

Scalarane-Based Sesterterpenes from an Indonesian Sponge *Strepsichordaia aliena*

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Received February 14, 2000

Investigation of the lipophilic extract of the sponge *Strepsichordaia aliena* revealed six new 20,24-bishomoscalarane sesterterpenes, honu'enone (**1**), phyllofolactones H–K (**3**–**6**), and phyllofenone C (**7**). Structure elucidation of these compounds was secured by spectroscopic methods, 1D and 2D NMR, and accurate mass measurements.

Pentaprenyl terpenoids (sesterterpenes) are widely distributed in fungi, lichens, higher plants, insects, and marine organisms. Their structures are derived from geranyl–farnesyl diphosphate.¹ Scalarane-based sesterterpenes possessing biological activities have been reported from sponges of the order Dictyoceratida.²

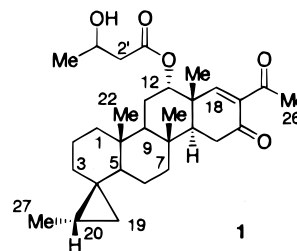
In a previous paper we reported the structures of 12 new sesterterpenes, honulactones A–L, from an Indonesian sponge *Strepsichordaia aliena* (family Thorectidae).³ Further investigation of *S. aliena* has led to the isolation and characterization of six new 20,24-bishomoscalarane sesterterpenes, honu'enone (**1**), phyllofolactones H–K (**3**–**6**), and phyllofenone C (**7**). Compounds **1** and **7** represent additional examples of 20,24-dimethyl-25-norscalarane sesterterpenes.

Results and Discussion

Honu'enone (**1**) was obtained as a colorless solid exhibiting a molecular ion peak (HRMS) at m/z 485.3267 corresponding to C₃₀H₄₄O₅. The ¹H and ¹³C NMR spectra of **1** indicated the presence of four singlets and two doublets belonging to methyl groups resonating at δ 0.80, 0.94, 1.08, 1.22, and 2.45; nine methylenes; seven methynes; four quaternary carbons; and a fully substituted quaternary sp² carbon (δ 136.7) incorporated into an α,β -unsaturated diketone (two carbonyl carbons at δ 197.6 and 199.3). Initial inspection of the ¹H NMR spectrum indicated cyclopropane and hydroxybutanoyl protons similar to those observed for honulactones A and B.³ However, the ¹H and ¹³C signals associated with the substituted α,β -unsaturated γ -lactone in honulactones A and B were missing in compound **1** (Table 1). Instead, compound **1** showed new signals at δ 7.33 (H-18) corresponding to a trisubstituted sp² carbon (δ_C 164.2) and δ 2.45 (H-26) indicative of a methyl ketone (δ 30.7, 199.3). Analysis of the COSY spectrum allowed us to establish the following structural units: C-1 to C-3, C-5 to C-7, C-9 to C-12, C-14 to C-15, C-19 to C-20 to C-27, and C-2' to C-4'.

Interpretation of the HMBC spectrum revealed correlations between H-3' (δ 4.15) to C-2' (δ 43.7)/C-4' (δ 22.5) and H-2' (δ 2.45) to C-1' (δ 171.4)/C-3' (δ 64.3)/C-4', confirming the presence of a 3-hydroxybutanoate moiety attached to

the oxygenated C-12 carbon [HMBC cross-peak correlation between H-12 (δ 5.09) and C-1']. Positioning of the methyl ketone at C-17 was based on HMBC correlations observed from H-18 to C-12/C-13/C-14/C-17/C-24 and H-26 to C-17/C-24, thus providing further evidence of the lack of a γ -lactone. HMBC cross-peaks between H-14/H-15 to C-16



(δ 197.6) located the second carbonyl carbon at C-16. The cyclopropane signals at C-19 were connected to C-20, and both were connected to C-4: H-19_{cis} and H-19_{trans} showed correlations to C-4/C-20. Finally, the C-27 methyl doublet was placed on the C-20 cyclopropane ring based on HMBC correlation between H-27 and C-4, C-19, and C-20.

The small J value observed for H-12 indicated an equatorial hydrogen, which was also corroborated by a strong ROESY cross-peak between H-12 and H-11_{eq}/H-11_{ax}/H-18/H-23. The C-20 cyclopropane carbon had β -orientation, as a strong ROESY cross-peak was observed between H-20 and H-22. Relative configuration of the CH₃-27 group was assigned as S^* supported by ROESY cross-peaks between H-27 and H-3_{ax}, C-20, C-22, and H-19_{trans}. The all-trans A–B–C–D ring system was also confirmed by cross-peaks observed in the ROESY spectrum: H-11_{ax} to H-21/H-22/H-23, H-15_{ax} to H-21/H-23, and H-9_{ax} to H-5_{ax}/H-14_{ax}.

The next five compounds were C-12 substituted C₄ and C₅ hydroxy esters of phyllofolactone A (**2**) previously isolated by Schmitz and co-workers from *Phyllospongia foliascens* collected in the South China Sea.^{4,5} The ¹H and ¹³C NMR spectra of compounds **3** and **4** indicated the presence of a 3-hydroxybutanoyl residue at C-12 in ring C, while phyllofolactones J (**5**) and K (**6**) showed a 3-hydroxypentanoyl moiety also attached to ring C at C-12 (Tables 2 and 3). Compounds **3** and **4** are stereoisomers at CH₃-26 configuration. 1D NOE experiments indicated that **3** is the β isomer; irradiation of H-24 produced a positive NOE on H-16_{ax} and H-26, while irradiation of H-26 produced a positive NOE on H-16_{eq} and H-24. On the other

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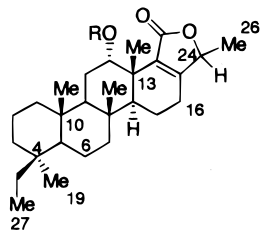
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Table 1. ¹H NMR and ¹³C NMR Data for Honu'enone (**1**) and Phyllofenone C (**7**)^{a,b}

position	honu'enone (1)		phyllofenone C (7)	
	¹³ C	¹ H (mult; <i>J</i> = Hz)	¹³ C	¹ H (mult; <i>J</i> = Hz)
1	39.6	eq: 1.68, m ax: 0.73, m	40.1	eq: 1.60, m ax: 0.68 (ddd; 4, 13, 13)
2	21.0	1.45, m	17.9	1.40, m
3	33.0	eq: 1.54, m ax: 1.22, m	36.6	eq: 1.67 (ddd; 3, 14, 14) ax: 0.83, m
4	23.1		36.2	
5	50.1	ax: 1.40, m	58.6	ax: 0.94 (dd; 2.2, 13)
6	17.2	1.05, m	18.2	eq: 1.55, m ax: 1.45, m eq: 1.71, m ax: 0.88, m
7	39.0	eq: 1.65, m ax: 1.00, m	41.0	
8	37.8		37.1	
9	50.9	ax: 1.27 (dd; 2.0, 15)	53.6	ax: 1.31 (dd; 3.1, 12.3)
10	36.9		36.8	
11	22.2	eq: 1.97 (dt; 2.6, 15) ax: 1.76 (ddd; 2.4, 15, 15)	22.2	1.79, m
12	76.4	eq: 5.09 (t; 2.6)	76.7	eq: 5.11 (t; 2.6)
13	41.3		41.2	
14	48.8	ax: 2.07 (dd; 3.9, 14)	44.1	ax: 1.76, m
15	34.8	eq: 2.52, m ax: 2.41, m	24.0	eq: 1.88 (d; 15) ax: 1.60 (ddd; 4.4, 15, 15)
16	197.6		65.1	5.75 (dd; 1.5, 4.2)
17	136.7		134.9	
18	164.2	7.33, s	153.0	6.70, s
19 _{cis}	13.6	0.59 (dd; 4.4, 8.9)	28.4	0.82, s
19 _{trans}		-0.48 (t; 5)		
20	13.3	0.69, m	24.5	a: 1.5, m b: 1.17, m
21	16.2	0.94, s	17.0	0.85, s
22	14.0	0.80, s	16.7	0.84, s
23	18.5	1.17, s	19.8	1.05, s
24	199.3		197.6	
25				
26	30.7	2.45, s	25.8	2.21, s
27	13.1	1.08 (d; 6.3)	8.6	0.74 (t; 7.3)
1'	171.4		171.9	
2'	43.7	2.45, m	43.7	a: 2.53 (dd; 3.3, 16) b: 2.46 (dd; 8.8, 16)
3'	64.3	4.15, m	64.6	4.18, m
3'-OH				2.85, s
4'	22.5	1.23 (d; 6.3)	22.8	1.25 (d; 6.4)
CH ₃ CO			170.1	
CH ₃ CO			21.2	2.04, s

^a Spectra of **1** and **7** were recorded in CDCl₃ at 500 MHz for ¹H NMR and 125 MHz for ¹³C NMR. ^b The numbering system follows that proposed by Kazlauskas et al.¹⁰

hand, 1D NOE experiments showed that CH₃-26 was α -oriented in phyllofolactone I (**4**): irradiation of H-24 produced a positive NOE on H-16_{eq} and H-26. Similar NOE



R = H	26 β -CH ₃	2
R = COCH ₂ CH(OH)CH ₃	26 β -CH ₃	3
R = COCH ₂ CH(OH)CH ₃	26 α -CH ₃	4
R = COCH ₂ CH(OH)CH ₂ CH ₃	26 β -CH ₃	5
R = COCH ₂ CH(OH)CH ₂ CH ₃	26 α -CH ₃	6

experiments indicated that CH₃-26 was β -oriented in phyllofolactone J (**5**), although it was α -oriented in compound **6**. In addition, the C-24 chemical shift was diagnostic in confirming the orientation of the CH₃-26: in compounds **4** and **6** (α CH₃-26), C-24 resonates at δ 78.1, as compared to compounds **3** and **5** (β CH₃-26), where it resonates at δ

77.8/77.9 (Table 3). The same carbon chemical shifts correlations were observed for honulactones A–L: C-24 resonates upfield when Me-26 is β -oriented compared to the α -oriented Me-26.³

Phyllofenone C (**7**)⁶ was obtained as an amorphous solid, [α]_D +16°, with the molecular formula C₃₂H₅₀O₆ as established by HRMS. The ¹³C NMR spectrum of **7** showed 32 signals accounting for three carbonyls (δ 170.1, 171.9, and 197.6), two olefinic carbons (δ 134.9 and 153.0), two methyl ketones (δ 21.2 and 25.8), and three oxymethines (δ 64.6, 65.1, and 76.7).

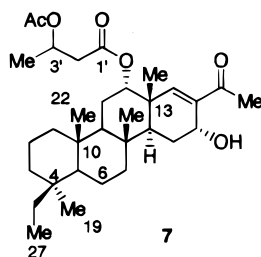
Some features in the ¹H NMR observed in phyllofolactones H and I (**3**, **4**) were present in compound **7**: four axial methyl groups (δ 0.82, H-19; 0.84, H-22; 0.85, H-21; and 1.05, H-23), an ethyl side chain; a methyl triplet at δ 0.74 (H-27) coupled to two multiplets at δ 1.17/1.5 (H-20), and a 3-hydroxybutanoyl unit. However, close inspection of the ¹H and ¹³C NMR spectra indicated that the signals associated with the substituted α,β -unsaturated γ -lactone present in phyllofolactones B–D^{4,5} and H–K were missing in compound **7** (Tables 2 and 3). Instead, compound **7** showed new signals at δ 6.70 (H-18) corresponding to a trisubstituted sp² carbon (δ _C 153), δ 2.04 associated with an acetyl

Table 2. ^1H NMR Data for Phyllofolactones H–K (3–6)^{a,b}

position	^1H (mult; $J = \text{Hz}$)			
	phyllofolactone H (3)	phyllofolactone I (4)	phyllofolactone J (5)	phyllofolactone K (6)
1	eq: 1.68, m ax: 0.58 (ddd; 4, 13, 13)	eq: 1.66, m ax: 0.58 (ddd; 4, 13, 13)	eq: 1.65, m ax: 0.59 (ddd; 4, 13, 13)	eq: 1.66, m ax: 0.59 (ddd; 4, 13, 13)
2	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>
3	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>
4				
5	ax: 0.86 (dd; 2, 13)	ax: 0.86 (dd; 2, 13)	ax: 0.86, m	ax: 0.87, m
6	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>
7	eq: 1.83 (dt; 3, 13) ax: 0.99 (ddd; 4, 13, 13)	eq: 1.83 (dt; 3, 13) ax: 1.01 (ddd; 4, 13, 13)	eq: 1.83 (dt; 3, 13) ax: 0.99 (ddd; 4, 13, 13)	eq: 1.83 (dt; 3, 13) ax: 1.01 (ddd; 4, 13, 13)
8				
9	ax: 1.16, m	ax: 1.17, m	ax: 1.17, m	ax: 1.18, m
10				
11	eq: 2.01 (dt; 3, 15) ax: 1.69, m	eq: 2.02 (dt; 3, 15) ax: 1.69, m	eq: 2.02 (dt; 3, 15) ax: 1.71, m	eq: 2.03 (dt; 3, 15) ax: 1.69, m
12	eq: 5.60 (t; 2.7)	eq: 5.58 (t; 3)	eq: 5.60 (t; 2.7)	eq: 5.58 (t; 2.7)
13				
14	ax: 1.49, m	ax: 1.50, m	ax: 1.50, m	ax: 1.50, m
15	eq: 1.91 (dd; 6.5, 12) ax: 1.55, m	eq: 1.91 (dd; 7, 13) ax: 1.56, m	eq: 1.91 (dd; 7, 12) ax: 1.54, m	eq: 1.91 (dd; 7, 12) ax: 1.53, m
16	eq: 2.35, m ax: 2.19 (ddd; 7, 12, 15)	eq: 2.31, m ax: 2.24, m	eq: 2.36, m ax: 2.20 (ddd; 7, 12, 15)	eq: 2.32, m ax: 2.24 (ddd; 7, 11, 15)
17				
18				
19	0.79, s	0.79, s	0.79, s	0.79, s
20	a: 1.51, m b: 1.17, m	a: 1.52, m b: 1.14, m	a: 1.50, m b: 1.15, m	a: 1.49, m b: 1.15, m
21	0.82, s	0.83, s	0.83, s	0.83, s
22	0.88, s	0.89, s	0.89, s	0.89, s
23	1.17, s	1.18, s	1.17, s	1.18, s
24	4.77 (q; 6.7)	4.75 (q; 6.5)	4.77 (q; 7)	4.76 (q; 6.6)
25				
26	1.35 (d; 7)	1.34 (d; 6.8)	1.36 (d; 6.8)	1.35 (d; 6.9)
27	0.73 (t; 7.4)	0.73 (t; 7.4)	0.73 (t; 7.4)	0.73 (t; 7.4)
1'				
2'	a: 2.36 (dd; 4, 16) b: 2.31 (dd; 8.5, 16)	2.33 (d; 6)	a: 2.38 (dd; 3, 16) b: 2.30 (dd; 9, 16)	a: 2.36 (dd; 3, 15.5) b: 2.30 (dd; 9, 15.5)
3'	4.09, m	4.11 (q; 6.3)	3.82, m	3.83, m
3'-OH	3.08, s	3.04, s	3.00, s	2.99, s
4'	1.18 (d; 6.3)	1.18 (d; 6.3)	1.45, m	1.45, m
5'			0.94 (t; 7.5)	0.94 (t; 7.4)

^aSpectra of 3–6 were recorded in CDCl_3 at 500 MHz. ^bThe numbering system follows that proposed by Kazlauskas et al.¹⁰
^cSuperimposing signals.

unit, δ 2.45 (H-26) indicative of a methyl ketone (δ_{C} 30.7, 199.3), and δ 5.75 (H-16) for an oxymethine proton.



Long-range heteronuclear correlations revealed the following connections: (a) attachment of the 3-hydroxybutanoate unit to ring C through C-12; (b) the singlet methyl (δ_{H} 2.45) is attached to C-24 (δ_{C} 197.6), and the latter is connected to ring D through C-17: HMBC correlation between H-26 to C-17; (c) the ethyl side chain and one angular methyl group were found to be attached to C-4 in ring A: HMBC cross-peaks between H-19/H-20/H-27 and C-4; (d) HMBC correlations placed the last oxymethine proton on C-16: cross-peaks between H-14/H-15/H-18 and C-16.

The small coupling constants for H-12 and H-16 revealed α -orientation for both oxymethine protons. The ethyl side chain was assigned β -orientation because a strong ROESY

cross-peak was observed between H-20 and H-22. Finally, the acetyl unit was connected to the butanoyl unit through the oxygen at C-3'.

Uncommon, but not unique, the lack of C-25 in phyllofenone C (7) is also found in phyllofenone A and other 25-norscalaranes isolated from sponges of the genus *Phyllospongia* (syn. *Carteriospongia*),⁷ *Strepsichordaia lendenfeldi*,^{2a} *Dictyoceratida* spp.,⁸ *Halichondria* spp.,⁸ and *Hyrtios erecta*.⁹ Further biological evaluation of compounds 1 and 3–7 is under way.

Experimental Section

Spectral Analysis. NMR spectra were determined on a General Electric GN Omega 500 spectrometer operating at 500 MHz for ^1H and 125 MHz for ^{13}C . ^1H chemical shifts are referred to CDCl_3 ; ^{13}C chemical shifts are referred to CDCl_3 (77.0 ppm). Homonuclear ^1H connectivities were determined by using the 2D double-quantum filtered COSY and 1D decoupling experiments. Homonuclear ^1H NOEs were obtained by difference NOE experiments using a 2-s irradiation period. One-bond heteronuclear ^1H – ^{13}C connectivities were determined by 2D proton-detected HMQC experiments; two- and three-bond ^1H – ^{13}C connectivities were determined by 2D proton-detected HMBC experiments. HRMS were determined in the DCI and FAB modes. Optical rotations were measured on a JASCO-DIP-700 instrument using CH_2Cl_2 at 20 °C at the sodium D line (589 nm).

Table 3. ^{13}C NMR Data for Phyllofolactones H–K (3–6)^{a,b}

position	phyllofolactone H (3)	phyllofolactone I (4)	phyllofolactone J (5)	phyllofolactone K (6)
1	40.0	40.0	40.0	40.0
2	18.0	18.0	18.0	18.0
3	36.5	36.5	36.5	36.6
4	36.1	36.1	36.1	36.1
5	58.7	58.7	58.7	58.7
6	18.1	18.1	18.1	18.1
7	41.7	41.7	41.5	41.6
8	37.5	37.5	37.5	37.5
9	53.4	53.5	53.4	53.5
10	37.0	37.0	37.0	37.0
11	21.0	20.9	20.9	21.0
12	74.5	74.6	74.5	74.6
13	38.4	38.4	38.4	38.4
14	51.1	51.4	51.1	51.4
15	16.9	17.0	16.9	17.0
16	24.0	24.4	24.0	24.4
17	164.2	164.3	164.1	164.3
18	132.7	132.6	132.7	132.6
19	28.4	28.5	28.5	28.5
20	24.4	24.5	24.5	24.5
21	16.7	16.6	16.7	16.6
22	16.8	16.7	16.8	16.7
23	21.4	21.2	21.4	21.2
24	77.9	78.1	77.8	78.1
25	171.3	171.3	171.3	171.3
26	18.6	18.6	18.6	18.6
27	8.6	8.6	8.6	8.6
1'	171.5	171.4	171.7	171.5
2'	43.4	43.4	41.8	41.7
3'	64.2	64.3	69.4	69.4
3'-OH				
4'	22.2	22.3	29.2	29.3
5'			10.0	10.0

^a Spectra of 3–6 were recorded in CDCl_3 at 125 MHz. ^b The numbering system follows that proposed by Kazlauskas et al.¹⁰

Animal Material. The sponge was collected at Turtle Bay, Sangakali, eastern Indonesia, at a depth of 23 m, in March 1996 (2° 04' 59" N, 118° 23' 41" E). In life, the sponge is fan-shaped to palmitate–digitate, with 2-mm diameter oscules on one surface; the opposite surface has radiating channels, both surfaces are covered with small conules. The texture is quite tough, but very flexible; the external color in life is maroon–purple; interior, cream. The skeleton consists of simple radiating cored primary fibers and golden vermiform tertiary fibers that are linked by short junctions. The surface has a layer of sand grains on it. The sponge is closely comparable to *S. aliena* (order Dictyoceratida, family Thorectidae, subfamily Phyllosponginae). A voucher specimen has been deposited in the Natural History Museum, London (BMNH 1999.7.12.1).

Extraction and Isolation. The freeze-dried sponge (81.0 g) was extracted in dichloromethane–isopropyl alcohol (DCM–IPA) (1:1; 1.0 L) overnight, filtered, and concentrated under reduced pressure to dryness yielding 3.03 g of crude extract. The crude extract was loaded on a Sephadex LH-20 column (30 × 2.5 cm) equilibrated in DCM. The column was eluted using a gradient profile as follows: (1) DCM, DCM/acetone (1:1), and methanol. Eight major fractions (A–H) were collected and concentrated to dryness. Reversed-phase HPLC (Phenomenex Ultracarb 10 ODS 30; 250 × 22 mm; 80% aqueous MeCN to 100% MeCN in 40 min at 6.0 mL/min and monitoring at 220 nm) of fraction B afforded six fractions [fraction 1 (35.2 mg), fraction 2 (77.2 mg), fraction 3 (32.4 mg), fraction 4 (118.1 mg), fraction 5 (44.7 mg), and fraction 6 (90.3 mg)]. Fractions 4 and 6 were further separated by normal-phase HPLC (Microsorb Si; 300 × 7.0 mm; solvent A = hexanes, solvent B = 1:1 hexanes/isopropyl alcohol, starting with solvent A at 0 min to 100% solvent B in 35 min at 2.0 mL/min and monitoring at 220 nm) to yield honu'enone (1.3 mg), phyllofolactone H (3.8 mg), phyllofolactone I (2.8 mg), phyllofolactone J (2.0 mg), phyllofolactone K (1.2 mg), and phyllofenone C (1.3 mg).

Honu'enone (1): colorless solid, 1.3 mg (0.0016% based on dry wt); $[\alpha]_{\text{D}} +16.0^\circ$ (*c* 0.4, CH_2Cl_2); ^1H and ^{13}C NMR data,

see Table 1; assignments made by interpretation of COSY, HMQC, and HMBC data; HRFABMS *m/z* obsd 485.3267 [$\text{M} + \text{H}$]⁺ ($\text{C}_{30}\text{H}_{45}\text{O}_5$, Δ 2.7 ppm).

Phyllofolactone H (3): amorphous solid, 3.8 mg (0.0047% based on dry wt); $[\alpha]_{\text{D}} +78.5^\circ$ (*c* 1.3, CH_2Cl_2); ^1H and ^{13}C NMR data, see Tables 2 and 3; assignments made by interpretation of COSY, HMQC, and HMBC data; HRDCIMS *m/z* obsd 518.38674 [$\text{M} + \text{NH}_4$]⁺ ($\text{C}_{31}\text{H}_{52}\text{NO}_5$, Δ -4.2 ppm).

Phyllofolactone I (4): amorphous solid, 2.8 mg (0.0035% based on dry wt); $[\alpha]_{\text{D}} +61.9^\circ$ (*c* 0.93, CH_2Cl_2); ^1H and ^{13}C NMR data, see Tables 2 and 3; assignments made by interpretation of COSY, HMQC, and HMBC data; HRDCIMS *m/z* obsd 518.383471 [$\text{M} + \text{NH}_4$]⁺ ($\text{C}_{31}\text{H}_{52}\text{NO}_5$, Δ 2.1 ppm).

Phyllofolactone J (5): amorphous solid, 2.0 mg (0.0025% based on dry wt); $[\alpha]_{\text{D}} +55.3^\circ$ (*c* 0.8, CH_2Cl_2); ^1H and ^{13}C NMR data, see Tables 2 and 3; assignments made by interpretation of COSY, HMQC, and HMBC data; HRDCIMS *m/z* obsd 532.398571 [$\text{M} + \text{NH}_4$]⁺ ($\text{C}_{32}\text{H}_{54}\text{NO}_5$, Δ 3.1 ppm).

Phyllofolactone K (6): amorphous solid, 1.2 mg (0.0015% based on dry wt); $[\alpha]_{\text{D}} +53.8^\circ$ (*c* 0.8, CH_2Cl_2); ^1H and ^{13}C NMR data, see Tables 2 and 3; assignments made by interpretation of COSY, HMQC, and HMBC data; HRDCIMS *m/z* obsd 532.399877 [$\text{M} + \text{NH}_4$]⁺ ($\text{C}_{32}\text{H}_{54}\text{NO}_5$, Δ 0.6 ppm).

Phyllofenone C (7): amorphous solid, 1.3 mg (0.0016% based on dry wt); $[\alpha]_{\text{D}} +16.0^\circ$ (*c* 0.4, CH_2Cl_2); ^1H and ^{13}C NMR data, see Table 1; assignments made by interpretation of COSY, HMQC, and HMBC data; HRFABMS *m/z* obsd 553.35051 [$\text{M} + \text{Na}$]⁺ ($\text{C}_{32}\text{H}_{50}\text{O}_6\text{Na}$, Δ 1.5 ppm).

Cytotoxicity Testing. Cytotoxicity assays were carried out by Instituto Biomar, S. A., Madrid, Spain.

Acknowledgment. We thank, NSF, the Sea Grant College Program, Instituto Biomar, S. A., and PharmaMar, S. A. for financial support.

Supporting Information Available: ^1H and ^{13}C NMR spectra for all compounds are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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