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Two New Constituents from the Soft Coral *Nephthea hainansis*

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Abstract: Two new compounds, namely 7α, 10α-dimethyl-3β-isopropene-1, 2-ene-octahydronaphthalene (**1**) and ethyl 5*Z*,8*Z*,11*Z*,14*Z*-nonadecatetraenoate (**2**) were isolated from the soft coral *Nephthea hainansis*. Compound **1** was a pseutosesquiterpene and **2** was a polyunsaturated fatty acid ethylate. Their structures were established on the basis of spectroscopic methods.

Keywords: Soft coral, *Nephthea hainansis*, sesquiterpene, polyunsaturated fatty acid ethylate.

Soft corals are a group of marine organisms deriving the metabolites of terpenoids with rich structural diversity, and some of the terpenoids possess interesting biological activities[1]. Previous investigations revealed that the metabolites of *Nephthea* genus mainly contained sesquiterpenes[2], diterpenes[3] and steroids[4]. However, a new species of the soft coral, *Nephthea hainansis*, distributed in South China Sea, has not been investigated chemically. This report intended to describe the structural elucidation of two new compounds from soft coral *N. hainansis*, collected off the inner coral reef near the Sanya, Hainan Province.

The MeOH extract (8.7 g) was subjected to repeated silica gel column chromatography eluting with the gradient of petroleum ether-acetone to obtain compounds **1** and **2**.

Compound **1**, $[\alpha]_D^{25}$ + 9.71 (*c* 0.27, $CHCl_3$), was obtained as colorless oil, and its molecular formula, $C_{15}H_{24}$, was established on the basis of HREIMS (*m/z* 204.1871 $[M]^+$, calcd. 204.1878). A weak IR absorption at 1670 cm^{-1} suggested the presence of vinyl group. The ^1H NMR spectrum of **1** exhibited three methyls at δ_H 0.86 (*d*, 3H, *J* = 6.6 Hz, H-14), 1.02 (*d*, 3H, *J* = 7.0 Hz, H-15), and 1.73 (*s*, 3H, H-13), an olefinic methylene at δ_H 4.78 (*s*, 1H, 12-Ha), 4.77 (*s*, 1H, 12-Hb), and an vinyl proton at δ_H 5.40 (*d*, 1H, *J* = 6.0 Hz). The ^{13}C NMR and DEPT spectra exhibited the carbons involving three methyls [δ_C 15.9 (C-14), 20.6 (C-15), and 21.7 (C-13)], five methylenes [δ_C 26.1 (C-4), 30.3 (C-5), 34.1 (C-8), 33.6 (C-9), and 110.9 (C-12)], five methines [δ_C 47.8 (C-3), 46.1 (C-6), 34.2 (C-7), 41.4 (C-10), and 122.6 (C-2)], and two quaternary carbons [δ_C 152.0 (C-1), 148.0 (C-11)]. Four unsaturations degrees of **1** indicated that the structure

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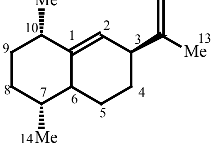
possessed two double bands and a bicyclic nucleus. The HMBC correlations traced from the methyl protons H-14 to C-6, C-7, C-8, methyl protons H-15 to C-1, C-10, and C-9, and from olefinic proton H-2 to C-10, C-6, C-3, and C-4, in association with COSY correlations, enabled to establish an 1,2-ene-octahydronaphthalene skeleton with two methyls attached at C-7 and C-10, respectively. Moreover, the HMBC correlations of olefinic methylene H_3-12 (δ4.78, 4.77) to C-13 (δ21.7, q) and C-3, and in turn, the third methyl protons H_3-13 correlated to C-11, C-12 and C-3, indicating an isopropene group located at C-3. The stereochemistry of **1** could be determined on the basis of NOESY spectrum. The NOE correlations observed between H-15 and H-2, between H-6 and H-12, H-10, as well as between H-3 and H-2 implied β-configurations for H-6 and H-10 and α-configuration for H-3. Moreover, The NOE correlation between H-6 and H-7 supposed a β-configurations for H-7. Accordingly, the structure of **1** was determined as 7α, 10α-dimethyl-3β-isopropene-1,2-ene-octahydronaphthalene.

Compound **2** was obtained as colorless oil. Its molecular formula, $C_{21}H_{34}O_2$, was proposed on the basis of EIMS (*m/z* 318 $[M]^+$) and in association with ^{1}H, ^{13}C NMR and DEPT spectra. The IR absorption suggested the presence of carbonyl group (1740 cm^{-1}). The ^{1}H NMR spectrum exhibited the resonances for olefinic protons at δ_H 5.40-5.42(8H, m), methylenes at δ_H 2.87 (m, 6H), 2.34 (*t*, 2H, *J* = 7.5 Hz), 2.14 (*m*, 2H), 2.09 (*dt*, 2H, *J* = 7.4, 7.4 Hz,), 1.72 (*m*, 2H), 1.61 (*m*, 2H), 1.27 (*m*, 4H), 1.61 (*m*, 2H) and methyls at δ_H 0.88 (*t*, 3H, *J* = 7.1 Hz), characteristic of a tetraene alkyl moiety. The additional protons at δ_H 1.27 (*t*, 3H, *J* = 7.1 Hz) and 4.15 (*q*, 2H, *J* = 7.1 Hz) were attributed to an ethoxy group. The HMQC spectrum assigned all protons and their associated carbons. The COSY correlations between the olefinic protons at δ_H 5.41 (m) and methylene protons at δ_H 2.87 (m), methylene protons at δ_H 2.14 (m), and 2.09 (m), suggested the presence of a trideca-tetraene moiety. The COSY cross peaks between δ_H 2.34 (*t*, 2H, *J* = 7.5 Hz) /1.72 (m, 2H,) and δ_H 1.73 (m, 2H,)/ 2.14 (m, 2H,), as well as the HMBC correlations between δ_H 2.34 and δ_C 174.0 (s, C-1), 25.2 (t, C-3), and 27.6 (t, C-4), and between δ_H 1.72 (m, 2H, H-3) and C-1, C-2 (δ34.1, t), C-4 (δ27.6, t), and C-5 (δ 128.0, d) led to the position of the first double bond at C-5/C-6, and in turn, the remaining three double bands should be located at C-8, C-11, and C-14. The remaining partial structure was consistent with a *n*-butanyl group, which was considered to link at C-15. The further HMBC correlation between methylene signals at δ_H 4.15(*q*, 2H, *J*=7.1Hz) and carbonyl carbon indicated that **2** was an ethylate. The geometries of double bonds were assigned as *Z* forms due to the coupling constant between olefinic protons less than 14 Hz. Accordingly, the structure of **2** was determined as ethyl 5*Z*, 8*Z*, 11*Z*, 14*Z*-nonadecatetraenoate.



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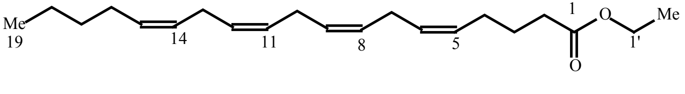

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Table 1 ^{1}H and ^{13}C NMR data of compound **1** (500 MHz, in $CDCl_3$, δ ppm, J_{HZ})

position	δ_H (*J*)	δ_C	HMBC(H→C)
1		152.0, s	
2	5.40, d (6.0)	122.6, d	C-3,C-6,C-10,C-11
3	2.84, m	47.8, d	C-1,C-2,C-4,C-11,C-12,C-13
4	1.78,m; 1.70,m	26.1 t	C-2, C-3, C-5, C-11
5	1.78, m; 1.60, m	30.3, t	
6	2.92, m	46.1, d	C-1,C-2,C-5,C-7,C-14
7	1.93, m	34.2, d	C-6,C-8,C-14
8	1.74, m; 1.25, m	34.1, t	C-6, C-8, C-14
9	1.88, m; 1.41, m	33.6, t	
10	2.52, m	41.4, d	C-1,C-6, C-9, C-15
11		148.0, s	
12	4.77, br; 4.78, br	110.9, t	C-3,C-13
13	1.73, s	21.7, q	C-3,C-11,C-12
14	0.86, d (6.6)	15.9, q	C-6,C-7,C-8
15	1.02, d (7.0)	20.6, q	C-1,C-9,C-10

Table 2 ^{1}H and ^{13}C NMR data of compound **2** (500 MHz, in $CDCl_3$, δ ppm, J_{HZ})

position	δ_H (*J*)	δ_C	HMBC(H→C)
1		174.0, s	
2	2.34, t (7.5)	34.1, t	C-1,C-3,C-4
3	1.72, t (7.4)	25.2, t	C-1,C-2,C-4,C-5
4	2.09, dt (7.4, 7.4)	27.6, t	C-2,C-3,C-6
5,6,8,9,11,12,14,15	5.40-5.42, m	130.9-128.0, d	C-7,C-10,C-13,C-4,C-16
7,10,13	2.87, m	26.0-25.0, t	
16	2.14, m	27.5, t	C-14,C-15,C-17
17	1.27, m	30.4, t	
18	1.61,m	25.1, t	
19	0.88, t (7.1)	14.6, q	C-17,C-18
1’	4.15, q (7.1)	60.6, t	C-1,C-2’
2’	1.27, t (7.1)	14.6, q	C-1’

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