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ARTICLE *in* JOURNAL OF NATURAL PRODUCTS · JANUARY 2005

Impact Factor: 3.8 · DOI: 10.1021/np0401314 · Source: PubMed

Novel Meroditerpenoid-Related Metabolites from the Formosan Soft Coral *Nephthea chabrolii*

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Received June 9, 2004

Nine new metabolites, including one novel naphthoquinone derivative, chabrolonaphthoquinone A (**1**), four tetraprenyltoluquinol-related metabolites, chabrolohydroxybenzoquinones A−D (**2**−**5**), and four tetraprenyltoluquinone-related compounds, chabrolobenzoquinones A−D (**6**−**9**), were isolated from the organic extract of a Taiwanese soft coral, *Nephthea chabrolii*. The structures of **1**−**9** were elucidated on the basis of spectral data.

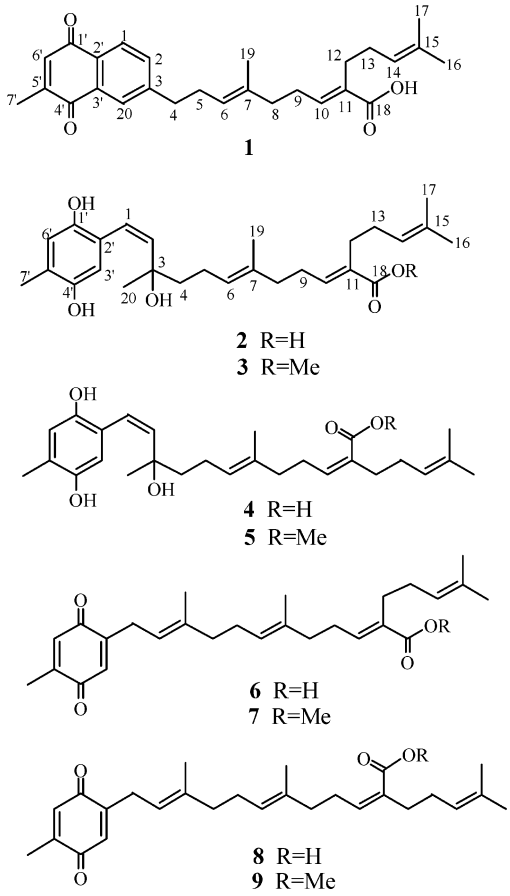
In previous studies a series of novel secondary metabolites, including cembranes and norditerpenes,[1] polyhydroxysteroids,[2] and sesquiterpenes,[3−5] have been isolated from the soft coral *Nephthea chabrolii* (Audouin). During the course of our investigation on new natural substances from Taiwanese marine invertebrates, we initiated a study on the chemical constituents of *N. chabrolii*, which has afforded nine meroditerpene-derived metabolites. These include one novel naphthoquinone derivative, chabrolonaphthoquinone A (**1**), four tetraprenyltoluquinol-related metabolites, chabrolohydroxybenzoquinones A−D (**2**−**5**), and four tetraprenyltoluquinones, chabrolobenzoquinones A−D (**6**−**9**). The structures of metabolites **1**−**9** were characterized by spectral analysis.

Results and Discussion

A collection of *N. chabrolii* was homogenized with EtOH, filtered, and further extracted with EtOH. The combined extracts were concentrated and subsequently subjected to further purification to yield the new compounds, **1**−**9** (see Experimental Section).

Chabrolonaphthoquinone A (**1**) was obtained as an optically inactive yellow oil. The HREIMS of **1** established the molecular formula $C_{27}H_{32}O_4$, implying 12 degrees of unsaturation. The EIMS showed peaks at *m/z* 420 $(M)^+$ and 374 $(M - HCOOH)^+$, suggesting the presence of a carboxyl group. The UV spectrum showed absorptions at 343, 266, and 257 nm, indicative of a 1,4-naphthoquinone moiety.[6] From the ^1H and ^{13}C NMR spectral data (Table 1), together with the HMQC data, 27 signals were assigned to four methyl, six sp^3 methylene, seven sp^2 methine, and seven sp^2 quaternary olefinic carbons, two carbonyls, and a carboxyl group. The ^1H NMR spectrum of **1** also showed signals of seven olefinic protons (δ 7.96, d, J = 8.0 Hz; 7.91, d, J = 1.5 Hz; 7.53, dd, J = 8.0, 1.5 Hz; 6.84, t, J = 7.5 Hz; 6.81, d, J = 1.5 Hz; 5.18, t, J = 7.0 Hz; 5.12, t, J = 7.5 Hz) and four methyls (δ 2.19, 3H, d, J = 1.5 Hz; 1.68, 3H, s; 1.59, 3H, s; 1.56, 3H, s).

The planar structure and all of the ^1H and ^{13}C chemical shifts of **1** were elucidated by 2D NMR experiments, especially the $^1H-^1H$ COSY and HMBC experiments (Figure 1). The proton sequence from H-1 to H-2 and the HMBC correlations from H-7′ to C-4′, C-5′, C-6′; H-1 to C-1′, C-3′, C-3; H-2 to C-2′; H-20 to C-2′, C-4′, C-2; and H_2-4 to C-2, C-3, C-20 suggested a naphthoquinone moiety in **1**. This together with an EIMS peak at *m/z* 185 $(C_{12}H_9O_2)^+$ further revealed this moiety (**10**) to be an important structural unit of **1** (Scheme 1). The structure of the side chain was elucidated by the $^1H-^1H$ COSY correlations from H_2-4 to H-6; H_2-8 to H-10; and H_2-12 to H-14 and the HMBC correlations from H_2-5 to C-3, C-7; H_2-8 to C-7; H_2-9 to C-7, C-11; H-10 to C-8, C-11; H_2-12 to C-10, C-11, C-14; H_3-16 to C-14, C-15; and H_3-17 to C-14, C-15, and thus the



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10.1021/np0401314 CCC: $27.50
Published on Web 12/03/2004

Table 1. ^{1}H and ^{13}C NMR Data for Compound **1**

C/H	δ_H[a]	δ_C[b]	
1′		185.0	(C)[d]
2′		130.3	(C)
3′		132.1	(C)
4′		185.9	(C)
5′		148.0	(C)
6′	6.81 d (1.5)[c]	135.7	(CH)
7′	2.19 d (1.5)	16.5	(CH_3)
1	7.96 d (8.0)	126.3	(CH)
2	7.53 dd (8.0, 1.5)	133.9	(CH)
3		148.8	(C)
4	2.78 t (7.5)	36.1	(CH_2)
5	2.38 m	29.2	(CH_2)
6	5.18 t (7.0)	123.6	(CH)
7		135.5	(C)
8	2.10 m	38.4	(CH_2)
9	2.28 m	27.3	(CH_2)
10	6.84 t (7.5)	144.9	(CH)
11		131.2	(C)
12	2.31 m	26.8	(CH_2)
13	2.10 m	27.6	(CH_2)
14	5.12 t (7.5)	123.6	(CH)
15		132.4	(C)
16	1.68 s	25.7	(CH_3)
17	1.59 s	17.6	(CH_3)
18		171.8	(C)
19	1.56 s	16.0	(CH_3)
20	7.91 d (1.5)	126.4	(CH)

[a] Spectra recorded at 500 MHz in $CDCl_3$. [b] 125 MHz in $CDCl_3$. [c] J values (in Hz) parentheses. [d] Deduced from DEPT.

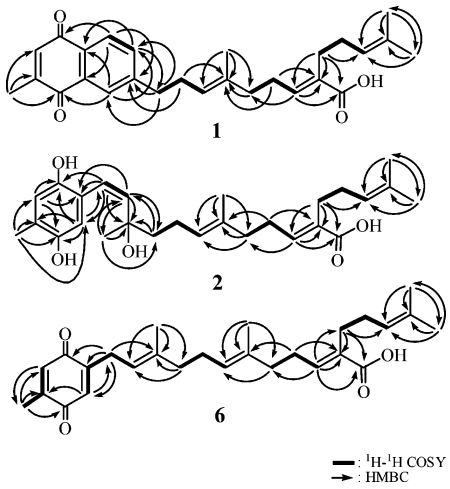
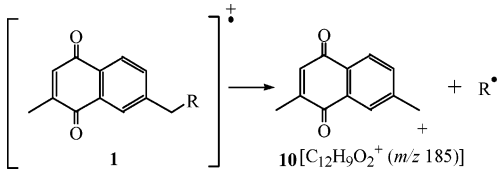


Figure 1. Key ^{1}H−^{1}H COSY and HMBC correlations for **1**, **2**, and **6**.

Scheme 1. Mode of Fragmentation of **1** in the EMS



connectivity from C-4 to C-17 was fully established. The methyl group attached at C-7 was confirmed by HMBC correlations between H_3-19/C-6, C-7, and C-8. The HMBC correlations between H-10/C-18 and H_2-12/C-18 revealed the attachment of a carboxyl group at C-11. On the basis of these findings, the skeleton of **1** was unambiguously established. The geometries of the double bonds between C-6/C-7 and C-10/C-11 were shown to be *E* and *Z*, respectively, by comparison with data for related compounds.[7,8] The abnormal downfield shift of H-10 (δ 6.84) probably arises from the strong anisotropic effect of the neighboring carboxyl group.

Chabrolohydroxybenzoquinone A (**2**) was obtained as a pale oil. The molecular formula $C_{27}H_{38}O_5$ for **2** was suggested by HREIMS data, which exhibited a peak at *m/z* 424.2614 [$C_{27}H_{36}O_4$, M − H_2O]$^+$, and^{13}C and ^{1}H NMR spectral data (Tables 2 and 3). The structure elucidation and full assignment of ^{1}H and ^{13}C NMR data of **2** were achieved by 2D NMR, including ^{1}H−^{1}H COSY, HMQC, and HMBC experiments. The HMBC of **2** (Figure 1) possessed correlations between H-3′ and C-1′, C-4′, C-5′; H-6′ and C-1′, C-2′, C-4′; and H-7′ and C-3′, C-4′, C-5′, C-6′, thus characterizing the 1,4-dihydroxy-5-methylbenzene subunit of **2**. In addition, a ^{1}H−^{1}H COSY correlation between H-1 and H-2 and the HMBC correlations from H-1 to C-1′, C-2′, C-3′, C-3; H-2 to C-2′, C-3, C-4, C-20; and H_3-20 to C-2, C-3, C-4 were consistent with an isoprene unit attached to the aromatic moiety. The configuration of the double bonds in **2** was assigned according to the ^{1}H NMR data. The *Z* geometry of the C-1/C-2 double bond was indicated by a 10.0 Hz coupling constant between H-1 and H-2. Comparison of 1D and 2D NMR data, particularly the ^{1}H−^{1}H COSY and HMBC correlations (Figure 1), showed that the partial structure of the side chain from C-5 to C-19 in **2** is very close to that of **1**. The structure of compound **2** could be then further established.

Chabrolohydroxybenzoquinone B (**3**) was isolated as a pale oil with the molecular formula $C_{28}H_{40}O_6$, which possesses nine units of unsaturation, as indicated by HREIMS (438.2768 *m/z*, [M − H_2O]$^+$) and NMR spectral data (Tables 2 and 3). The ^{1}H and ^{13}C NMR spectral data of **3** revealed that the structure of metabolite **3** should be very similar to that of **2**. Also, comparison of the spectral data of both compounds showed that the carboxylic acid attached at the C-11 position of compound **2** was replaced by a carbomethoxyl group in **3**.

HREIMS and NMR spectral data indicated that chabrolohydroxybenzoquinone C (**4**) has the same molecular formula, $C_{27}H_{38}O_5$, as that of **2** (Tables 2 and 3). The ^{1}H NMR spectral data of **4** were found to be similar to those of **2**, except that the signal of H-10 of **4** (δ 5.99) was shifted significantly to upper field in comparison with that of **2** (δ 6.87), and the methylene protons H_2-9 (δ 2.59) were found to show downfield shifted resonance in comparison with that of **2** (δ 2.28). Thus, **4** was found to be the 10*Z* isomer of **2**. Also, we isolated a metabolite, chabrolohydroxybenzoquinone D (**5**), possessing structure similar to that of **4**. The NMR spectral data of **5** (Tables 2 and 3) are almost identical with those of **4** except for the presence of an additional oxymethyl group (δ_H 3.73, 3H, s) in **5**. Also, the ^{13}C NMR spectrum of **5** showed the same number of methylene, methine, and quaternary carbons as that of **4**, except for the presence of one more oxymethyl carbon, which showed a signal at δ_C 51.1 (q). Furthermore, the oxymethyl protons gave an HMBC cross-peak with a carbonyl carbon (δ 168.5, s), indicating the presence of the carbomethoxyl group in **5**. All of the data indicated that **5** is the methyl ester of **4**.

The new metabolite chabrolobenzoquinone A (**6**) was obtained as a pale oil. Its molecular formula, $C_{27}H_{36}O_4$, was established by HREIMS (*m/z* 424.2607, [M]$^+$). Thus, 10 degrees of unsaturation were determined for **6**. It displayed UV (λ_{max} 251 nm) and IR (ν_{max} 1657 and 1614 cm^{-1}) absorptions characteristic of benzoquinones.[7,9] The ^{1}H NMR spectrum of **6** (Table 4) showed signals for two quinone protons (δ 6.59, d, J = 1.5 Hz; 6.49, s) and four olefinic protons (δ 6.87, t, J = 7.5 Hz; 5.16, t, J = 7.0 Hz; 5.14, m; 5.13, m). The ^{13}C NMR spectra (Table 5) of **6** contained a total of 27 resonances for five methyl, seven methylene,

Table 2. ^{1}H NMR Chemical Shifts for Compounds **2**−**5**[a]

	2	**3**	**4**	**5**
3′	6.42 s	6.43 s	6.42 s	6.42 s
6′	6.56 s	6.56 s	6.56 s	6.56 s
7′	2.18 s	2.18 s	2.18 s	2.18 s
1	6.25 d (10.0)[b]	6.26 d (10.0)	6.25 d (9.5)	6.25 d (9.5)
2	5.53 d (10.0)	5.53 d (10.0)	5.53 d (9.5)	5.53 d (9.5)
4	1.64 m; 1.71 m	1.64 m; 1.71 m	1.64 m; 1.71 m	1.64 m; 1.71 m
5	2.12 m	2.12 m	2.13 m	2.12 m
6	5.15 t (7.5)	5.14 t (7.0)	5.14 t (7.0)	5.13 t (7.2)
8	2.08 m	2.06 m	2.06 m	2.04 m
9	2.28 m	2.25 q (7.5)	2.59 q (7.5)	2.50 q (7.5)
10	6.87 t (7.5)	6.72 t (7.5)	5.99 t (7.5)	5.84 t (7.5)
12	2.31 m	2.30 m	2.26 m	2.24 m
13	2.11 m	2.08 m	2.12 m	2.08 m
14	5.14 t (7.5)	5.13 t (7.0)	5.09 t (7.0)	5.08 t (7.2)
16	1.68 s	1.68 s	1.68 s	1.68 s
17	1.59 s	1.59 s	1.58 s	1.57 s
19	1.59 s	1.59 s	1.59 s	1.57 s
20	1.36 s	1.36 s	1.36 s	1.36 s
COO*Me*		3.73 s		3.73 s

[a] Spectra recorded at 500 MHz in $CDCl_3$. [b] *J* values (in Hz) in parentheses.

Table 3. ^{13}C NMR Chemical Shifts for Compounds **2**−**5**[a]

	2	**3**	**4**	**5**
1′	146.6 (C)[b]	146.7 (C)	146.7 (C)	146.7 (C)
2′	119.5 (C)	119.6 (C)	119.6 (C)	119.6 (C)
3′	112.5 (CH)	112.4 (CH)	112.5 (CH)	112.4 (CH)
4′	147.4 (C)	147.4 (C)	147.4 (C)	147.4 (C)
5′	124.6 (C)	124.5 (C)	124.5 (C)	124.4 (C)
6′	118.1 (CH)	118.1 (CH)	118.1 (CH)	118.1 (CH)
7′	15.9 (CH_3)	15.9 (CH_3)	15.9 (CH_3)	15.9 ((CH_3)
1	122.5 (CH)	122.5 (CH)	122.4 (CH)	122.4 (CH)
2	129.7 (CH)	129.7 (CH)	129.7 (CH)	129.8 (CH)
3	77.9 (C)	77.9 (C)	77.9 (C)	77.9 (C)
4	40.8 (CH_2)	40.8 (CH_2)	40.9 (CH_2)	40.9 (CH_2)
5	22.6 (CH_2)	22.7 (CH_2)	22.6 (CH_2)	22.6 (CH_2)
6	125.1 (CH)	125.0 (CH)	124.9 (CH)	124.7 (CH)
7	133.9 (C)	134.1 (C)	134.3 (C)	134.5 (C)
8	38.3 (CH_2)	38.5 (CH_2)	39.0 (CH_2)	39.1 (CH_2)
9	27.4 (CH_2)	27.2 (CH_2)	28.1 (CH_2)	28.0 (CH_2)
10	145.3 (CH)	142.7 (CH)	145.7 (CH)	142.1 (CH)
11	131.2 (C)	131.8 (C)	130.4 (C)	131.4 (C)
12	26.7 (CH_2)	27.0 (CH_2)	34.5 (CH_2)	34.7 (CH_2)
13	27.6 (CH_2)	27.7 (CH_2)	27.9 (CH_2)	27.8 (CH_2)
14	123.6 (CH)	123.7 (CH)	123.4 (CH)	123.5 (CH)
15	132.3 (C)	132.2 (C)	132.3 (C)	132.1 (C)
16	25.7 (CH_3)	25.7 (CH_3)	25.7 (CH_3)	25.7 (CH_3)
17	17.6 (CH_3)	17.6 (CH_3)	17.7 (CH_3)	17.7 (CH_3)
18	173.2 (C)	168.4 (C)	172.8 (C)	168.5 (C)
19	15.9 (CH_3)	15.9 (CH_3)	15.8 (CH_3)	15.8 (CH_3)
20	26.0 (CH_3)	26.1 (CH_3)	26.1 (CH_3)	26.1 (CH_3)
COO*Me*		51.6 (CH_3)		51.1 (CH_3)

[a] Spectra recorded at 125 MHz in $CDCl_3$. [b] Deduced by DEPT.

Table 4. ^{1}H NMR Chemical Shifts for Compounds **6**−**9**

	6[a]	**7**[a]	**8**[b]	**9**[a]
3′	6.49 s	6.49 s	6.50 s	6.50 s
6′	6.59 d (1.5)[c]	6.59 d (1.5)	6.59 d (1.5)	6.59 s
7′	2.03 d (1.5)	2.03 d (1.5)	2.04 d (1.5)	2.04 s
1	3.11 d (7.0)	3.11 d (7.5)	3.11 d (7.2)	3.11 d (7.0)
2	5.16 t (7.0)	5.15 m[d]	5.15 t (7.2)	5.15 t (7.0)
4	2.08 m	2.07 m	2.08 m	2.08 m
5	2.13 m	2.12 m	2.12 m	2.13 m
6	5.14 m[d]	5.14 m[d]	5.13 t (7.2)	5.12 t (7.0)
8	2.12 m	2.11 m	2.13 m	2.10 m
9	2.30 m	2.28 m	2.60 m	2.52 m
10	6.87 t (7.5)	6.73 t (7.5)	6.00 t (7.5)	5.86 t (7.5)
12	2.31 m	2.32 m	2.26 m	2.25 m
13	2.10 m	2.08 m	2.10 m	2.08 m
14	5.13 m[d]	5.13 m[d]	5.10 t (7.2)	5.09 t (7.5)
16	1.67 s	1.67 s	1.67 s	1.68 s
17	1.59 s	1.59 s	1.59 s	1.58 s
19	1.62 s	1.62 s	1.60 s	1.60 s
20	1.62 s	1.62 s	1.62 s	1.62 s
COO*Me*		3.72 s		3.74 s

[a] Spectra recorded at 500 MHz in $CDCl_3$. [b] Spectra recorded at 300 MHz in $CDCl_3$. [c] *J* values (in Hz) in parentheses. [d] Overlapping of signals was observed.

and six methine groups and nine quaternary carbons, including a carbonyl group (δ 173.1, s) and two quinone carbonyls (δ 187.9, s; 188.3, s). The ^{1}H−^{1}H COSY (Figure 1) showed correlations of H_3-7′/H-6′ and H-3′/H_2-1, and the HMBC spectrum (Figure 1) showed long-range correlations from H_2-1 to C-1′, C-2′, C-3′; H-3′ to C-5′; H-6′ to C-7′; and H_3-7′ to C-4′, C-5′, C-6′ and established the 5′-methylquinone structural unit of **6** and an isoprene unit attached to the quinone moiety. The ^{13}C NMR chemical shift of the allylic methyl H_3-20 (δ 16.0) established the *E* configuration of the C-2/C-3 double bond. Careful analyses of the NMR data (^{1}H and ^{13}C) showed that the partial structure of the side chain from C-5 to C-19 in **6** should be very similar to that of **2**, and the structure of compound **6** was further established. Furthermore, a metabolite **7** (optically inactive pale oil) with a structure closely related to **6** was found. The molecular formula of chabrolobenzoquinone B (**7**) was assigned as $C_{28}H_{38}O_4$ from the HREIMS. The NMR data (Tables 4 and 5) of **7** were similar to those of **6**. However, an additional methoxyl group (δ_H 3.72, 3H, s; δ_C 51.5, q) was observed in **7**. In addition, the methoxyl group positioned at C-18 was confirmed by the connectivity between the oxymethyl (δ_H 3.72) and the carbonyl carbon (δ_C 168.4, s, C-18). All of the above information suggested that chabrolobenzoquinone B (**7**) is the methyl ester of **6**.

Compound **8** (chabrolobenzoquinone C), with a molecular formula of $C_{27}H_{36}O_4$ (HREIMS), was obtained as an optically inactive oil. Careful comparison of its ^{1}H and ^{13}C NMR data (Tables 4 and 5) with those of **6** suggested that metabolite **8** is the 10*Z* isomer of **6**. Similarly, HREIMS and ^{1}H and ^{13}C NMR data of compound **9**, an optically inactive pale oil, revealed that this metabolite has the molecular formula $C_{28}H_{38}O_4$. Comparison of its ^{1}H and ^{13}C NMR (Tables 4 and 5) with those of **7** also clearly indicated that **9** is the 10*Z* isomer of **7**.

The biosynthetic pathways of the concerned meroditerpenoidal carboxylic acids were proposed as shown in Scheme 2. The oxidation of the 1,4-dihydroxybenzene unit of a proposed intermediate **11** would lead to the formation of 1,4-benzoquinone **6** and the following isomer **8** (pathway a). Isomerization of the 2,3-double bond of **11** to the 1,2-double bond and the subsequent hydroxylation at C-3

Scheme 2. Proposed Biosynthetic Pathways of the Related Meroditerpenoids

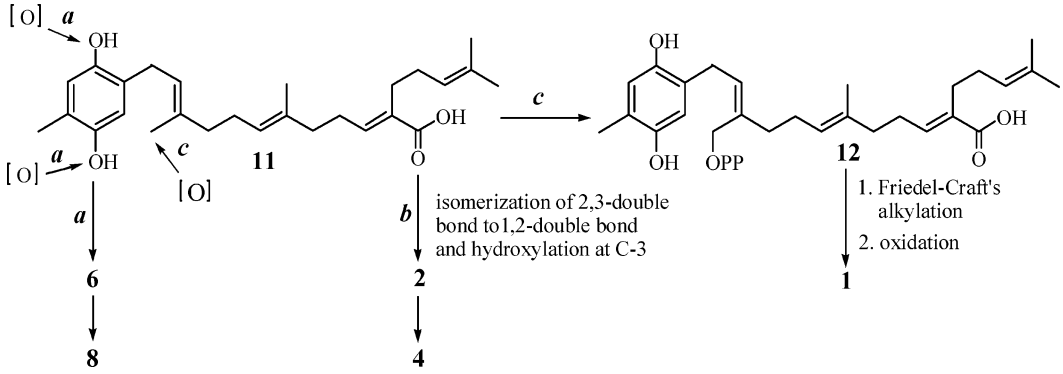


Table 5. ^{13}C NMR Chemical Shifts for Compounds **6**–**9**

	6[a]	**7**[a]	**8**[b]	**9**[a]
1′	187.9 (C)[c]	187.9 (C)	187.9 (C)	187.9 (C)
2′	148.4 (C)	148.4 (C)	148.6 (C)	148.4 (C)
3′	132.3 (CH)	132.3 (CH)	132.4 (CH)	132.3 (CH)
4′	188.3 (C)	188.3 (C)	188.5 (C)	188.4 (C)
5′	145.6 (C)	145.6 (C)	145.7 (C)	145.6 (C)
6′	133.5 (CH)	133.5 (CH)	133.6 (CH)	133.5 (CH)
7′	15.4 (CH_3)	15.5 (CH_3)	15.5 (CH_3)	15.5 ((CH_3)
1	27.4 (CH_2)	27.2 (CH_2)	27.2 (CH_2)	27.1 (CH_2)
2	118.0 (CH)	118.0 (CH)	118.0 (CH)	117.9 (CH)
3	139.7 (C)	139.8 (C)	139.9 (C)	139.9 (C)
4	39.5 (CH_2)	39.5 (CH_2)	39.6 (CH_2)	39.6 (CH_2)
5	26.3 (CH_2)	26.4 (CH_2)	26.4 (CH_2)	26.4 (CH_2)
6	124.8 (CH)	124.7 (CH)	124.4 (CH)	124.4 (CH)
7	134.2 (C)	134.3 (C)	134.7 (C)	134.7 (C)
8	38.3 (CH_2)	38.5 (CH_2)	39.1 (CH_2)	39.1 (CH_2)
9	27.1 (CH_2)	27.1 (CH_2)	28.3 (CH_2)	27.9 (CH_2)
10	145.3 (CH)	142.6 (CH)	145.4 (CH)	142.2 (CH)
11	131.2 (C)	131.8 (C)	130.6 (C)	131.4 (C)
12	26.7 (CH_2)	27.1 (CH_2)	34.6 (CH_2)	34.7 (CH_2)
13	27.6 (CH_2)	27.7 (CH_2)	27.9 (CH_2)	28.0 (CH_2)
14	123.6 (CH)	123.7 (CH)	123.5 (CH)	123.5 (CH)
15	132.3 (C)	132.2 (C)	132.3 (C)	132.1 (C)
16	25.7 (CH_3)	25.7 (CH_3)	25.7 (CH_3)	25.7 (CH_3)
17	17.6 (CH_3)	17.6 (CH_3)	17.8 (CH_3)	17.7 (CH_3)
18	173.1 (C)	168.4 (C)	172.6 (C)	168.5 (C)
19	16.1 (CH_3)	16.1 (CH_3)	16.2 (CH_3)	16.1 (CH_3)
20	16.0 (CH_3)	16.0 (CH_3)	16.0 (CH_3)	15.9 (CH_3)
COO*Me*		51.5 (CH_3)		51.1 (CH_3)

[a] Spectra recorded at 125 MHz in $CDCl_3$. [b] Spectra recorded at 75 MHz in $CDCl_3$. [c] Deduced by DEPT.

would afford **2** and the following isomer **4** (pathway b). Furthermore, oxidation at C-20 of **11** formed intermediate **12**, which could be ring-closed and subsequently oxidized to afford a naphthoquinone **1** (pathway c). To the best of our knowledge, the incorporation of a methyl group of the related meroditerpene to form a naphthoquinone was here found for the first time.

Experimental Section

General Experimental Procedures. IR spectra were recorded on a Jasco FT-5300 infrared spectrophotometer. Ultraviolet spectra were recorded on a Hitachi U-3210 UV spectrophotometer. NMR spectra were recorded on a Bruker AVANCE DPX300 FT-NMR at 300 MHz for ^{1}H and 75 MHz for ^{13}C or on a Varian Unity INOVA 500 FT-NMR at 500 MHz for ^{1}H and 125 MHz for ^{13}C, respectively, in $CDCl_3$. EIMS was obtained with a VG Quattro GC/MS spectrometer. HREIMS spectra were recorded on a Finnigan MAT-95XL mass spectrometer. Silica gel (Merck, 230–400 mesh) was used for column chromatography. Precoated silica gel plates (Merck, Kieselgel 60 F-254, 0.2 mm) were used for analytical TLC.

Animal Material. The soft coral *N. chabrolii* was collected by hand using scuba off the coast of Pingtung County, southern Taiwan, in July 2001, at depths of 15–20 m, and stored in a freezer until extraction. A voucher sample was deposited at the Department of Marine Resources, Sun Yat-Sen University.

Extraction and Separation. The sliced bodies of *N. chabrolii* (1.8 kg, wet wt) were homogenized with EtOH and filtered. The ground organism was repeatedly extracted with EtOH. The combined extract was concentrated under vacuum to afford a dark brown viscous residue (20.8 g). The residue was triturated with *n*-hexane first to afford an *n*-hexane-soluble layer and then with EtOAc. The combined EtOAc extract was evaporated under vacuum to yield an oily residue (15.8 g), which was subjected to column chromatography on silica gel, using *n*-hexane, *n*-hexane, and EtOAc mixtures of increasing polarity, and finally pure EtOAc, to yield 28 fractions. Fractions 7 and 9 eluted with *n*-hexane–EtOAc (15:1) and were further purified on silica gel using *n*-hexane–acetone (gradient, 30:1 to 20:1) to yield **7** (8.9 mg) and **9** (3.1 mg) from fraction 7 and **3** (2.5 mg) and **5** (3.7 mg) from fraction 9. Fraction 12 eluted with *n*-hexane–EtOAc (8:1) and was purified by normal-phase HPLC using *n*-hexane–acetone (12:1) to afford **6** (50.2 mg), **8** (8.2 mg), and **1** (8.0 mg). Fraction 15 eluted with *n*-hexane–EtOAc (4:1) and was purified by normal-phase HPLC using *n*-hexane–acetone (1:8) to afford **2** (150.2 mg) and **4** (15.2 mg).

Chabrolonaphthoquinone A (1): yellow oil; UV (MeOH) λ_{max} (log ϵ) 343 (2.79), 266 (3.63), 257 (3.69) nm; IR (neat) ν_{max} 3292, 2922, 1680, 1662, 1631, 1601 cm^{-1}; ^{1}H ($CDCl_3$, 500 MHz) and ^{13}C ($CDCl_3$, 125 MHz) NMR, see Table 1; EIMS (30 eV) *m/z* 420 (4, [M]$^+$), 402 (3), 374 (0.5), 185 (11); HREIMS *m/z* 420.2288 (calcd for $C_{27}H_{32}O_4$, 420.2302).

Chabrolohydroxybenzoquinone A (2): pale oil; UV (MeOH) λ_{max} (log ϵ) 332 (3.69), 266 (3.65) nm; IR (neat) ν_{max} 3398, 2926, 1684, 1637 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz), see Tables 2 and 3; EIMS (30 eV) *m/z* 424 (0.9, [M − H_2O]$^+$), 409 (0.5), 378 (0.2), 175 (100), 137 (4), 69 (14); HREIMS *m/z* 424.2614 (calcd for $C_{27}H_{36}O_4$, M$^+$ − H_2O, 424.2615).

Chabrolohydroxybenzoquinone B (3): pale oil; UV (MeOH) λ_{max} (log ϵ) 331 (3.72), 266 (3.70) nm; IR (neat) ν_{max} 3433, 2924, 1712, 1680, 1641 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz), see Tables 2 and 3; EIMS (30 eV) *m/z* 438 (0.4, [M − H_2O]$^+$), 423 (0.2), 392 (0.5), 175 (100), 137 (4), 69 (13); HREIMS *m/z* 438.2768 (calcd for $C_{28}H_{38}O_4$, M$^+$ − H_2O, 438.2771).

Chabrolohydroxybenzoquinone C (4): pale oil; UV (MeOH) λ_{max} (log ϵ) 330 (3.77), 267 (3.80) nm; IR (neat) ν_{max} 3396, 2926, 1684, 1637 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz), see Tables 2 and 3; EIMS (30 eV) *m/z* 424 (0.9, [M − H_2O]$^+$), 409 (0.4), 378 (0.3), 175 (100), 137 (8), 69 (13); HREIMS *m/z* 424.2611 (calcd for $C_{27}H_{36}O_4$, M$^+$ − H_2O, 424.2615).

Chabrolohydroxybenzoquinone D (5): pale oil; UV (MeOH) λ_{max} (log ϵ) 331 (3.67), 267 (3.70) nm; IR (neat) ν_{max} 3422, 2924, 1714, 1684, 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz), see Tables 2 and 3; EIMS (70 eV) *m/z* 438 (1, [M − H_2O]$^+$), 423 (0.4), 392 (0.2), 175 (100), 137 (5), 69 (64); HREIMS *m/z* 438.2769 (calcd for $C_{28}H_{38}O_4$, M$^+$ − H_2O, 438.2771).

Chabrolobenzoquinone A (6): pale oil; UV (MeOH) λ_{max} (log ϵ) 251 (4.00) nm; IR (neat) ν_{max} 3273, 2924, 1684, 1657, 1614 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz), see Tables 4 and 5; EIMS (30 eV) *m/z* 424 (0.7, $[M]^+$), 409 (0.4), 378 (0.2), 175 (92), 137 (54), 69 (100); HREIMS *m/z* 424.2607 (calcd for $C_{27}H_{36}O_4$, 424.2615).

Chabrolobenzoquinone B (7): pale oil; UV (MeOH) λ_{max} (log ϵ) 252 (4.02) nm; IR (neat) ν_{max} 2924, 1712, 1657, 1614 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz), see Tables 4 and 5; EIMS (30 eV) *m/z* 438 (0.6, $[M]^+$), 423 (0.3), 392 (0.2), 175 (93), 137 (93), 69 (100); HREIMS *m/z* 438.2741 (calcd for $C_{28}H_{38}O_4$, 438.2771).

Chabrolobenzoquinone C (8): pale oil; UV (MeOH) λ_{max} (log ϵ) 251 (4.06) nm; IR (neat) ν_{max} 3271, 2924, 1684, 1657, 1614 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) and ^{13}C NMR ($CDCl_3$, 75 MHz), see Tables 4 and 5; EIMS (30 eV) *m/z* 424 (0.8, $[M]^+$), 409 (0.4), 378 (0.2), 175 (94), 137 (76), 69 (100); HREIMS *m/z* 424.2605 (calcd for $C_{27}H_{36}O_4$, 424.2615).

Chabrolobenzoquinone D (9): pale oil; UV (MeOH) λ_{max} (log ϵ) 251 (4.03) nm; IR (neat) ν_{max} 2924, 1712, 1657, 1614 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 125 MHz), see Tables 4 and 5; EIMS (30 eV) *m/z* 438 (1, $[M]^+$), 423 (0.4), 392 (0.7), 175 (93), 137 (92), 69 (100); HREIMS *m/z* 438.2768 (calcd for $C_{28}H_{38}O_4$, 438.2771).

Acknowledgment. This work was supported by a grant from the National Science Council (Contract No. NSC 92-2323-B-110-003), Republic of China, awarded to J.-H.S.

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NP0401314