 (1H, d, J = 15.5 Hz, H-7), 6.36 (1H, d, J = 15.5 Hz, H-8), 7.02 (1H, s, H-10), 5.72 (1H, s, H-12), 1.23 (3H, s, H-16), 0.98 (3H, s, H-17), 1.22 (3H, s, H-18), 2.22 (3H, s, H-22), 4.32 (1H, m, H-3'), 6.03 (1H, s, H-8'), 1.08 (3H, s, H-16'), 1.39 (3H, s, H-17'), 1.36 (3H, s, H-18'), and 1.81 (3H, s, H-19'); ^{13}C-NMR ($CDCl_3$, 125 MHz) see table 1.

(8*R*,69*R*)-Peridininol-5,8-furanoxide (3): Reddish solid; ESI-MS *m/z* 589 $[M+H]^+$ ($C_{37}H_{48}O_6$). ^{1}H-NMR ($CDCl_3$, 500 MHz) and ^{13}C-NMR ($CDCl_3$, 125 MHz) see table 1.



1 R = Ac
2 R = H

3 R = H
3a R = Ac

Fig. 1: Structures of **1** - **3**

Table 1: The NMR data of **1** - **3** and reported compounds

C	#δ_C	**1**		@δ_C	**2**	&δ_C	**3**	
		δ_C[a,b]	δ_H[a,c] mult. (J = Hz)		δ_C[a,b]		δ_C[a,b]	δ_H[a,c] mult. (J = Hz)
1	35.3	35.28	-	35.29	35.31	33.9	33.91	-
2	47.1	47.03	1.26 m/1.63 m	47.05	47.09	46.6	46.64	1.49 m/1.77m
3	64.2	64.06	3.90 m	64.15	64.18	67.7	67.66	4.32 m
4	40.9	40.88	1.62 m/ 2.39 dd (5.0, 14.5)	40.88	40.93	47.5	47.57	1.93 m/2.19 m
5	67.5	67.53	-	67.50	**67.49**	**87.8**	**87.82**	-
6	70.5	70.50	-	71.05	**70.48**	**153.8**	**153.81**	-
7	133.6	133.63	7.16 d (15.5)	133.58	**133.62**	**117.8**	**117.89**	5.53 br s
8	121.8	121.78	6.37 d (15.5)	121.78	**121.81**	**77.2**	**77.01**	5.61 br s
9	124.8	124.75	-	124.74	**124.79**	**132.4**	**132.35**	-
10	136.3	136.33	7.02 s	136.31	136.30	138.2	138.23	7.16 d (1.0)
11	146.8	146.77	-	146.74	146.78	146.7	146.72	-
12	119.2	119.23	6.44 s	119.24	119.22	118.8	118.88	5.69 s
13	134.0	133.95	-	133.90	134.08	133.8	133.60	-
14	138.0	138.06	6.45 brd (10.8)	138.05	138.04	137.8	137.84	6.47*
15	137.2	137.24	6.51 dd (10.8, 14.3)	131.54	137.26	128.8	128.78	6.59*
16	29.5	29.49	1.21 s	29.29	29.50	28.6	28.63	1.33 s
17	24.9	24.91	0.97 s	24.87	24.92	31.3	31.29	1.16 s
18	19.9	19.88	1.20 s	19.85	19.88	28.7	30.91	1.66 s
19	168.7	168.74	-	168.75	168.75	168.9	168.90	-
20	15.4	15.37	2.22 s	15.36	15.37	15.4	15.39	2.21 s
1'	35.8	35.78	-	35.84	35.78	35.8	35.89	-
2'	45.4	45.44	1.40 m 1.09 brd (12.8)	49.37	49.45	45.4	49.48	1.33 m/1.95m
3'	67.9	68.08	5.37 m	64.23	64.25	67.9	64.29	4.24 m
4'	45.2	45.30	1.50 t (12.0)/2.27	48.86	48.94	45.2	48.89	1.40 m/2.25 m
5'	72.7	72.53	-	72.95	72.97	72.7	72.99	-
6'	117.6	117.58	-	117.80	117.89	117.6	117.80	-
7'	202.6	202.67	-	-	202.73	202.6	202.72	-
8'	103.3	103.27	6.05 s	103.14	103.17	103.3	103.18	6.03 s
9'	133.9	133.88	-	134.00	133.91	133.6	134.01	-
10'	128.1	128.10	6.10 d (11.5)	127.98	128.00	128.1	127.99	6.10 d (11.5)
11'	131.5	131.50	6.61 dd (11.5, 14.3)	132.92	131.55	131.4	131.47	6.60*
14'	133.0	132.99	6.35 dd (11.5, 14.3)	128.85	132.94	133.0	132.90	6.37*
15'	128.9	128.90	6.61 dd (11.5, 14.3)	137.25	128.87	137.1	137.13	6.50*
16'	32.1	32.06	1.07 s	32.11	32.14	31.3	29.34	1.33 s
17'	29.2	29.14	1.38 s	29.48	29.32	32.1	32.16	1.07 s
18'	31.3	31.18	1.35 s	31.32	31.35	29.2	31.38	1.33 s
19'	14.0	13.98	1.80 s	13.97	13.98	14.0	13.99	1.79 s
$\underline{C}OCH_3$	170.4	170.48	-			170.4		
$CO\underline{C}H_3$	21.4	21.36	2.04 s			21.4		

[a]Measured in $CDCl_3$, [b]125MHz, [c]500 MHz, #δ_C of peridinin [7], @δ_C of peridininol [8], &δ_C of all-trans-(8R,69R)-peridinin-5,8-furanoxide (**3a**) [7], *overlapped signals

III - RESULTS AND DISCUSSION

Compound **1** was isolated as purple crystals suggesting that it is a carotenoid pigment. Its ^{1}H-NMR spectrum showed typical signals of two oxymethine [δ 3.90 (1H, m, H-3) and 5.37 (1H, m, H-3')], eleven olefinic protons, and nine tertiary methyl protons [δ 1.21 (H-16), 0.97 (H-17), 1.20 (H-18), 2.22 (H-20), 1.07 (H-16'), 1.38 (H-17'), 1.35 (H-18'), 1.80 (H-19'), and 2.04 ($COCH_3$), each 3H, s]. The ^{13}C-NMR spectrum revealed 39 carbon signals, including nine methyl, four methylene, 13 methine, and thirteen quaternary carbons detected by DEPT experiments. An acetoxy group was indicated by carbon signals at δ 170.48 (C)/21.36 (CH_3). Beside the two oxymethine groups at δ 64.06 (CH, C-3) and 68.08 (CH, C-3'), three oxygenated quaternary carbons were identified by carbon signals at δ 67.53 (C, C-5), 70.50 (C, C-6), and 72.53 (C, C-5'). In addition, the presence of an allene group was indicated by the low-field ^{13}C-NMR signal at δ 202.67 (C, C-7'). The carbon signal at δ 168.74 (C) showed the presence of an ester group. From above evidence, the ^{13}C-NMR data of **1** were compared with those of peridinin [7] and found to match completely (Table 1). To confirm the structure of **1**, the HSQC, HMBC, and COSY spectra were recorded. The ^{1}H-^{1}H COSY experiment allowed the assignment of the connectivity of C-2/C-3/C4, C-14/C-15/C-15'/C-14'/C-11', and C-2'/C-3'/C-4'. The epoxy group at C-5/C-6 was identified by HMBC correlations between H-18 (δ 1.20) and C-4 (δ 40.88)/C-5 (δ 67.53)/C-6 (δ 70.50). Detailed analysis of the other HMBC correlations led to confirm the gross structure of **1** (Fig. 1). Moreover, the ESI-MS exhibited an ion peak at *m/z* 631 $[M+H]^+$ corresponding to the molecular formula of $C_{39}H_{50}O_7$. Thus, **1** was elucidated to be peridinin.

The ^{1}H and ^{13}C-NMR data of **2** were identical to those of **1** except for the absence of the acetoxy group. The good agreement of the ^{13}C-NMR data of **2** with the reported data (table 1) allowed the elucidation of **2** as peridininol [8].

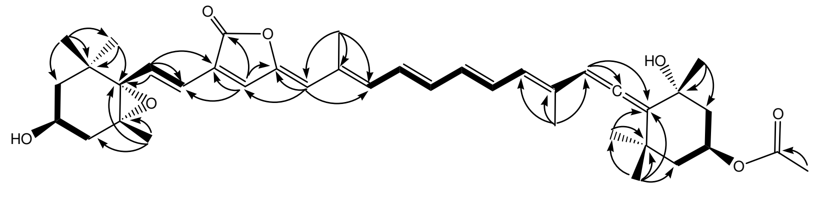


Fig. 2: Key HMBC (⟶) and ^{1}H-^{1}H COSY (▬) correlations of **1**

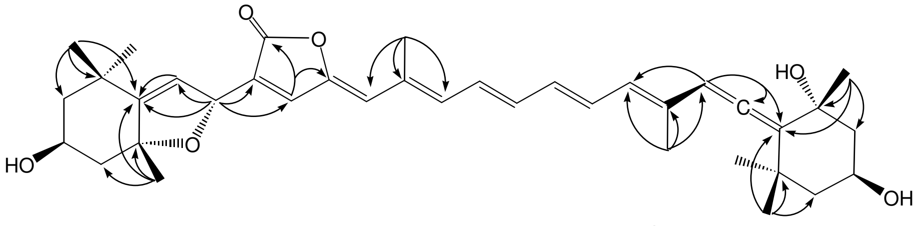


Fig. 3: Key HMBC correlations of **3**

Compound **3** was purified as a reddish solid. Its NMR data were similar to those of **2**, except for the signals due to C-6 to C-9. The di-substituted double bond in **2** [δ 133.62 (CH, C-7) and 121.81 (CH, C-8)] was changed to tri-substituted double bond in **3** [δ 153.82 (C, C-6) and 117.89 (CH, C-7). This evidence, and the presence of one quaternary oxygenated carbon and an oxymethine group at δ 87.82 (C, C-5) and 77.01 (CH, C-8), respectively, indicated that **3** have a 5,8-furanoxide structure [7]. The NMR data of **3** were first assigned by comparison with those of **2** and all-*trans*-peridinin-5,8-furanoxide (**3a**) [7], and further confirmed by HSQC and HMBC experiments (Fig. 3). Moreover, the ESI-MS exhibited an ion peak at *m/z* 589 $[M+H]^+$ corresponding to the molecular formula of $C_{37}H_{48}O_6$. Consequently, compound **3** was elucidated as all-*trans*-peridininol-5,8-furanoxide. This compound was previously isolated from the fresh water clam *Corbicula japonia* [9]. However, this is the first report of **3** from soft corals and the ^{13}C-NMR data were presented here for the first time.

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