

A novel chlorinated norsesquiterpenoid and two related new metabolites from the soft coral *Paralemnalia thyrsoides*

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Abstract—A structurally unique chlorinated norsesquiterpenoid, paralemnolin A (**1**), along with two new metabolites, paralemnolin B (**2**) and C (**3**), have been isolated from the soft coral *Paralemnalia thyrsoides*. Their structures were determined by extensive spectroscopic analyses. Single-crystal X-ray diffraction analysis of **1** further establish the absolute stereochemistry of **1**.

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Soft coral of the genus *Paralemnalia* have been found to be a rich source of bioactive secondary metabolites.^{1–4} During the course of our investigation on the bioactive chemical constituents from marine invertebrates,^{5–7} two new norsesquiterpenoids (**1** and **2**), and one sesquiterpenoid (**3**) have been isolated from the soft coral *Paralemnalia thyrsoides*, collected by hand using scuba at Green Island, located off the southeast coast of Taiwan. We describe herein the structure elucidation of these compounds, and also the proposed biosynthesis pathway for the chlorinated metabolite **1** (Fig. 1).

The organism of *P. thyrsoides* was frozen immediately after collection and the freeze-dried organism was extracted sequentially with EtOAc. The EtOAc extract (33.0 g) was fractionated by open column chromatography on silica gel using *n*-hexane, *n*-hexane/EtOAc, and EtOAc/MeOH mixtures of increasing polarity. A fraction eluted with EtOAc/*n*-hexane (1:15) was further purified by normal-phase HPLC using EtOAc/*n*-hexane (1:50) to afford compound **1** (20.9 mg). Compounds **2**

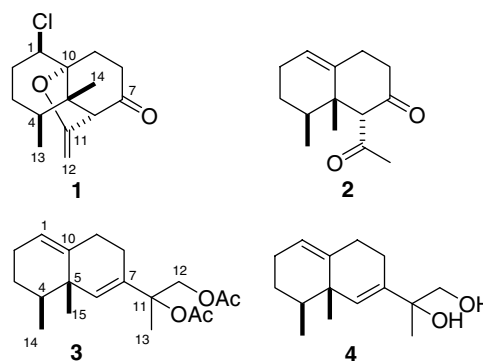


Figure 1. Structures of metabolites 1–4.

(27.3 mg) and **3** (35.5 mg) were eluted with EtOAc/*n*-hexane (1:10) and further purified by normal-phase HPLC using EtOAc/*n*-hexane (1:30).

ESIMS of paralemnolin A (**1**)⁸ exhibited two ion peaks at m/z 277 $[M+Na]^+$ /279 $[M+2+Na]^+$ (in a ratio ca. 1:0.3) in accordance with the presence of one chlorine atom (Table 1). A molecular formula of $C_{14}H_{19}ClO_2$ for **1** was established by HRESIMS, indicating five degrees of unsaturation. The NMR spectral data suggested the presence of one ketone (δ_C 206.6 qC), one 1-alkyl,

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Table 1. ^1H and ^{13}C NMR spectral data of compounds **1–3**

C/H	1		2		3	
	$^{13}\text{C}^{\text{a}}$	$^1\text{H}^{\text{b}}$	$^{13}\text{C}^{\text{a}}$	$^1\text{H}^{\text{b}}$	$^{13}\text{C}^{\text{a}}$	$^1\text{H}^{\text{b}}$
1	60.0 d ^c	4.28 t (3.0) ^d	124.3 d ^c	5.67 m	120.3 d ^c	5.34 br s
2	30.6 t	1.92 m	25.7 t	1.99 m	25.4 t	1.98 m
		2.27 m		2.13 m		
3	23.3 t	1.39 m	27.2 t	1.39 m	27.4 t	1.48 m
		1.69 m		1.43 m		
4	33.5 d	1.71 m	35.1 d	1.71 m	37.0 d	1.50 m
5	49.2 s		46.7 s		38.4 s	
6	65.6 d	3.10 s	75.0 d	3.89 s	131.4 d	5.62 d (2.7) ^d
7	206.6 s		207.3 s		135.2 s	
8	34.1 t	α 2.77 m	38.3 t	α 2.86 m	27.4 t	1.88 m
		β 2.35 m		β 2.29 m		2.16 m
9	32.9 t	α 2.01 m	31.7 t	α 2.56 m	30.0 t	α 2.10 m
		β 2.65 m		β 2.64 m		β 2.29 m
10	87.2 s		136.3 s		141.8 s	
11	158.8 s		204.4 s		82.9 s	
12	84.4 t	4.01 d (2.1)	33.9 q	2.22 s	68.1 t	4.15 d (11.1)
		4.32 d (2.1)				4.24 d (11.4)
13	16.4 q	0.85 d (6.6)	16.1 q	0.93 d (6.9) ^d	21.5 q	1.59 s
14	13.1 q	1.04 s	20.0 q	0.95 s	15.9 q	0.93 d (5.7)
15					20.8 q	0.93 s
OAc					170.9 s	
					21.2 q	2.08 s
					169.7 s	
					22.1 q	2.01 s

^a Spectra recorded at 75 MHz in CDCl_3 at 25 °C.

^b Spectra recorded at 300 MHz in CDCl_3 at 25 °C.

^c Multiplicity are deduced by HSQC and DEPT spectra and indicated by usual symbol.

^d J value (in Hz) in parentheses.

1-alkoxy-disubstituted carbon–carbon double bond (δ_{C} 158.8 qC and 84.4 CH₂; δ_{H} 4.01 and 4.32, each d, $J=2.1$ Hz), one oxygenated quaternary carbon (δ_{C} 87.2), and one secondary alkyl chloride (δ_{C} 60.0; δ_{H} 4.28, dd, $J=3.0, 3.0$ Hz). The above functionalities also account for two of the five degrees of unsaturation, suggesting a tricyclic structure in **1**.

The gross structure of **1** was established by 2D NMR spectroscopic analyses. From ^1H – ^1H COSY spectrum of **1**, it was possible to establish the proton sequences by the following cross-peaks: H-1/H₂-2, H₂-2/H₂-3; H₂-3/H-4, H-4/H₃-13, H₂-8/H₂-9 (Fig. 2). Its HMBC spectrum showed many informative correlations, such

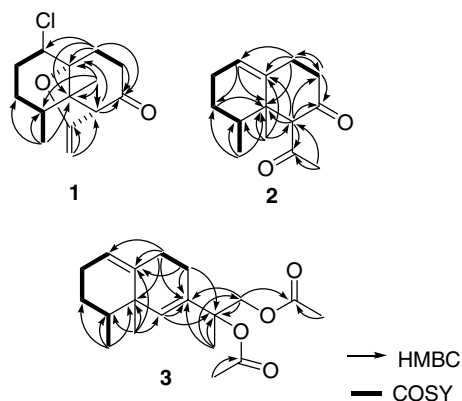


Figure 2. Selective ^1H – ^1H COSY and HMBC correlations of **1–3**.

as H-6/C-7 and C-10; H₂-8/C-7 and C-10; H₂-9/C-1, C-5, C-7, C-8, and C-10; H₂-12/C-11 and C-6; H₃-13/C-3, C-4, and C-5; and H₃-14/C-4, C-5, C-6, and C-10 (Fig. 2). Thus, the unusual planar structure of **1** with an α -methylene THF structural unit was established unambiguously.

The relative stereochemistry of **1** was elucidated from the NOE interactions observed in a NOESY experiment (Fig. 3). In the NOESY experiment of **1**, H₃-14 was found to show NOE interactions with H-6, H₃-13, and one proton of H₂-9 (δ_{H} 2.65, m), but not with H-1 and H-4. Furthermore, the other proton of H₂-9 (δ_{H} 2.01, m) showed a NOE interaction with H-1, suggesting that H₃-14, H₃-13, and H-6 should be positioned on the same face and arbitrarily assigned as β -protons, and H-1 and H-4 were assigned as α -protons. To confirm the structure of **1** and establish its absolute configuration, a single-crystal X-ray crystallographic analysis was undertaken.⁹ The crystal structure (ORTEP diagram)

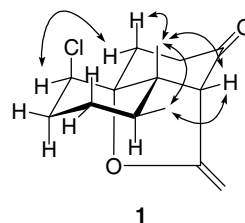


Figure 3. Key NOESY correlations of **1**.

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