Five New Polyacetylenes from a Sponge of the Genus *Petrosia*

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Petrocortynes D−H, novel C_{46} polyacetylenes, were isolated from a sponge of the genus *Petrosia* collected from Keomun Island, Korea. Petrocortyne D (**2**) is a 4,5-dihydro derivative of a diastereomer of petrocortyne A (**1**), and petrocortynes E−H (**3**−**6**) possess an additional allylic-hydroxyl group. The structures of these compounds were determined by combined chemical and spectral methods, and absolute configurations of most of the asymmetric carbon centers were determined by the modified Mosher's method. Limitations on the application of Mosher's method to allylic alcohols is discussed. Petrocortynes D−H exhibited moderate cytotoxicity and inhibitory activity against PLA_2.

Linear acetylenes and polyacetylenes are widely recognized as one of the most frequently encountered groups of sponge metabolites. Despite their relatively limited distribution among sponges, compounds of this structural class possess great structural variations on both chain-lengths and functionalities.[1] Several sponge-derived acetylenes and polyacetylenes exhibit potent antimicrobial, antiviral, cytotoxic, RNA-cleaving, and enzyme-inhibitory activities as well as brine-shrimp lethality.[2−15] In addition, some of these compounds have important ecological functions, including metamorphosis-inducing and antifouling effects against larvae of benthic invertebrates.[13]

In our continuing search for bioactive substances from marine animals, we recently reported the structures and bioactivities of petrocortynes A−C from an undescribed sponge of the genus *Petrosia* collected from Keomun Island, South Sea, Korea.[15,16] These compounds are C_{46} linear tetraacetylenes (petrocortynes A and B) and a diacetylene containing a γ-pyrone ring (petrocortyne C) structurally related to petroformynes previously isolated from the Mediterranean sponge *P. ficiformis*.[11,12,17,18] However, the structures of these compounds are distinguished from each other in the location of a diacetylenic carbinol group in carbon framework as well as the stereochemistry of asymmetric carbon centers.

In addition to petrocortynes A−C, ^{1}H NMR analysis and cytotoxicity tests of silica vacuum flash chromatographic fractions of the crude extract of the above sponge revealed the presence of structurally related metabolites as minor constituents in more polar fractions. Consequently, we pursued these compounds by a large-scale extraction and a bioactivity-guided separation. Herein we report the structures and bioactivities of petrocortynes D−H, novel linear C_{46} tetraacetylenes.

Results and Discussion

The sponge was collected and processed as described in the Experimental Section to yield petrocortynes D−H. Petrocortyne D (**2**, Chart 1) was isolated as a colorless gum that analyzed for $C_{46}H_{72}O_2$ by combined HRFABMS and ^{13}C NMR analysis. The NMR data of this compound were very similar to those of petrocortyne A (**1**). The only significant difference in the ^{13}C NMR spectrum was the replacement of olefinic carbon signals at δ 128.5 (C-4) and 134.3 (C-5) of **1** by those of upfield methylenes in **2** (Table 1). Corresponding changes were also observed in the ^{1}H NMR spectrum in which the olefinic proton signals at δ 5.61 (H-4) and 5.90 (H-5) of **1** disappeared. In addition, the signal of a methine proton (H-3) was shifted upfield from δ 4.83 (1H, br d, J = 5.9 Hz) to 4.37 (1H, ddd, J = 6.4, 6.4, 2.0 Hz) in **2** (Table 2). These changes were readily accommodated by hydrogenation of the C-4 double bond of **1** and were confirmed by a combination of ^{1}H COSY, TOCSY, HSQC, HETCOR, and HMBC experiments. Thus, the structure of **2** was defined as a 4,5-dihydro derivative of **1**.

Compound **2** possessed asymmetric carbons at the same positions (C-3 and C-14) as **1**. The stereochemistry at these carbons was assigned on the basis of the modified Mosher's method.[19,20] The ^{1}H NMR spectra of **2*S*** and **2*R***, the (*S*)- and (*R*)-MTPA esters of **2**, respectively, were obtained, and the difference $\Delta(\delta\mathbf{2S} - \delta\mathbf{2R})$ was measured. These values established the *R* configuration at C-14, identical with **1** (H-11, +13 Hz; H-17, −15 Hz). However, the same method revealed that the absolute configuration at C-3 of **2** was *S*, opposite that of **1** (H-1, +23 Hz; H-4, −31 Hz). Although details of biosynthetic mechanism are not clear, stereochemical reversal at this center is thought to be closely related to the hydrogenation (or dehydrogenation) process. The same phenomenon was observed for petrosiacetylenes, linear C_{30} polyacetylenes isolated from the identical specimens chosen for this study.[15]

Petrocortyne E (**3**) was isolated as a colorless gum. The molecular formula for this compound was deduced as $C_{46}H_{70}O_3$ by combined HRFABMS and ^{13}C NMR spectrometry. The spectral data for **3** were highly compatible with those of **1**. Careful examination of the NMR data, however, revealed several significant differences. The most noticeable change in the ^{13}C NMR data was the appearance of the signal of a new hydroxyl-bearing carbon at δ 86.6 (CH). The corresponding proton signal was also observed at δ 4.28 (1H, ddd, J = 8.3, 6.8, 5.9 Hz) in the ^{1}H NMR spectrum. A combination of proton decoupling and ^{1}H COSY experiments showed that this proton was directly spin-coupled to an olefinic proton at δ 5.39 (1H, m), thus forming an ene-ol functionality. Based upon 15.6 Hz vicinal coupling constant of this proton with an olefinic one at δ 5.78 (1H, dt, J = 15.6, 6.8 Hz), the *E* geometry was assigned for the new double bond. With the aid of this information, the structure of **3** was determined by combined 2D NMR experiments. The HMBC experiment was particularly helpful in locating the ene-ol group in carbon framework (Figure 1). Long-range correlations of the methylene carbon signal at δ 24.6 (C-19) with the α-acety-

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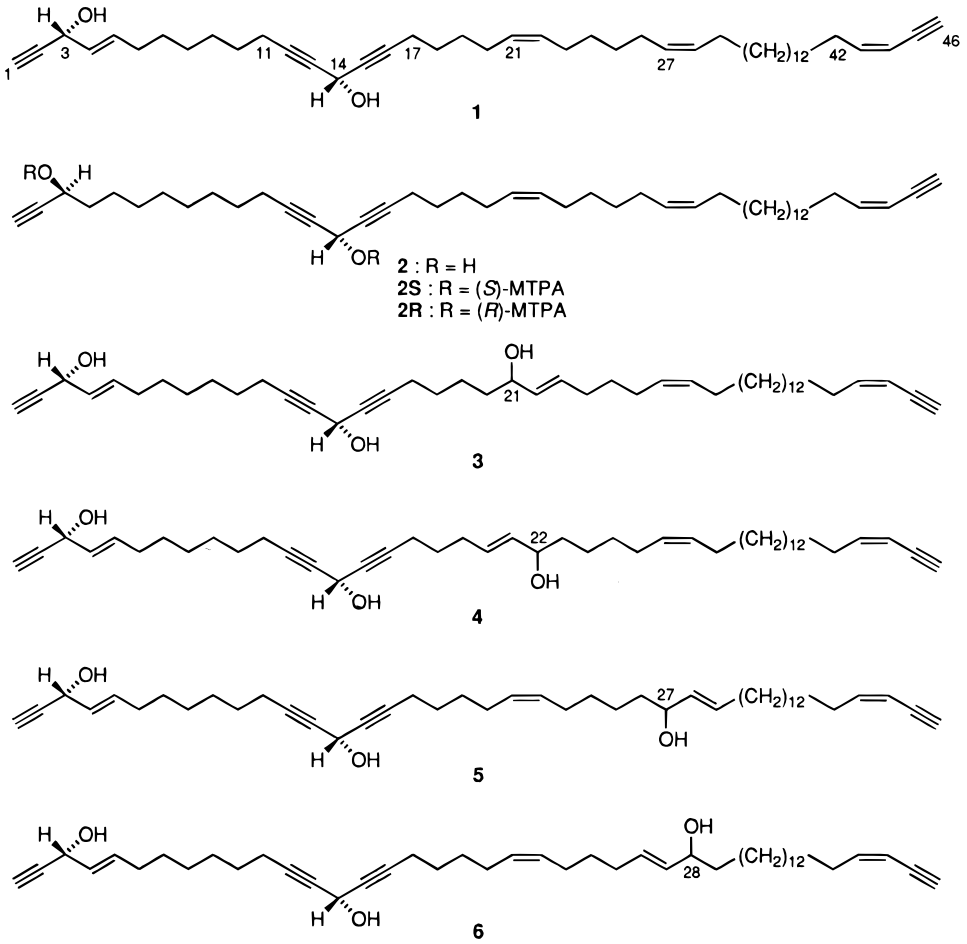
Chart 1



lenic and methine proton signals at δ 2.23 (H-17) and 4.28 (H-21), respectively, showed that the ene-ol and diacetylenic carbinol groups were connected to each other by a chain composed of four methylenes. Similarly, long-range correlations of the olefinic proton signals with neighboring carbon signals secured the connection between the trans and cis double bonds via three methylenes, which was confirmed by TOCSY data. Thus, the structure of a long-chain subunit (**a**), consisting of 21 carbons, was confidently defined. In addition, two subunits (**b** and **c**), located at the termini of the molecule, were readily assigned by the HETCOR and HMBC experiments (Figure 1).

The connection between the partial structures **a** and **b** was determined by the TOCSY data in that correlations of the signals of the α-olefinic (H-6) and β-acetylenic (H-10) protons with those of three common methylene protons (H-7−H-9) were clearly observed. Because the connectivity between two of three partial structures was determined by spectral methods, the remaining one between **b** and **c** must consist of a chain of 11 methylene carbons. This interpretation was supported by HREIMS data in that peaks at *m/z* 341($C_{25}H_{41}^+$, rel int 13), 287 ($C_{21}H_{35}^+$, 30), 273 ($C_{20}H_{33}^+$, 23), containing the right part of the molecule, were observed. Thus, the structure of petrocortyne E (**3**) was determined as a C_{46} tetraacetylenic tetraene-triol with three asymmetric carbons at C-3, C-14, and C-21.

Petrocortyne F (**4**) was isolated as a colorless gum. The molecular formula for this compound was established as $C_{46}H_{70}O_3$ by combined HRFABMS and ^{13}C NMR spectrometry. Although the spectral data of **4** were almost identical with those of **3**, careful examination of the ^1H and ^{13}C NMR data of both compounds showed considerable discrepancies in the region C-15−C-28; differences were ^{13}C 1.2−0.5 ppm, ^1H 0.04−0.02 ppm. Therefore, the partial structure **a** of **3** must be structurally modified to a different one, which was determined by combined 2D NMR experiments. The ^1H COSY and HSQC data showed that **4** possessed the same trans ene-ol group as **3**. On the basis of mutual HMBC correlations of the α- and β-acetylenic methylenes (C-17 and C-18) with the allylic methylene and olefinic methine, respectively, the trans double bond and hydroxyl group were assigned to C-20 and C-22, respectively (Experimental Section). Similarly, HMBC correlations of the carbon signal at δ 25.3, shifted upfield by the γ-effect of the hydroxyl group, with the allylic proton signal at δ 2.02 placed the cis double bond at C-27, identical with **3**. Thus, the structure of **4** was determined to be a derivative of **3** possessing a reversed ene-ol functionality, except for the stereochemistry of asymmetric carbons.

The molecular formula of petrocortyne G (**5**) was analyzed for $C_{46}H_{70}O_3$, identical with those of **3** and **4**, by combined HRFABMS and ^{13}C NMR analysis. The NMR data of **5** were also very similar to those obtained for **3** and **4**. Comparison of the NMR data, however, revealed that the signals of carbons and protons in the region of C-15−C-28 were noticeably shifted from those of other petrocortynes. A combination of 2D NMR experiments revealed that **5** contained the same cis double bond and trans ene-ol group as other compounds. The HMBC data showed that the allylic-hydroxyl group was separated from the cis double bond by four methylenes, as with **4**; however, the same experiment showed that, instead of the ene-ol group, the cis double bond was connected to the diacetylenic carbinol functionality by four methylenes. This interpreta-

Table 1. Carbon NMR Assignments for Compounds **1**−**6**[a]

no.	1	2	3	4	5	6
1	74.0 d	72.8 d	74.0 d	74.0 d	74.0 d	74.0 d
2	83.3 s	85.0 s	83.3 s	83.3 s	83.3 s	83.3 s
3	62.8 d	62.3 d	62.8 d	62.8 d	62.8 d	62.8 d
4	128.5 d	37.6 t	128.5 d	128.5 d	128.5 d	128.5 d
5	134.3 d	24.9 t	134.4 d	134.3 d	134.3 d	134.3 d
6	31.8 t	29.1 t	31.8 t	31.8 t	31.8 t	31.8 t
7	28.6 t	28.9 t	28.6 t	28.6 t	28.6 t	28.6 t
8	28.5 t	29.3 t	28.5 t	28.5 t	28.5 t	28.5 t
9	28.6 t	28.8 t	28.6 t	28.6 t	28.5 t	28.6 t
10	28.2 t	28.3 t	28.2 t	28.2 t	28.2 t	28.2 t
11	18.7 t	18.7 t	18.7 t	18.7 t	18.6 t	18.7 t
12	78.1 s	78.0 s[b]	78.1 s	78.1 s	78.1 s[b]	78.1 s[b]
13	85.0 s	85.1 s[c]	85.1 s	85.1 s	85.0 s[c]	85.1 s[c]
14	52.6 d	52.6 d	52.5 d	52.5 d	52.5 d	52.5 d
15	85.0 s	84.9 s[c]	84.7 s	84.4 s	84.9 s[c]	84.9 s[c]
16	78.1 s	78.1 s[b]	78.3 s	78.6 s	78.2 s[b]	78.2 s[b]
17	18.7 t	18.7 t	18.6 t	18.6 t	18.6 t	18.6 t
18	28.0 t	28.0 t	28.1 t	27.5 t	27.9 t	27.9 t
19	28.9 t	28.9 t	24.6 t	31.4 t	28.8 t	28.8 t
20	26.7 t	26.7 t	31.9 t	135.3 d	26.7 t	26.7 t
21	129.6 d	129.6 d	86.6 d	129.7 d	129.5 d	129.7 d[d]
22	130.2 d	130.2 d	136.8 d	86.8 d	130.0 d	129.8 d[d]
23	27.1 t	27.1 t	128.5 d	32.4 t	27.0 t	27.0 t
24	29.4 t	29.4 t	31.9 t	25.3 t	29.5 t	29.1 t
25	NA[f]	NA[f]	29.1 t	NA[f]	24.9 t	31.9 t
26	27.2 t[e]	27.2 t[e]	26.7 t	27.1 t	32.3 t	136.5 d
27	129.3 d	129.3 d	129.1 d	129.3 d	87.0 d	128.9 d
28	130.1 d	130.0 d	130.5 d	130.2 d	128.4 d	87.0 d
29	27.3 t[e]	27.3 t[e]	27.3 t	27.3 t	137.2 d	32.5 t
30	29.8 t	29.8 t	29.8 t	29.8 t	32.3 t	25.4 t
31	NA[f]	NA[f]	NA[f]	NA[f]	29.1 t	NA[f]
40	29.2 t	29.2 t	29.2 t	29.2 t	29.2 t	29.2 t
41	28.7 t	28.8 t	28.8 t	28.8 t	28.7 t	28.8 t
42	30.3 t	30.3 t	30.3 t	30.3 t	30.3 t	30.3 t
43	146.3 d	146.2 d	146.3 d	146.3 d	146.3 d	146.3 d
44	107.9 d	107.9 d	107.9 d	107.9 d	107.9 d	107.9 d
45	80.6 s	80.6 s	80.6 s	80.6 s	80.6 s	80.6 s
46	81.1 d	81.1 d	81.1 d	81.1 d	81.1 d	81.1 d

[a] Measured in $CDCl_3$ solutions at 125 MHz; δ in ppm; TMS as internal standard. Assignments were aided by DEPT, HETCOR, HSQC, and HMBC experiments. [b−e] Interchangeable signals. [f] NA: not assigned.

tion was supported by TOCSY data in that correlations containing the signals of both α-acetylenic (C-17) and allylic methylene protons (C-20) were clearly observed. Thus, the structure of **5** was defined as a C_{46} linear polyacetylene containing a trans ene-ol group at C-27.

The molecular formula of petrocortyne H (**6**) was established as $C_{46}H_{70}O_3$ by HRFABMS and ^{13}C NMR analysis. Combined 2D NMR data revealed that **6** possessed the same partial structure as C-21−C-29 of **3**. However, a series of HMBC and TOCSY correlations containing the signals of carbon and protons of the C-17 α-acetylenic methylene revealed that the cis double bond was connected to the diacetylenic carbinol group via four methylenes, as observed for **5**. Thus, the structure of petrocortyne H (**6**) was defined as a derivative of **5** containing a reversed trans ene-ol functionality.

Compounds **3**−**6** contained three asymmetric carbons at C-3, C-14, and that bearing an allylic-hydroxyl group. The stereochemical assignment for these centers was approached by the modified Mosher's method; however, two unusual phenomena were observed from the MTPA esterification process. First, the standard condition using dry pyridine as reaction solvent was found to be unsuitable for the esterification of these compounds. Only **6** was esterified in good yield (55 and 48% for **6*S*** and **6*R***, respectively), while other compounds were either esterified in much lower yield (24 and 29% for **5*S*** and **5*R***, respectively) or totally decomposed (**3** and **4**). Lowering the temperature was not particularly helpful because the reactants were still rapidly decomposed. This problem was partially solved by changing the reaction solvent from dry pyridine to a 1:3 mixture of pyridine and 30% EtOAc in hexane. In this condition, the MTPA esters of **4**−**6** were obtained in good yield (56−81%), while **3** was still totally decomposed. Comparison of the results showed that both the yields of the reactions and the stability of the polyacetylenes were closely related to the distance between the allylic-hydroxyl and diacetylenic carbinol group at C-12. Compound **6**, having the hydroxyl group at C-28, was esterified in the highest yield, while **5** and **4**, having the same group at C-27 and C-22, respectively, were obtained in much lower yields, with that for **5** being higher than that for **4**. Compound **3**, containing the hydroxyl group at C-21 was rapidly decomposed. These results suggested that, although the detailed mechanism is not known, the electron-rich diacetylenic carbinol group at C-12 significantly influences the esterification process.

Another important finding was the structures of products. The molecular formula for both of the MTPA esters of **6**, **6*S*** and **6*R***, was deduced as $C_{66}H_{82}F_6O_7$ by HRFABMS, which was different from $C_{76}H_{91}F_9O_9$ for the expected triester. Examination of the NMR data revealed that only two of the three hydroxyl groups were esterified, and the remaining portion of the molecule contained a new carbonyl group; ^{13}C δ 200.9 (C). A combination of ^1H COSY, TOCSY, HSQC, and HMBC experiments revealed that the C-3 and C-14 hydroxyl groups were converted to the corresponding MTPA esters, while the trans ene-ol functionality at C-26 was converted to an α,β-unsaturated ketone (Figure 2). The same phenomenon was observed for **4** and **5**, in that only the C-3 and C-14 hydroxyl groups were esterified, and the trans ene-ol groups were changed to the corresponding α,β-unsaturated ketones (Figure 3). Our results demonstrated that the absolute stereochemistry of a molecule possessing an allylic-hydroxyl group cannot be determined by Mosher's method because it would be either oxidized (**4**−**6**) or rapidly decomposed (**3**) during ester formation. It is not known whether the same phenomenon would occur in a molecule containing a cis ene-ol group. Based upon the differences $\Delta(\delta\boldsymbol{S} - \delta\boldsymbol{R})$, the absolute configurations at C-3 and C-14 were assigned as 3*R*,14*R* for **4**, **5**, and **6** (Experimental Section).

Comparison of the molecular structures showed that petrocortynes D−H (**3**−**6**) were biosynthetically related to petrocortyne A (**1**), the major metabolite from the specimens. Two double bonds located in the middle of the carbon framework of **1** are readily attacked by a hydroxyl group, and concomitant migration of the double bond and removal of an allylic hydride would form the corresponding triols. Thus, the addition of a hydroxyl group to C-21, C-22, C-27, and C-28 would transform **1** to **3**, **4**, **5**, and **6**, respectively. An alternative mechanism of removal of an allylic proton and subsequent attachment of a hydroxyl group to a carbocation would be much less feasible because none of the corresponding triols containing a hydroxyl group at C-20, C-23, C-26, or C-29 was isolated from the specimens.

Sponge-derived acetylenes and polyacetylenes are widely recognized for their diverse and potent bioactivities. For recent examples, petrocortynes A−C and petrosiacetylenes A−D from the same specimens of *Petrosia* exhibited significant cytotoxicity and RNA-cleaving activity as well as moderate inhibitory activity against PLA_2, Na^+/K^+-ATPase, and/or reverse transcriptase (RT). In our measurement, petrocortynes D−H exhibited moderate cytotoxicity against a human leukemia cell-line (K-562); LC_{50} 45,

Table 2. Proton NMR Assignments for Compounds **2**−**6**[a]

no.	2	3	4	5	6
1	2.47 d (2.0)	2.57 d (1.5)	2.57 d (2.4)	2.57 d (2.0)	2.57 d (2.0)
3	4.37 dt (2.0, 6.4)	4.84 br d (5.5)	4.84 br d (5.9)	4.84 br d (5.9)	4.84 br d (5.9)
4	1.71 m	5.62 ddt (15.1, 6.4, 1.5)	5.62 ddt (15.1, 6.4, 1.5)	5.62 ddt (15.1, 5.9, 1.5)	5.62 ddt (15.6, 5.9, 1.0)
5	1.46 m	5.91 ddt (15.1, 1.0, 6.8)	5.91 ddt (15.1, 1.0, 6.8)	5.91 ddt (15.1, 1.0, 6.6)	5.91 ddt (15.6, 1.0, 6.8)
6	1.32 m	2.11 m	2.12 dt (6.8, 7.3)	2.10 dt (6.6, 7.3)	2.12 m
7	1.28 m	1.41 m	1.41 m	1.42 m	1.41 m
8	1.32 m	1.34−1.31 m	1.33−1.31 m	1.33−1.31 m	1.34−1.31 m
9	1.38 m	1.39 m	1.39 m	1.39 m	1.39 m
10	1.51 m	1.52 p (7.3)	1.52 p (7.3)	1.51 m	1.51 m
11	2.22 dt (2.0, 6.8)	2.22 dt (2.0, 7.3)	2.23 dt (2.0, 7.3)	2.22 dt (2.0, 7.3)	2.22 dt (2.0, 7.3)
14	5.09 br s	5.09 br s	5.09 br s	5.09 br s	5.09 br s
17	2.23 dt (2.0, 6.8)	2.23 dt (2.0, 7.3)	2.26 dt (2.0, 7.3)	2.23 dt (2.0, 7.3)	2.24 dt (2.0, 7.3)
18	1.53 m	1.54 m	1.65 p (7.3)	1.53 m	1.53 m
19	1.44 m	1.46 m	2.20 ddt (7.3, 1.0, 7.3)	1.45 m	1.44 m
20	2.05 m	1.66 m, 1.48 m	5.75 dt (15.1, 7.3)	2.03 m	2.03 m
21	5.34 m	4.28 ddd (8.3, 6.8, 5.9)	5.43 m	5.36−5.33 m	5.37 m
22	5.38 m	5.39 m	4.27 dt (7.3, 7.3)	5.36−5.33 m	5.35 m
23	2.03 m	5.78 dt (15.6, 6.8)	1.64 m, 1.44 m	2.01 m	2.05 m
24	1.36 m	2.10 m	1.34 m	1.36 m	1.46 m
25	1.36 m	1.46 m	1.36 m	1.34 m	2.10 m
26	2.01 m	2.04 m	2.02 m	1.64 m, 1.43 m	5.77 dt (15.1, 6.8)
27	5.36 m	5.33 m	5.32 m	4.27 dt (7.8, 6.8)	5.38 (15.1, 7.8, 1.5)
28	5.36 m	5.37 m	5.34 m	5.38 ddt (15.6, 7.8, 1.5)	4.27 dt (7.8, 6.8)
29	2.01 m	2.01 dt (6.4, 7.3)	2.00 m	5.77 dt (15.6, 6.8)	1.63 m, 1.41 m
30	1.34 m	1.34−1.31 m	1.33−1.31 m	2.08 dt (6.8, 7.3)	1.34−1.31 m
31	1.30−1.25 m	1.30−1.25 m	1.30−1.25 m	1.38 m	1.30−1.25 m
40	1.34 m	1.34−1.31 m	1.33−1.31 m	1.33−1.31 m	1.34−1.31 m
41	1.42 m	1.41 m	1.41 m	1.42 m	1.41 m
42	2.32 ddt (7.3, 1.5, 7.3)	2.32 ddt (7.3, 1.0, 7.3)	2.32 ddt (7.3, 1.0, 7.3)	2.32 ddt (7.3, 1.0, 7.3)	2.32 ddt (7.3, 1.0, 7.3)
43	6.00 br dt (10.7, 7.3)	6.00 ddt (10.7, 1.0, 7.3)	6.00 ddt (10.7, 1.0, 7.3)	6.00 ddt (10.7, 1.0, 7.3)	6.00 ddt (10.7, 1.0, 7.3)
44	5.44 ddt (10.7, 2.0, 1.5)	5.44 ddt (10.7, 2.4, 1.0)	5.44 ddt (10.7, 2.0, 1.5)	5.44 ddt (10.7, 2.0, 1.5)	5.44 ddt (10.7, 2.0, 1.5)
46	3.07 d (2.0)	3.07 d (2.4)	3.07 d (2.0)	3.07 d (2.0)	3.07 d (2.0)

[a] Measured in $CDCl_3$ solutions at 500 MHz; δ in ppm (J in Hz); TMS as internal standard. Assignments were aided by ^1H COSY and TOCSY experiments.

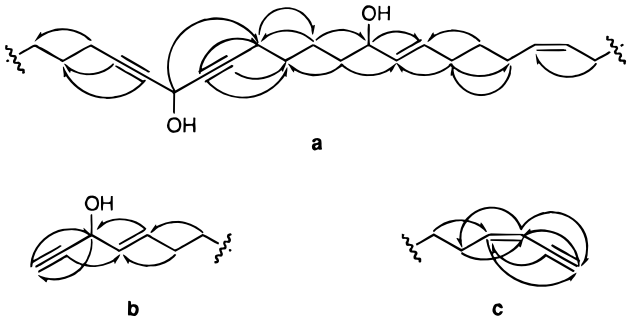


Figure 1. Partial structures and key HMBC correlations of **3** (two-bond correlations are omitted).

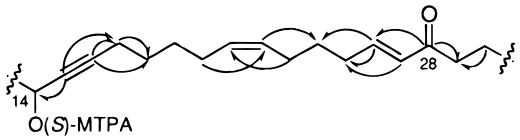


Figure 2. Selected HMBC correlations of compound **6S**.

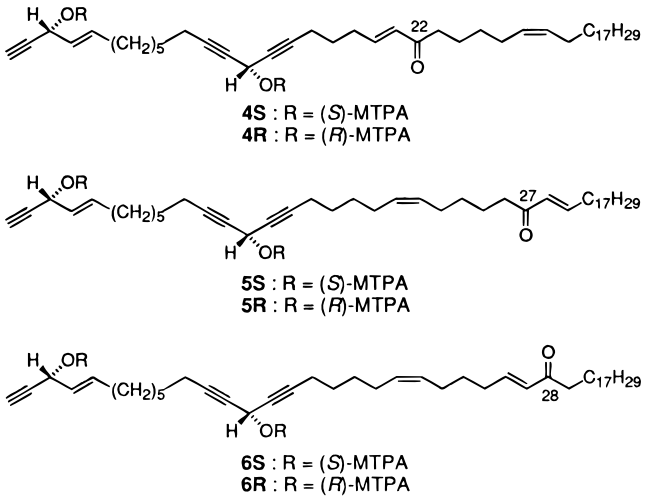


Figure 3. Products of MTPA-esterification of compounds **4**−**6**.

7, 21, 30, and 11 μM for **2**−**6**, respectively. In addition, **3**−**6** inhibited PLA_2 at a concentration of 50 μg/mL by 48, 25, 36, and 32%, respectively.

Experimental Section

General Experimental Procedures. NMR spectra were recorded in $CDCl_3$ solutions on a Varian Unity 500 spectrometer. Proton and carbon NMR spectra were measured at 500 and 125 MHz, respectively. All of the chemical shifts were recorded with respect to internal Me_4Si. IR spectra were recorded on a Mattson GALAXY spectrophotometer. UV spectra were obtained in MeOH using a Milton−Roy spectrophotometer. HRFABMS were obtained by using a JEOL JMS−HX 110 mass spectrometer provided by Korea Basic Science Institute, Taejeon, Korea. The optical rotations were measured on a JASCO digital polarimeter using a 5-cm cell. All solvents used were spectral grade or were distilled from glass prior to use.

Animal Material. The specimens of *Petrosia* sp. (sample number 94K-13) were collected by hand using scuba at 20−30 m depth in October 1994, and November 1995, along the offshore of Keomun Island, South Sea, Korea.[16] Morphological characters of the specimens were highly compatible with those of *P. corticata*; however, these were distinguished from *P. corticata* in possessing only oxeas and no large strongylotes as spicules. Details of morphological characters were reported previously.[15]

Extraction and Isolation. The freshly collected samples were immediately frozen and kept at −25 °C until chemically investigated. The sponge (5.5 kg, wet wt) was defrosted,

macerated, and extracted with MeOH (6 L × 2) and CH_2Cl_2 (6 L × 2). The combined extracts (353.41 g) were partitioned between CH_2Cl_2 and H_2O. The CH_2Cl_2 layer (100.61 g) was concentrated in vacuo, and the residue was repartitioned between *n*-hexane (71.20 g) and 25% aqueous MeOH (28.53 g). The hexane layer was dried and subjected to silica vacuum flash chromatography by using sequential mixtures of *n*-hexane and EtOAc as eluents. Fractions eluted with nonpolar solvents (20−30% EtOAc−*n*-hexane) were combined and separated by semipreparative silica HPLC (YMC silica column, 20% EtOAc−hexane) to yield a mixture of petrocortynes D−H as a single peak. Further separation of petrocortynes was made by reversed-phase HPLC (YMC ODS column, 10% aqueous MeOH) to afford each compound as an isolated peak. Final purification was made by reversed-phase HPLC (YMC ODS−H80 column, 100% CH_3CN) to yield 9.4, 7.5, 5.1, 5.0, and 6.5 mg of **2**−**6**, respectively.

Petrocortyne D (2): a colorless gum; $[\alpha]^{25}_D$ −0.8° (*c* 0.14, MeOH); UV (MeOH) λ_{max} (log ϵ) 223 (4.09) nm; IR (KBr) ν_{max} 3400−3300 (br), 2925, 2855, 1460, 1295, 1000, 970 cm^{-1}; ^{13}C and ^1H NMR values, see Tables 1 and 2, respectively; HMBC correlations H-1/C-3; H-3/C-1, C-2, C-4, C-5; H-4/C-2, C-3, C-5, C-6; H-10/C-11; H-11/C-9, C-12, C-13, C-14; H-14/C-12, C-13, C-15, C-16; H-17/C-14, C-15, C-16, C-18, C-19; H-18/C-17, C-20; H-19/C-17; H-20 and/or H-23/C-21, C-22; H-26 and/or H-29/C-27, C-28; H-42/C-40, C-43, C-44; H-43/C-41, C-42, C-44; H-44/C-42, C-43; H-46/C-43, C-44; HRFABMS $[M + Na]^+$ *m*/*z* 679.5452 (calcd for $C_{46}H_{72}O_2Na$ 679.5430).

Petrocortyne E (3): a colorless gum; $[\alpha]^{25}_D$ +3.0° (*c* 0.15, MeOH); UV (MeOH) λ_{max} (log ϵ) 224 (4.15) nm; IR (KBr) ν_{max} 3450−3300 (br), 2925, 2855, 2205, 2100, 1625, 1460, 1245, 1005, 970 cm^{-1}; ^{13}C and ^1H NMR values, see Tables 1 and 2, respectively; HMBC correlations H-1/C-3; H-3/C-1, C-2, C-4, C-5; H-4/C-2, C-3, C-6; H-5/C-3, C-6, C-7; H-6/C-8; H-9/C-11; H-10/C-12, C-13; H-11/C-10, C-12, C-13, C-14; H-17/C-14, C-15, C-16, C-19; H-18/C-15, C-16, C-17, C-19, C-20; H-19/C-17; H-21/C-19, C-20, C-22; H-22/C-20, C-21, C-24; H-23/C-21, C-24; H-24/C-25, C-26; H-26/C-24, C-25; H-27/C-29; H-42/C-41, C-43, C-44; H-43/C-41, C-42, C-45; H-44/C-42, C-46; H-46/C-43, C-44; HRFABMS $[M + Na]^+$ *m*/*z* 693.5232 (calcd for $C_{46}H_{70}O_3Na$ 693.5223).

Petrocortyne F (4): a colorless gum; $[\alpha]^{25}_D$ +8.5° (*c* 0.03, MeOH); UV (MeOH) λ_{max} (log ϵ) 223 (4.14) nm; IR (KBr) ν_{max} 3450−3300(br), 2925, 2855, 1570, 1460, 1115, 1010, 970 cm^{-1}; ^{13}C and ^1H NMR values, see Tables 1 and 2, respectively; HMBC correlations H-1/C-3; H-3/C-1, C-2, C-4, C-5; H-4/C-2, C-3, C-6; H-5/C-3, C-6, C-7; H-6/C-8; H-10/C-9, C-11; H-11/C-10, C-12, C-13, C-14; H-17/C-15, C-16, C-18, C-19; H-18/C-15, C-17, C-19, C-20; H-19/C-17, C-18; H-20/C-18, C-19, C-22; H-21/C-19; H-22/C-20, C-23, C-24; H-23/C-24; H-25/C-24, C-26; H-26/C-24; H-27/C-26; H-28/C-26; H-29/C-28, C-30; H-42/C-43, C-44; H-43/C-41, C-42, C-45, C-46; H-46/C-44; HRFABMS $[M + Na]^+$ *m*/*z* 693.5225 (calcd for $C_{46}H_{70}O_3Na$ 693.5223).

Petrocortyne G (5): a colorless gum; $[\alpha]^{25}_D$ +8.3° (*c* 0.04, MeOH); UV (MeOH) λ_{max} (log ϵ) 223 (4.00) nm; IR (KBr) ν_{max} 3450−3300 (br), 2925, 2855, 1570, 1460, 1115, 1010, 970 cm^{-1}; ^{13}C and ^1H NMR values, see Tables 1 and 2, respectively; HMBC correlations H-3/C-2, C-4, C-5; H-4/C-2, C-3, C-6; H-5/C-3, C-6, C-7; H-6/C-7; H-11/C-10, C-12, C-13, C-14; H-17/C-14, C-15, C-16, C-18, C-19; H-18/C-17; H-19/C-21; H-23/C-21, C-22, C-25; H-24/C-25; H-26/C-25; H-27/C-25, C-26, C-29; H-28/C-30; H-29/C-27, C-30, C-31; H-30/C-28, C-29; H-42/C-41, C-43, C-44; H-43/C-42, C-45; H-44/C-42; H-46/C-43, C-44; HRFABMS $[M + Na]^+$ *m*/*z* 693.5245(calcd for $C_{46}H_{70}O_3Na$ 693.5223).

Petrocortyne H (6): a colorless gum; $[\alpha]^{25}_D$ +4.4° (*c* 0.07, MeOH); UV (MeOH) λ_{max} (log ϵ) 223 (4.17) nm; IR (KBr) ν_{max} 3400−3300 (br), 2925, 2850, 1570, 1450, 1115, 1010, 970 cm^{-1}; ^{13}C and ^1H NMR values, see Tables 1 and 2, respectively; HMBC correlations H-1/C-3; H-3/C-1, C-2, C-4, C-5; H-4/C-2, C-3, C-6; H-5/C-3, C-6, C-7; H-6/C-4, C-5; H-10/C-12; H-11/C-10, C-12, C-13, C-14; H-14/C-12, C-16; H-17/C-14, C-15, C-16, C-18; H-18/C-16, C-19; H-20/C-21; H-21/C-19, C-20, C-23; H-22/C-20, C-23, C-24; H-23/C-21, C-22, C-25; H-25/C-23, C-26, C-27; H-26/C-24, C-25, C-28; H-27/C-25, C-28; H-28/C-26, C-27, C-30; H-29/C-30; H-42/C-41; H-43/C-41, C-42; H-44/C-42; H-46/C-43, C-44; HRFABMS $[M + Na]^+$ *m*/*z* 693.5245 (calcd for $C_{46}H_{70}O_3Na$ 693.5223).

Preparation of MTPA esters. To a stirred solution of a polyacetylene (1−2 mg) in dry pyridine (0.3 mL) was added (*S*)- or (*R*)-MTPA chloride (20 μL). After stirring the mixture under N_2 at room temperature for 1 h, the solvent was removed by blowing with N_2. The residue was redissolved in 30% EtOAc−*n*-hexane (2 mL) and filtered through Sepak silica column. After removing the solvent under vacuum, the residue was separated by reversed-phase HPLC (YMC ODS column, 100% MeCN) to afford MTPA esters of either a polyacetylene (**2**) or polyacetylenic α,β-unsaturated ketones (**5** and **6**). In this manner, the MTPA esters of **2** and **6** were obtained in good yield (71 and 85% for **2*S*** and **2*R***, respectively; 55 and 41% for **6*S*** and **6*R***, respectively), while those of **5** were obtained in lower yield (24 and 29% for **5*S*** and **5*R***, respectively). MTPA treatments of **3** and **4**, however, resulted in rapid decomposition of the reactants.

The polyacetylenes were dissolved in a mixture of dry pyridine (0.1 mL) and 30% EtOAc−*n*-hexane (0.3 mL). The other processes were identical with the first scenario. In this manner, all of the MTPA esters of polyacetylenes (except **3**) were obtained in good yield (56−81%), while **3** was decomposed rapidly.

(*S*)-MTPA ester (2*S*) of 2: ^1H NMR ($CDCl_3$) δ 7.54 (4H, m, Ar), 7.41−7.36 (6H, m, Ar), 6.21 (1H, tt, 2.0, 2.0, H-14), 6.00 (1H, br dt, 10.7, 7.3, H-43), 5.53 (1H, dt, 2.0, 6.8, H-3), 5.44 (1H, ddt, 10.7, 2.4, 1.5, H-44), 5.37−5.34 (3H, m, H-22, H-27, H-28), 5.33 (1H, m, H-21), 3.59 (6H, s, OMe), 3.06 (1H, d, 2.4, H-46), 2.54 (1H, d, 2.0, H-1), 2.32 (2H, ddt, 7.3, 1.5, 7.3, H-42), 2.22 (2H, dt, 2.0, 7.3, H-11), 2.20 (2H, dt, 2.0, 7.3, H-17), 2.04 (2H, m, H-20), 2.03−2.00 (6H, m, H-23, H-26, H-29), 1.79 (2H, m, H-4), 1.50 (2H, m, H-18), 1.49 (2H, m, H-10), 1.41 (4H, m, H-19, H-41), 1.36 (4H, m, H-24, H-25), 1.34 (2H, m, H-30), 1.31 (4H, m, H-5, H-19); HRFABMS $[M + Na]^+$ *m*/*z* 1111.6267 (calcd for $C_{66}H_{86}F_6O_6Na$ 1111.6226).

(*R*)-MTPA ester (2*R*) of 2: ^1H NMR ($CDCl_3$) δ 7.54 (4H, m, Ar), 7.42−7.37 (6H, m, Ar), 6.21 (1H, tt, 2.0, 2.0, H-14), 6.00 (1H, br dt, 10.7, 7.3, H-43), 5.51 (1H, dt, 2.0, 6.6, H-3), 5.44 (1H, ddt, 10.7, 2.0, 1.5, H-44), 5.38−5.34 (3H, m, H-22, H-27, H-28), 5.33 (1H, m, H-21), 3.59 (3H, s, OMe), 3.55 (3H, s, OMe), 3.06 (1H, d, 2.4, H-46), 2.49 (1H, d, 2.0, H-1), 2.32 (2H, ddt, 7.3, 1.5, 7.3, H-42), 2.24 (2H, dt, 2.0, 7.3, H-17), 2.19 (2H, dt, 2.0, 7.3, H-11), 2.04 (2H, m, H-20), 2.03−2.00 (6H, m, H-23, H-26, H-29), 1.85 (2H, m, H-4), 1.52 (2H, m, H-18), 1.47 (2H, m, H-10), 1.44 (2H, m, H-5), 1.42 (4H, m, H-19, H-41), 1.36 (4H, m, H-24, H-25), 1.34 (2H, m, H-30), 1.32 (2H, m, H-9).

(*S*)-MTPA ester (4*S*) of 4: ^1H NMR ($CDCl_3$) δ 7.54 (4H, br t, 8.7, Ar), 7.41−7.36 (6H, m, Ar), 6.75 (1H, dt, 16.1, 6.8, H-20), 6.21 (1H, tt, 2.0, 2.0, H-14), 6.09 (1H, br d, 16.1, H-21), 6.06 (1H, dt, 15.6, 6.8, H-5), 6.00 (1H, br d, 6.8, H-3), 6.00 (1H, dt, 10.7, 7.3, H-43), 5.60 (1H, ddt, 15.6, 6.8, 1.5, H-4), 5.44 (1H, ddt, 10.7, 2.4, 1.0, H-44), 5.36 (1H, m, H-28), 5.33 (1H, m, H-27), 3.59 (3H, s, OMe), 3.55 (3H, s, OMe), 3.06 (1H, d, 2.4, H-46), 2.59 (1H, d, 2.0, H-1), 2.51 (2H, t, 7.3, H-23), 2.32 (2H, br dt, 7.3, 7.3, H-42), 2.26 (2H, dt, 6.8, 7.3, H-19), 2.25 (2H, dt, 2.0, 7.1, H-17), 2.22 (2H, dt, 2.0, 7.1, H-11), 2.08 (2H, br dt, 6.8, 7.3, H-6), 2.04 (2H, dt, 7.3, 7.3, H-26), 2.01 (2H, dt, 6.8, 6.8, H-29), 1.66 (2H, p, 7.3, H-18), 1.62 (2H, p, 7.3, H-24), 1.50 (2H, p, 7.3, H-10), 1.40 (2H, m, H-41), 1.38 (2H, m, H-7), 1.35 (4H, m, H-9, H-25), 1.33 (2H, m, H-30), 1.30 (2H, m, H-8); HRFABMS $[M + Na]^+$ *m*/*z* 1123.5858 (calcd for $C_{66}H_{82}F_6O_7$-Na 1123.5862).

(*R*)-MTPA ester (4*R*) of 4: ^1H NMR ($CDCl_3$) δ 7.54 (4H, m, Ar), 7.42−7.37 (6H, m, Ar), 6.76 (1H, dt, 15.6, 6.8, H-20), 6.20 (1H, tt, 2.0, 2.0, H-14), 6.10 (1H, br d, 15.6, H-21), 6.03 (1H, br d, 6.8, H-3), 6.00 (1H, dt, 15.6, 6.8, H-6), 6.00 (1H, dt, 10.7, 7.3, H-43), 5.50 (1H, ddt, 15.6, 6.8, 1.5, H-5), 5.44 (1H, ddt, 10.7, 2.4, 1.0, H-44), 5.36 (1H, m, H-28), 5.33 (1H, m, H-27), 3.59 (3H, s, OMe), 3.58 (3H, s, OMe), 3.06 (1H, d, 2.4, H-46), 2.63 (1H, d, 2.0, H-1), 2.51 (2H, t, 7.3, H-23), 2.32 (2H, br dt, 7.3, 7.3, H-42), 2.28 (2H, dt, 6.8, 7.3, H-19), 2.27 (2H, dt, 2.0, 7.1, H-17), 2.20 (2H, dt, 2.0, 7.1, H-11), 2.04 (4H, dt, 6.8, 7.3, H-6, H-26), 2.00 (2H, dt, 6.8, 6.8, H-29), 1.68 (2H, p,

7.3, H-18), 1.61 (2H, p, 7.3, H-24), 1.47 (2H, p, 7.3, H-10), 1.39 (2H, m, H-41), 1.35 (4H, m, H-7, H-25), 1.32 (4H, m, H-9, H-30), 1.27 (2H, m, H-8); HRFABMS $[M + Na]^+$ *m/z* 1123.5871 (calcd for $C_{66}H_{82}F_6O_7Na$ 1123.5862); $\Delta(\delta$**4*S*** $- \delta$**4*R***$)$ H-1, −21 Hz; H-4, +51 Hz; H-5, +29 Hz; H-6, +19 Hz; H-10, +14 Hz; H-11, +16 Hz; H-17, −13 Hz; H-18, −11 Hz; H-19, −10 Hz, H-20, −4 Hz; H-21, −4 Hz.

(*S*)-MTPA ester (5*S*) of 5: ^{1}H NMR ($CDCl_3$) δ 7.54 (4H, m, Ar), 7.41−7.36 (6H, m, Ar), 6.82 (1H, dt, 15.6, 6.8, H-29), 6.21 (1H, tt, 2.4, 2.4, H-14), 6.08 (1H, dt, 15.6, 1.5, H-28), 6.06 (1H, ddt, 15.6, 1.0, 6.8, H-5), 6.00 (1H, br d, 6.8, H-3), 6.00 (1H, ddt, 10.7, 1.0, 7.3, H-43), 5.60 (1H, ddt, 15.6, 6.8, 1.5, H-4), 5.44 (1H, ddt, 10.7, 2.4, 1.5, H-44), 5.35 (1H, m, H-22), 5.32 (1H, m, H-21), 3.59 (3H, d, 1.0, OMe), 3.55 (3H, d, 1.0, OMe), 3.06 (1H, d, 2.4, H-46), 2.59 (1H, d, 2.0, H-1), 2.52 (2H, t, 7.3, H-26), 2.32 (2H, ddt, 7.3, 1.5, 7.3, H-42), 2.22 (2H, dt, 2.0, 7.3, H-11), 2.21 (2H, dt, 2.0, 7.3, H-17), 2.20 (2H, ddt, 6.8, 1.5, 7.3, H-30), 2.08 (2H, br dt, 6.8, 7.3, H-6), 2.03 (2H, dt, 7.3, 7.3, H-23), 2.01 (2H, dt, 7.3, 7.3, H-20), 1.61 (2H, p, 7.3, H-25), 1.49 (2H, m, H-10), 1.49 (2H, p, 7.3, H-18), 1.45 (2H, m, H-31), 1.42 (2H, m, H-19), 1.40 (4H, m, H-7, H-41), 1.38 (2H, m, H-9), 1.36 (2H, m, H-24), 1.32 (2H, m, H-8); ^{13}C NMR ($CDCl_3$) δ 147.42 (CH, C-29), 146.29 (CH, C-43), 138.61 (CH, C-5), 130.26 (CH, C-28), 129.78 (CH, C-21), 129.53 (CH, C-22), 123.53 (CH, C-4), 100.89 (CH, C-44), 87.26 (C, C-13/-15), 87.21 (C, C-13/-15), 81.12 (CH, C-46), 78.40 (C, C-2), 75.84 (CH, C-1), 73.56 (C, C-12/-16), 73.54 (C, C-12/-16), 66.29 (CH, C-3), 56.01 (CH, C-14), 39.94 (CH_2, C-27), 32.46 (CH_2, C-30), 31.86 (CH_2, C-6), 30.26 (CH_2, C-42), 27.97 (CH_2, C-10/-18), 27.63 (CH_2, C-10/-18), 27.06 (CH_2, C-23), 26.61 (CH_2, C-20), 23.94 (CH_2, C-25), 18.64 (CH_2, C-11/-17), 18.59 (CH_2, C-11/-17); HRFABMS $[M + Na]^+$ *m/z* 1123.5863 (calcd for $C_{66}H_{82}F_6O_7Na$ 1123.5862).

(*R*)-MTPA ester (5*R*) of 5: ^{1}H NMR ($CDCl_3$) δ 7.54 (4H, m, Ar), 7.41−7.36 (6H, m, Ar), 6.82 (1H, dt, 15.6, 6.8, H-29), 6.21 (1H, tt, 2.0, 2.0, H-14), 6.08 (1H, dt, 15.6, 1.5, H-28), 6.03 (1H, br d, 6.8, H-3), 6.00 (1H, br dt, 15.6, 6.8, H-5), 6.00 (1H, br dt, 10.7, 7.3, H-43), 5.50 (1H, ddt, 15.6, 6.8, 1.5, H-4), 5.44 (1H, ddt, 10.7, 2.0, 1.5, H-44), 5.35 (1H, m, H-22), 5.32 (1H, m, H-21), 3.59 (6H, br s, OMe), 3.06 (1H, d, 2.0, H-46), 2.63 (1H, d, 2.0, H-1), 2.52 (2H, t, 7.3, H-26), 2.32 (2H, ddt, 7.3, 1.5, 7.3, H-42), 2.23 (2H, dt, 2.0, 7.3, H-17), 2.20 (2H, m, H-30), 2.19 (2H, dt, 2.0, 7.3, H-11), 2.04 (2H, m, H-6), 2.03 (2H, m, H-23), 2.01 (2H, m, H-20), 1.61 (2H, p, 7.3, H-25), 1.51 (2H, m, H-18), 1.46 (4H, m, H-10, H-31), 1.42 (2H, m, H-19), 1.40 (2H, m, H-41), 1.37 (2H, m, H-24), 1.35 (4H, m, H-7, H-9), 1.29 (2H, m, H-8); HRFABMS $[M + Na]^+$ *m/z* 1123.5856 (calcd for $C_{66}H_{82}F_6O_7Na$ 1123.5862); $\Delta(\delta$**5*S*** $- \delta$**5*R***$)$ H-1, −21 Hz; H-4, +50 Hz; H-5, +36 Hz; H-6, +19 Hz; H-11, +17 Hz; H-17, −14 Hz.

(*S*)-MTPA ester (6*S*) of 6: ^{1}H NMR ($CDCl_3$) δ 7.54 (4H, m, Ar), 7.42−7.37 (6H, m, Ar), 6.81 (1H, dt, 15.6, 6.8, H-26), 6.09 (1H, br d, 15.6, H-27), 6.07 (1H, dt, 15.6, 6.8, H-5), 6.00 (1H, br d, 6.8, H-3), 6.00 (1H, dt, 10.7, 7.3, H-43), 5.60 (1H, ddt, 15.6, 6.8, 1.5, H-4), 5.44 (1H, ddt, 10.7, 2.0, 1.5, H-44), 5.36 (1H, m, H-22), 5.34 (1H, m, H-21), 3.59 (3H, br s, OMe), 3.55 (3H, br s, OMe), 3.06 (1H, d, 2.0, H-46), 2.59 (1H, d, 2.0, H-1), 2.51 (2H, t, 7.3, H-29), 2.32 (2H, ddt, 7.3, 1.0, 7.3, H-42), 2.22 (2H, dt, 2.0, 7.3, H-11), (2.21, 2H, dt, 2.0, 7.3, H-17), 2.20 (2H, m, H-25), 2.08 (2H, m, H-6), 2.04 (2H, m, H-23), 2.02 (2H, m, H-20), 1.59 (2H, p, 7.3, H-30), 1.53 (2H, m, H-24), 1.51 (2H, m, H-10), 1.50 (2H, p, 7.3, H-18), 1.43 (2H, m, H-19), 1.41 (6H, m, H-7, H-9, H-41), 1.32 (2H, m, H-8); ^{13}C NMR ($CDCl_3$) δ 200.91 (C, C-28), 146.82 (CH, C-26), 146.31 (CH, C-43), 138.60 (CH, C-5), 130.44 (CH, C-27), 129.64 (CH, C-21), 129.20 (CH, C-22), 123.53 (CH, C-4), 107.88 (CH, C-44), 87.28 (C, C-13/-15), 87.14 (C, C-13/-15), 81.12 (CH, C-46), 78.41 (C, C-2), 75.84 (CH, C-1), 73.73 (C, C-12/-16), 73.59 (C, C-12/-16), 66.29 (CH, C-3), 56.00 (CH, C-14), 55.53 (CH_3 × 2, OMe), 40.20 (CH_2, C-29), 31.95 (CH_2, C-25), 31.86 (CH_2, C-6), 30.27 (CH_2, C-43), 28.67 (CH_2, C-19), 27.97 (CH_2, C-18), 27.66 (CH_2, C-24), 26.70 (CH_2, C-20/-23), 26.67 (CH_2, C-23), 24.32 (CH_2, C-30), 18.65 (CH_2, C-11/-17), 18.58 (CH_2, C-11/-17); HRFABMS $[M + Na]^+$ *m/z* 1123.5863 (calcd for $C_{66}H_{82}F_6O_7Na$ 1123.5862).

(*R*)-MTPA ester (6*R*) of 6: ^{1}H NMR ($CDCl_3$) δ 7.54 (4H, m, Ar), 7.42−7.36 (6H, m, Ar), 6.81 (1H, dt, 15.6, 6.8, H-26), 6.21 (1H, tt, 2.0, 2.0, H-14), 6.09 (1H, br d, 15.6, H-27), 6.03 (1H, m, H-3), 6.00 (1H, br dt, 15.6, 6.8, H-5), 6.00 (1H, dt, 10.7, 7.3, H-43), 5.50 (1H, ddt, 15.6, 6.8, 1.5, H-4), 5.44 (1H, ddt, 10.7, 2.0, 1.5, H-44), 5.36 (1H, m, H-22), 5.34 (1H, m, H-21), 3.59 (6H, br s, OMe), 3.07 (1H, d, 2.0, H-46), 2.63 (1H, d, 2.4, H-1), 2.51 (2H, t, 7.3, H-29), 2.32 (2H, br dt, 7.3, 7.3, H-42), 2.24 (2H, dt, 2.0, 7.3, H-17), 2.21 (2H, m, H-25), 2.19 (2H, dt, 2.0, 7.3, H-11), 2.06 (2H, m, H-6), 2.04 (2H, m, H-23), 2.01 (2H, m, H-20), 1.59 (2H, m, H-30), 1.52 (2H, p, 7.3, H-18), 1.52 (2H, m, H-24), 1.46 (2H, m, H-10), 1.43 (2H, m, H-19), 1.41 (2H, m, H-41), 1.39 (2H, m, H-7), 1.34 (2H, m, H-9), 1.28 (2H, m, H-8); ^{13}C NMR ($CDCl_3$) δ 200.91 (C, C-28), 146.82 (CH, C-26), 146.31 (CH, C-43), 138.24 (CH, C-5), 130.44 (CH, C-27), 129.64 (CH, C-21), 129.20 (CH, C-22), 123.37 (CH, C-4), 107.88 (CH, C-44), 87.25 (C, C-13/-15), 87.18 (C, C-13/-15), 81.12 (CH, C-46), 78.62 (C, C-2), 75.90 (CH, C-1), 73.80 (C, C-16), 73.52 (C, C-12), 65.98 (CH, C-3), 56.00 (CH, C-14), 55.53 (CH_3 × 2, OMe), 40.20 (CH_2, C-29), 31.95 (CH_2, C-25), 31.81 (CH_2, C-6), 30.27 (CH_2, C-42), 27.93 (CH_2, C-18), 27.66 (CH_2, C-24), 26.70 (CH_2, C-20/-23), 26.67 (CH_2, C-20/-23), 24.32 (CH_2, C-30), 18.64 (CH_2, C-11/-17), 18.61 (CH_2, C-11/-17); HRFABMS $[M + Na]^+$ *m/z* 1123.5859 (calcd for $C_{66}H_{82}F_6O_7Na$ 1123.5862); $\Delta(\delta$**6*S*** $- \delta$**6*R***$)$ H-1, −22 Hz; H-4, +51 Hz; H-5, +36 Hz; H-6, +19 Hz; H-11, +16 Hz; H-17, −13 Hz.

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