Sesquiterpenes from the Formosan Stolonifer *Tubipora musica*

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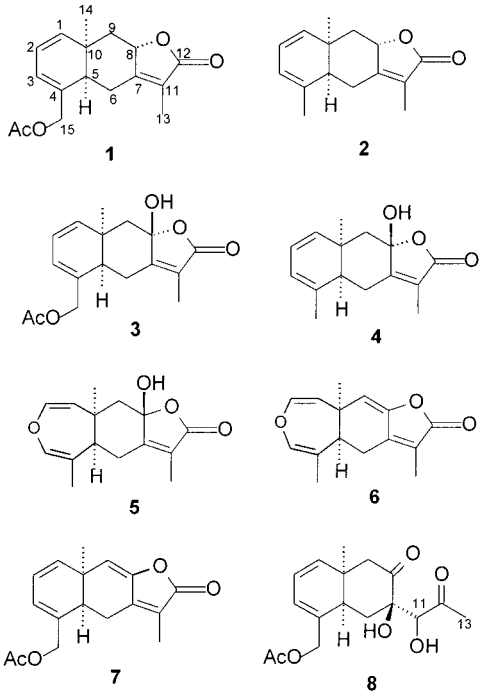
Received May 7, 2001

Eight new sesquiterpenes, tubipolides A−G (**1**−**7**) and tubiporone (**8**) (novel carbon skeleton), and a known sesquiterpene, spirotubipolide, have been isolated from the Formosan stolonifer *Tubipora musica*. The structures of compounds **1**−**8** were determined by 1D and 2D NMR spectral analysis.

Previously, Iguchi et al. reported three furanosesquiterpenoids, tubipofuran, 15-acetoxytubipofuran, and spirotubipolide, from the Japanese stolonifer *Tubipora musica*.[1,2] As part of our search for bioactive substances from marine organisms, the Formosan stolonifer *Tubipora musica* Linnaeus (Stolonifera) was studied based on the CH_2Cl_2 extracts, showing significant cytotoxicity in P-388 (mouse lymphocytic leukemia) cell cultures as determined by standard procedures.[3,4] Bioassay-guided fractionations resulted in the isolation of eight new sesqeuterpenes, tubipolide A−G (**1**−**7**) and tubiporone (**8**) (novel carbon skeleton), and a known sesquiterpene, spirotubipolide.[2] Compounds **2**, **7**, and spirotubipolide exhibited cytotoxicity against the P-388 cell line.



Results and Discussion

Tubipolide A (**1**) was shown to have the molecular formula $C_{17}H_{20}O_4$ as indicated by HREIMS and NMR data. Its UV absorption at λ_{max} (log ϵ) 262 nm (3.08) exhibited the presence of a conjugated homoannular diene system, which was further confirmed by ^{1}H NMR [δ 5.66 (H-1), 6.02 (H-2,) 6.00 (H-3)] and ^{13}C NMR (δ 134.4, 123.8, 121.1, 136.7).[3,4] The ^{1}H NMR and ^{13}C NMR spectra also showed signals due to an acetoxymethyl (δ_H 2.12, 4.66, δ_C 20.9, 66.1, 170.8), a methyl on a quaternary carbon (δ_H 0.98, δ_C 24.6, 36.5), and two methylenes [δ_H 2.11 (H-6β), 2.85 (H-6α), 2. 47 (H-9β), 1.25 (H-9α), δ_C 27.1, 45.4].

The presence of a α-methyl-α,β-unsaturated-γ-lactone moiety was indicated by the following spectral data: IR 1746 cm^{-1}; UV 226 (4.26) nm; ^{1}H NMR 1.82 (H-13), 4.66 (H-8); ^{13}C NMR 8.3 (C-13), 78.4 (C-8), 119.6 (C-11), 160.1 (C-7), 175.0 (C-12). These spectral data closely resembled those of the known α-methyl-α,β-unsaturated-γ-lactone.[5] COSY correlations from H-5 to H_2-6 and H-8 to H_2-9, as well as HMBC correlations (Figure 1) from H_2-6 to C-7 and C-11 and from H_2-9 to C-10, C-1, and C-14, confirmed the connection of ring A and ring C through C-6 and C-9. The relative stereochemistry of **1** was established by a 2D NOESY experiment, as shown in Figure 2. The NOESY correlations between the angular methyl (H_3-14) and the H-5 signal indicated the *cis* A/B ring juction. H-8 was assigned as β based on NOEs between H_3-14 and H-9α; H-9β and H-8.

Tubipolide B (**2**) had a molecular fomula of $C_{15}H_{18}O_2$ (HREIMS and NMR). The UV and IR spectra indicated the presence of conjugated homoannular diene and α,β-unsaturated-γ-lactone moieties. The ^{13}C and ^{1}H NMR spectra of **2** were quite similar to those of **1**, except the acetoxymethyl was replaced by a methyl group (δ_H 1.86, δ_C 22.4) in **2**. HMBC correlations between H_3-15 and C-3, C-4 as well as COSY correlations between H-15 and H-3 confirmed this assignment. The relative stereochemistry of **2** was established by a 2D NOESY experiment. The NOESY correlations between the angular methyl (H_3-14) and the H-5 signal indicated the *cis* A/B ring junction. H-8 was assigned as β based on NOEs between H-14 and H-9α; H-9β and H-8.

HREIMS and NMR data revealed tubipolide C (**3**) to have a molecular formula of $C_{17}H_{20}O_5$. The presence of a α-methyl-α,β-unsaturated-γ-hydroxy-γ-lactone moiety was indicated by the following spectral data: IR 3504, 1747 cm^{-1}; UV 236 (4.28) nm; ^{1}H NMR 1.79 (H-13); ^{13}C NMR 8.3 (C-13), 103.2 (C-8), 121.3 (C-11), 158.9 (C-7), 172.5 (C-12). The ^{13}C and ^{1}H NMR spectra of **3** resembled those of **1** except a hydroxy group replaced the proton at C-8 (δ_C 103.2) in **3**. The assignment of a hydroxy group at C-8 was confirmed by HMBC correlations between H-9 and C-8; H-6 and C-4, C-5, C-7, C-8, C-10; and OH-8 and C-7, C-8, C-9. The relative stereochemistry at C-5 and C-10 of **3** was determined by NOESY correlations between H-5 and H_3-14, H-6α, H_3-15. The hydroxy group at C-8 was assigned

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10.1021/np010228f CCC: $20.00 © 2001 American Chemical Society and American Society of Pharmacognosy
Published on Web 11/03/2001

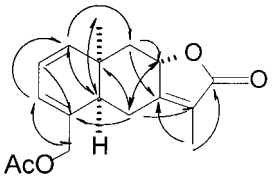

Figure 1. HMBC correlations of **1**.

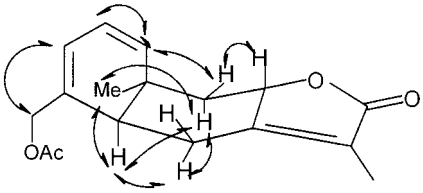

Figure 2. NOESY correlations of **1**.

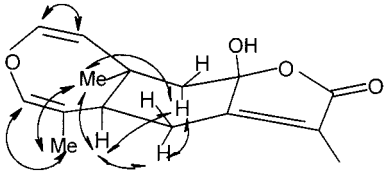

Figure 3. NOESY correlations of **5**.

as β based on the chemical shift of H_3-14, as it was not influced by a deshielding effect of the hydroxyl.

Tubipolide D (**4**) had a molecular formula of $C_{15}H_{18}O_3$ as indicated by HREIMS and NMR data. The presence of a α-methyl-α,β-unsaturated-γ-hydroxy-γ-lactone moiety was indicated by the following spectral data: IR 3461, 1743 cm^{-1}; UV 235 (4.29) nm; ^1H NMR 1.85 (H-13), ^{13}C NMR 8.3 (C-13), 103.0 (C-8), 121.2 (C-11), 159.0 (C-7), 172.0 (C-12). The ^{13}C and ^1H NMR spectra of **4** exhibited close similarity to **3** except the acetoxyl methyl group at C-4 was replaced by a methyl (δ_H 1.87, δ_C 22.2). HMBC correlation between H_3-15 and C-5, C-3, C-4 confirmed this assignment. The relative stereochemistry at C-5 and C-10 of **4** was determined by NOESY correlations between H-5 and H_3-14, H-6α.

Tubipolide E (**5**) showed a higher molecular weight by 16 mass units than **4**. The presence of an α-methyl-α,β-unsaturated-γ-hydroxy-γ-lactone moiety was indicated by the following spectral data: IR 3556, 1746 cm^{-1}; UV 242 (4.28) nm; ^1H NMR 1.87 (H-13); ^{13}C NMR 8.3 (C-13), 102.9 (C-8), 122.1 (C-11), 159.7 (C-7), 171.9 (C-12). The ^{13}C and ^1H NMR data of **5** were similar to those of **4** except the presence of an enol ether linkage between C-2 (δ_C 139.9, δ_H 6.14) and C-3 (δ_C 139.6, δ_H 6.24).[6,7] HMBC correlations from H-2 to C-1, C-3, and C-10; from H-1 to C-2 and C-5; and from H_3-15 to C-3, C-4, and C-5 confirmed the assignment of a oxepine ring. The *cis* A/B ring junction was determined by NOESY correlation between H_3-14 and H-5.

Tubipolide F (**6**) had a molecular formula of $C_{15}H_{16}O_3$ as determined by HREIMS. The presence of a α-methyl-α,β-unsaturated-γ-lactone moiety was indicated by the following spectral data: IR 1739 cm^{-1}; UV 246 (4.24) nm; ^1H NMR 1.91 (H-13); ^{13}C NMR 8.5 (C-13), 149.0 (C-8), 120.6 (C-11), 148.0 (C-7), 171.3 (C-12). The structure of **6** was determined by comparing the ^1H NMR spectra with those of **5**. Vinylic protons at δ 6.25 (H-3), 6.06 (H-2), and 4.47 (H-1) indicated the same ring A structure. The lack of the lactonic proton as well as of the isolated methylene protons at C-9 and the presence of an olefinic singlet at δ 5.65 (H-9) indicated a double bond at $\Delta^{8,9}$. HMBC correlations between H-9 and C-7, C-5, C-14; H_3-14 and C-1, C-5, C-9, C-10; H_2-6 and C-7, C-8; and H-5 and C-10, C-9 confirmed this assignment.

The molecular formula of tubipolide G (**7**) was determined as $C_{17}H_{18}O_4$ from HRFABMS. The ^{13}C and ^1H NMR data of **7** were analogous to those of **1** except the methylene (C-9) and a lactone methine (C-8) were replaced by an olefin at $\Delta^{8,9}$ (δ_H 5.54, δ_C 112.8, 147.4). HMBC correlations between H_2-9 and C-5, C-7, C-8, C-10, C-14; H_3-14 and C-5, C-9, C-10; and H_2-6 and C-4, C-5, C-8, C-10, C-11 confirmed the position of the double bond ($\Delta^{8,9}$). The relative stereochemistry at C-5 and C-10 of **7** was determined by NOESY correlations between H_3-14 and H-5.

Tubiporone (**8**) was obtained as a colorless oil, $[\alpha]^{25}_D$ +3.4° (*c* 0.03, $CHCl_3$). Analysis of HRFABMS revealed a molecular formula of $C_{17}H_{22}O_6$. Its IR spectrum (KBr) suggested the presence of an ester carbonyl (1746 cm^{-1}) and a ketone carbonyl (1724 cm^{-1}) group. The presence of a conjugated homoannular diene system in **1** was indicated by UV absorption at λ_{max} (log ϵ) 262 nm (3.26) and ^1H NMR [δ 5.50 (H-1), 5.89 (H-2), 5.95 (H-3)]. The ^1H and ^{13}C NMR spectra also showed signals due to an acetoxymethyl (δ_H 2.12, 4.58, 4.78, δ_C 21.0, 66.3, 171.0), a methyl on a quaternary carbon (δ_H 1.14, δ_C 25.7, 42.4), a methine (δ_H 2.58, δ_C 40.3), two methylenes [δ_H 1.68 (H-6β), 2.49 (H-6α), 2.56 (H-9β), 2.78 (H-9α); δ_C 38.2, 49.3], and a ketone [δ_C 207.7]. The COSY correlation (H-5 to H_2-6) and HMBC correlations (H_3-14 to C-1, C-5, C-9, and C-10; H-5 to C-3, C-4, C-6, C-7, and C-15; H_2-9 to C-1, C-5, C-7, C-8, C-10, and C-14; H_2-6 to C-4, C-5, C-7, C-8, and C-11) confirmed the relationships of the protons and carbons on the rings A and B. The presence of a 3-hydroxy-2-propanone side chain was indicated by the following spectral data: ^1H NMR δ 2.40 (H-13), 4.55 (H-11), 3.62 (OH-11); ^{13}C NMR 28.0 (C-13), 78.7 (C-11), 206.2 (C-12). HMBC correlations from H-13 to C-11 and C-12; H-11 to C-7 and C-8; H_2-6 to C-4, C-5, C-7, C-8, and C-11; H_2-9 to C-1, C-5, C-7, C-8, C-10, and C-14; and H-5 to C-3, C-4, C-6, C-7, and C-15 confirmed the attachment of the 3-hydroxy-2-propanone side chain at C-7. The relative stereochemistry at C-5, C-7, C-10 was established by NOESY correlations from H-5 to H_3-14, H-6α, and H-11; and from H-11 to H-6α, H-9α, and H-13.

The *cis* stereochemistry between the angular C-5 and C-10 positions for **1**−**8** was different from the *trans* form of eudesmanolides found in higher plants.[6−11] Tubipolide B (**2**), tubipolide G (**7**), and spirotubipolide exhibited cytotoxicity against the P-388 cell line with ED_{50} values of 3.69, 4.01, and 3.24 μg/mL, respectively.

Experimental Section

General Experimental Procedures. Melting points were determined using a Yanagimoto micromelting point apparatus and are reported uncorrected. Optical rotations were determined on a JASCO DIP-181 polarimeter. UV spectra were obtained on a Shimadzu UV-160A spectrophotometer, and IR spectra were recorded on a Hitachi 26-30 spectrophotometer. The NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C, respectively, in $CDCl_3$ using TMS as internal standard. EIMS spectra were obtained with a JEOL JMS-SX/SX 102A mass spectrometer at 70 eV. Silica gel 60 (Merck, 230−400 mesh) was used for column chromatography; precoated silica gel plates (Merck, Kieselgel 60 F_{254}, 0.25 mm) were used for TLC analysis.

Animal Material. The stolonifer *T. musica* was collected at Green Island, off Taiwan, in September 1999, at a depth of 20 m and was stored for 2 days in a freezer until extraction. A voucher specimen, NSUGN-032, was deposited in the

Table 1. ^{1}H NMR Spectral Data[a] of **1**−**8** in $CDCl_3$

	1	2	3	4	5	6	7	8
1	5.66 d (9.0)	5.49 d (9.6)	5.83 d (9.5)	5.64 d (9.6)	4.70 dd (7.8, 1.8)	4.47 dd (7.8, 1.2)	5.54 d (9.0)	5.50 br d (9.3)
2	6.02 dd (9.0, 5.2)	5.95 dd (9.6, 5.2)	5.87 dd (9.5, 5.0)	5.85 dd (9.3, 5.1)	6.14 d (7.8)	6.06 d (7.8)	5.93 dd (9.0, 5.1)	5.89 dd (9.3, 5.4)
3	6.00 br d (5.2)	5.71 br d (5.2)	5.95 d (5.0)	5.70 br d (5.1)	6.24 br s	6.25 br s	5.98 br d (5.1)	5.95 br d (5.4)
5	1.89 dd (13.2, 4.8)	1.73 dd (13.4, 4.8)	1.86 dd (13.5, 4.0)	1.72 dd (15.2, 4.5)	1.78 m	2.26 dd (13.5, 4.0)	2.25 dd (16.5, 4.3)	2.58 m
6α	2.85 dd (13.2, 4.8)	2.80 dd (13.4, 4.8)	2.65 dd (13.5, 4.0)	2.65 dd (15.2, 4.5)	2.72 m	2.74 t (13.5)	2.78 dd (16.5, 4.3)	2.49 dd (12.9, 4.2)
6*β*	2.11 t (13.2)	2.03 t (13.4)	2.37 t (13.5)	2.33 t (15.2)	2.72 m	2.82 dd (13.5, 4.0)	2.45 t (16.5)	1.68 t (12.9)
8	4.66 m	4.67 dd (12.6, 6.0)						
9α	1.25 t (12.6)	1.22 t (12.6)	1.59 d (13.8)	1.60 d (14.1)	1.49 d (14.1)	5.65 s	5.54 s	2.78 d (13.5)
9*β*	2.47 dd (12.6, 5.7)	2.43 dd (12.6, 6.0)	2.50 d (13.8)	2.47 d (14.1)	2.38 d (14.1)			2.56 d (13.5)
11								4.55 d (4.8)
13	1.82 br s	1.84 br s	1.79 br s	1.85 br s	1.87 br s	1.91 br s	1.88 br s	2.40 s
14	0.98 s	0.99 s	0.96 s	1.00 s	1.24 s	1.39 s	1.11 s	1.14 s
15	4.66 m	1.86 br s	4.58 d (13.0) 4.64 d (13.0)	1.87 br s	1.74 br s	1.75 br s	4.60 d (13.2) 4.71 d (13.2)	4.58 d (12.8) 4.78 d (12.8)
OAc	2.12 s		2.06 s					2.12 s
OH-7								4.14 s
OH-11								3.62 br d (4.8)

[a] Chemical shift assignment was confirmed by DEPT, COST, HMBC, and HSQC experiments. [b] *J* values (in Hz) in parentheses.

Table 2. ^{13}C NMR Spectral Data[a] (*δ*) of **1**−**8** in $CDCl_3$

	1	2	3	4	5	6	7	8
1	134.4 d	130.9 d	37.2 d	133.2 d	112.3 d	110.0 d	132.4 d	134.4 d
2	123.8 d	124.0 d	120.7 d	121.9 d	139.9 d	138.7 d	132.4 d	123.5 d
3	121.0 d	117.9 d	121.7 d	118.2 d	139.6 d	139.3 d	121.4 d	121.6 d
4	136.7 s	139.6 s	133.8 s	136.7 s	118.0 s	118.8 s	135.0 s	135.3 s
5	43.4 d	47.7 d	44.9 d	49.2 d	54.3 d	50.2 d	41.1 d	40.3 d
6	27.1 t	45.5 t	25.6 t	25.2 t	27.9 t	26.1 t	23.8 t	38.2 t
7	160.1 s	160.9 s	158.9 s	159.0 s	159.7 s	148.0 s	149.1 s	80.7 s
8	78.4 d	78.8 d	103.2 s	103.0 s	102.9 s	149.0 s	147.4 s	207.7 s
9	45.4 t	26.9 t	48.9 t	49.1 t	51.4 t	117.4 d	112.8 d	49.3 t
10	36.5 s	36.5 s	36.5 s	36.5 s	39.0 s	40.1 s	37.1 s	42.4 s
11	119.6 s	110.8 s	121.3 s	121.2 s	122.1 s	120.6 s	120.6 s	78.7 d
12	175.0 s	176.0 s	172.5 s	172.0 s	171.9 s	171.3 s	171.0 s	206.2 s
13	8.3 q	8.3 q	8.3 q	8.3 q	8.3 q	8.5 q	8.5 q	28.0 q
14	24.6 q	24.9 q	25.2 q	25.6 q	31.2 q	30.5 q	25.3 q	25.7 q
15	66.1 t	22.4 q	66.4 t	22.2 q	21.5 q	21.4 q	66.0 t	66.3 t
OAc	20.9 q		20.9 q				20.9 q	21.0 q
	170.8 s		171.1 s				170.8 s	171.0 s

[a] Chemical shift assignment was confirmed by DEPT, COST, HMBC, and HSQC experiments.

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Extraction and Isolation. The bodies of the stolonifer *T. musica* were freeze-dried to give 0.56 kg of a solid, which was extracted with CH_2Cl_2 (2.0 L × 3). After removal of solvent in vacuo, the residue (12.4 g) was subjected to silica gel column chromatography using *n*-hexane, *n*-hexane−CH_2Cl_2 (5:1 to 1:5), CH_2Cl_2, CH_2Cl_2−EtOAc (5:1 to 1:1), EtOAc, and acetone as eluting solvents. The collected fractions were evaporated in vacuo and examined by TLC. Homogeneous fractions, showing similar spots on TLC, were pooled to give 10 major fractions (F1−F10). Fraction F5 [0.41 g, eluted from CH_2Cl_2−EtOAc (5:1)] was further fractionated on a open column of silica gel to give **1** [4 mg, eluted from CH_2Cl_2−acetone (6:1)] and **8** [3 mg, eluted from CH_2Cl_2−acetone (5:1)]. Fraction F4 (6.15 g, eluted from CH_2Cl_2) was further subjected to silica gel CC using CH_2Cl_2, CH_2Cl_2−EtOAc, EtOAc, and acetone as eluting solvent to give six subfractions (F4.1−F4.6). Subfraction F4.2 [0.90 g, eluted from CH_2Cl_2−EtOAc (20:1)] was further chromatographed to give **6** [2 mg, eluted from *n*-hexanes−EtOAc (10:1)]. Subfraction F4.4 [1.04 g, eluted from CH_2Cl_2−acetone (5:1)] was further subjected to an open column of silica gel to give spirotubipolide [3 mg, eluted from *n*-hexanes−EtOAc (2:1)], **7** [2 mg, eluted from *n*-hexanes−EtOAc (1:1)], **2** [3 mg, eluted from *n*-hexanes−EtOAc (1:2)], and **3** (4 mg, eluted from EtOAc). Subfraction F4.5 [1.18 g, eluted from CH_2Cl_2−acetone (2:1)] was chromatographed further to give **4** [2 mg, eluted from *n*-hexanes−EtOAc (5:3)], **8** [2 mg, eluted from *n*-hexanes−EtOAc (5:4)], and **5** [3 mg, eluted from *n*-hexanes−EtOAc (1:1)].

Tubipolide A (1): colorless oil (4 mg); $[\alpha]^{25}_D$ −72.4° (*c* 0.03, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 226 (4.26), 262 (3.08) nm; IR (KBr) ν_{max} 1746 cm^{-1}; ^{1}H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m*/*z* 288 $[M]^+$ (9), 256 (6), 246 (5), 228 (30), 215 (18), 213 (28), 199 (29), 185 (24), 171 (23), 129 (27), 118 (58), 105 (100); HREIMS *m*/*z* 288.1361 (calcd for $C_{17}H_{20}O_4$, 288.1356).

Tubipolide B (2): colorless oil (3 mg); $[\alpha]^{25}_D$ −51.6° (*c* 0.02, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 225 (4.20), 266 (3.12) nm; IR (KBr) ν_{max} 1747 cm^{-1}; ^{1}H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m*/*z* 230 $[M]^+$ (37), 215 (12), 202 (2), 197 (7), 185 (14), 170 (12), 162 (30), 128 (13), 124 (29), 119 (100); HREIMS *m*/*z* 230.1307 (calcd for $C_{15}H_{18}O_2$, 230.1302).

Tubipolide C (3): colorless oil (4 mg); $[\alpha]^{25}_D$ −79.7° (*c* 0.05, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 236 (4.28), 268 (3.13) nm; IR (KBr) ν_{max} 3504, 1747 cm^{-1}; ^{1}H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m*/*z* 304 $[M]^+$ (4), 286 (1), 256 (1), 245 (5), 244 (19), 227 (23), 226 (63), 213 (44), 211 (46), 198 (63), 183 (32), 171 (39), 155 (40), 141 (22), 118 (100); HREIMS *m*/*z* 304.1308 (calcd for $C_{17}H_{20}O_5$, 304.1305).

Tubipolide D (4): colorless oil (2 mg); $[\alpha]^{25}_D$ −29.6° (*c* 0.04, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 235 (4.29), 262 (3.16) nm; IR (KBr) ν_{max} 3461, 1743 cm^{-1}; ^{1}H NMR, see Table 1; ^{13}C NMR,

see Table 2; EIMS *m/z* 246 $[M]^+$ (41), 229 (10), 228 (321), 213 (49), 200 (25), 199 (14), 186 (17), 185 (100), 173 (21), 157 (60), 142 (21), 127 (28), 120 (54), 119 (65), 105 (95), 77 (44); HREIMS *m/z* 246.1258 (calcd for $C_{15}H_{18}O_3$, 246.1251).

Tubipolide E (5): colorless oil (2 mg); $[\alpha]^{25}_D$ +7.0° (*c* 0.04, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 242 (4.28) nm; IR (KBr) ν_{max} 3556, 1746 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 262 $[M]^+$ (25), 244 (4), 229 (3), 216 (4), 215 (3), 201 (5), 189 (4), 178 (6), 162 (9), 146 (24), 95 (100); HREIMS *m/z* 262.1202 (calcd for $C_{15}H_{18}O_4$, 262.1200).

Tubipolide F (6): colorless oil (2 mg); $[\alpha]^{25}_D$ −8.7° (*c* 0.03, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 246 (4.24) nm; IR (KBr) ν_{max} 1739 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 244 $[M]^+$ (16), 229 (27), 216 (8), 215 (20), 213 (13), 201 (18), 188 (7), 187 (14), 174 (6), 173 (30), 162 (66), 149 (42), 134 (59), 128 (29), 105 (35), 91 (90), 77 (59), 53 (100); HREIMS *m/z* 244.1096 (calcd for $C_{15}H_{16}O_3$, 244.1095).

Tubipolide G (7): colorless oil (2 mg); $[\alpha]^{25}_D$ +22.6° (*c* 0.02, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 246 (4.24), 263 (3.27) nm; IR (KBr) ν_{max} 1742 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 271 $[M - 15]^+$ (1), 256 (2), 244 (3), 226 (19), 214 (18), 213 (100), 212 (31), 211 (70), 198 (16), 197 (20), 185 (17), 183 (22), 156 (25), 141 (20), 128 (22), 115 (28), 91 (20); HRFABMS *m/z* 287.1284 (calcd for $C_{17}H_{19}O_4$, 287.1278).

Tubiporone (8): colorless oil (2 mg); $[\alpha]^{25}_D$ +3.4° (*c* 0.03, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 262 (3.26) nm; IR (KBr) ν_{max} 1724, 1746 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m/z* 322 $[M]^+$ (1), 304 (1), 279 (3), 263 (19), 219 (18), 201 (27), 189 (38), 173 (26), 159 (28), 145 (43), 131 (33), 119 (64), 105 (86), 91 (100), 77 (65); HRFABMS *m/z* 323.1491 (calcd for $C_{17}H_{23}O_6$, 323.1488).

Cytotoxicity Testing. P-388 cells were kindly supplied by Prof. J. M. Pezzuto. Cytotoxic assays were carried out according to the procedure described previously.[3]

Acknowledgment. We thank Prof. J. M. Pezzuto, Program for Collaborative Research in Pharmaceutical Sciences, College of Pharmacy, University of Illinois at Chicago, for the provision of the P-388 cell line. This work was supported by a grant from the National Science Council of Taiwan awarded to C.-Y.D.

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NP010228F