Novel Meroditerpenes from the Brown Alga *Cystoseira* sp.

Guillermo Navarro, José J. Fernández, and Manuel Norte*

Instituto Universitario de Bio-Orgánica "Antonio González", Universidad de La Laguna, Astrofísico Francisco Sánchez 2, 38206 La Lguna, Tenerife, Spain
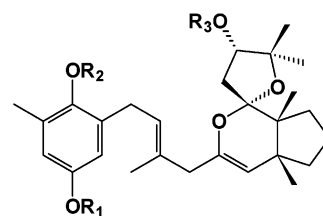
Five new meroditerpenes have been isolated from a brown alga of the genus *Cystoseira* collected around the Canary Islands. One, cystoseirone diacetate (**3**), possesses a new rearranged structure with an unusual ether linkage in the diterpene side chain. Its biogenetic origin was explained as derived from the oxidation of amentol chromane diacetate (**2**) and subsequent cyclization. Structures were determined through the interpretation of the spectral data and by means of chemical transformations. The relative stereochemistry was proposed on the basis of ROESY correlations.

Over 55 different species of the genus *Cystoseira* collected in the Mediterranean sea have been studied for their chemistry by Italian and French groups and have yielded an array of metabolites, mainly diterpenes derived from geranylgeranyltoluquinol by oxidation and cyclization.[1−3] By comparison, species from the eastern Atlantic coast have barely been studied, chemical investigations of only six species from north Morocco[3] and two from the Canary Islands having been previously reported.[4,5]
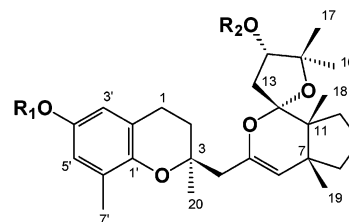
This paper describes the further investigation of the alga *Cystoseira* sp. collected at Montaña Clara Island by scuba at −10 m and then dried and extracted with acetone.

Amentol (**1**)[6] was the major known compound to be isolated, together with five new meroditerpenes, most of them studied in their acetate form due to instability: amentol chromane diacetate (**2**), cystoseirone diacetate (**3**), preamentol triacetate (**4**), 14-*epi*-amentol triacetate (**5**), and 14-methoxyamentol chromane (**6**), which was isolated from selected nonacetylated fractions.
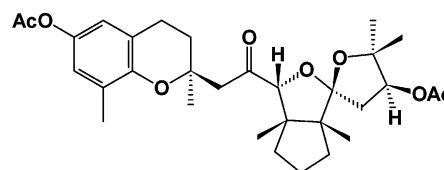
HREIMS data obtained for amentol chromane diacetate (**2**) gave its molecular formula as $C_{31}H_{42}O_7$. The IR spectrum showed absorption bands at 1764 and 1739 cm^{-1}, indicating carbonyl ester groups, while the presence of a chromane moiety was suggested by UV absorptions at 280 and 220 nm. In the ^{1}H NMR spectrum, the presence of two aromatic protons at δ_H 6.61 (H-5′) and 6.67 (H-3′), an aromatic methyl group at δ_H 2.15 (H$_3$-7′), and the aromatic acetyl group H$_3$-Ac-4′ (δ_H 2.32) characterized the mono-acetoxy-methyl-hydroquinone unit (Table 1). Two coupled methylene groups were also recorded at δ_H 1.78 (H-2β), 1.85 (H-2α), and 2.73 (H$_2$-1) and a methyl group attached to an oxygenated quaternary carbon at δ_H 1.36 (H$_3$-20, s). These features, in conjunction with the presence of the corresponding quaternary carbon at δ_C 76.0 (C-3) and the MS fragment at m/z 219.1032 (calcd for $[C_{13}H_{15}O_3]^+$, 219.1021), were also consistent with a chromane moiety. The ^{1}H NMR signals corresponding to the remainder of the diterpene fragment consisted of an ABX system centered at δ_H 2.20 (H-13β, dd, J = 4.5 and 14.3 Hz), 2.46 (H-13α, dd, J = 7.0 and 14.3 Hz), and 5.15 (H-14, dd, J = 4.5 and 7.0 Hz) for a −CH$_2$−CH−OAc− fragment; an isolated methylene group at δ_H 2.28 (H$_2$-4); an olefinic proton at δ_H 4.33 (H-6, s); four methyl groups attached to quaternary carbons at δ_H 1.15 (H$_3$-16), 1.35 (H$_3$-17), 1.01 (H$_3$-18), and 1.10 (H$_3$-19); and finally, three coupled methylene groups at δ_H

* To whom correspondence should be addressed. Tel: 34 922 318586. Fax: 34 922 318571. E-mail: mnorte@ull.es.

Amentol, R$_1$=R$_2$=R$_3$=H (1)
Amentol triacetate, R$_1$=R$_2$=R$_3$=Ac (8)

Amentol chromane diacetate, R$_1$=R$_2$=Ac (2)
14-Methoxy-amentol chromane, R$_1$=H; R$_2$=CH$_3$ (6)

Cystoseirone diacetate (3)

1.45 (H-8α), 1.70 (H-8β), 1.50 (H$_2$-9), and 1.25 (H-10β), 1.85 (H-10α). The ^{1}H and ^{13}C assignments were secured from HSQC and HMBC correlations.
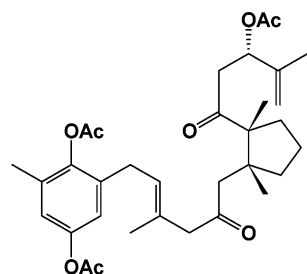
The relative configurations of the stereocenters C-7, C-11, C-12, and C-14 were established on the basis of ROESY correlations as R^*, R^*, R^*, and S^*, respectively, proving similar to those found in amentol (**1**).[6] The relative stereochemistry at C-3 was assigned as S^* in agreement with the cross-peaks observed in the ROESY experiment between H-6 and H-2β, H$_2$-4, H-8α, H$_3$-19, and protons H$_3$-20 and H-2α, H$_2$-4 (Figure 1).

Cystoseirone diacetate (**3**) was isolated as an oil. The high-resolution mass spectrum of this compound showed a peak at m/z 542.2875 to give $C_{31}H_{42}O_8$. IR bands at 1759, 1745, and 1715 cm^{-1} corresponded to two carbonyl esters and a ketone. Comparison of the NMR spectral data with those of compound **2** showed that cystoseirone diacetate
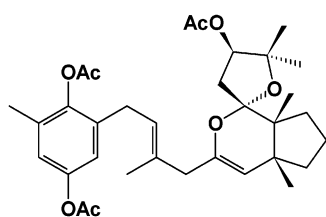
Isocystoseirone diacetate (7)

Preamentol triacetate (4)

14-*epi*-Amentol triacetate (5)

Table 1. ¹H NMR Data for Compounds **2**−**6**

proton	**2**	**3**	**4**	**5**	**6**
3′	6.67	6.61	6.83	6.83	6.46
5′	6.61	6.68	6.79	6.83	6.38
7′	2.15	2.16	2.14	3.21	2.11
1	2.73	2.73	3.24	5.32	2.61/2.90
2	1.78/1.85	1.95/2.08	5.27	5.32	1.71/1.82
4	2.28	2.83/2.93	3.06	2.68	2.22/2.34
6	4.33	4.13	2.26/2.43	4.30	4.32
8	1.45/1.70	1.35/1.45	1.71	1.45/1.72	1.45/1.70
9	1.50	1.40	1.79	1.51	1.70
10	1.25/1.85	1.35/1.60	1.52	1.25/1.75	1.35/1.80
13	2.20/2.46	2.07/2.66	2.65/2.94	2.08/2.49	2.04/2.50
14	5.15	5.18	5.60	5.00	3.36
16	1.15	1.30	4.90/4.99	1.32	1.34
17	1.35	1.12	1.67	1.36	1.26
18	1.01	0.93	1.18	1.09	0.93
19	1.10	1.22	1.14	0.94	1.12
20	1.36	1.40	1.75	1.66	1.26
COOC*H₃*-1′		2.07	2.33	2.34	
COOC*H₃*-4′	2.32	2.25	2.27	2.26	
COOC*H₃*-14	2.06		2.00	2.03	
*H₃*CO-14					3.36
*H*O-4′					4.31

Figure 1. Lowest energy conformation of amentol chromane diacetate (**2**) and significant ROE correlations.

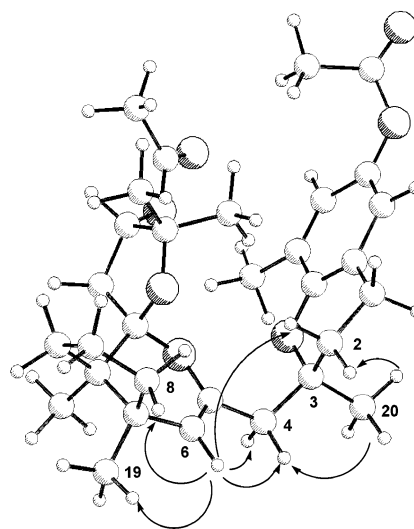(**3**) also has a chromane moiety. Although the rest of the diterpene side chain contained most of the typical systems observed for this series, there were some significant differences in the chemical shifts. In the ¹H NMR spectrum, the ABX system due to the C-13 to C-14 fragment, centered at δ_H 2.07 (H-13α, dd, $J = 7.0$ and 14.0 Hz), 2.66 (H-13β, dd, $J = 7.0$ and 14.0 Hz), and 5.18 (H-14, dd, $J = 7.0$ and 7.0 Hz), two angular methyl groups at δ_H 1.30 (H₃-16, s) and 1.12 (H₃-17, s), a −CH₂−CH₂−CH₂− moiety, a C-8 to C−10 fragment centered at δ_H 1.35 and 1.45 (H₂-8), 1.40 (H₂-9), 1.60 and 1.35 (H₂-10), all of which are common to this series, were observed. The most remarkable differences in comparison with compound **2** were those of the signals centered at δ_H 2.83 (d, $J = 16.5$ Hz) and 2.93 (d, $J = 16.5$ Hz) assigned to H₂-4 and at δ_H 4.13 assigned to H-6 (s). Comparison of the ¹³C NMR spectra revealed that the signals for carbons C-4 (δ_C 44.7), C-5 (δ_C 144.5), and C-6 (δ_C 111.7) in **2** were replaced by new signals at δ_C 49.1, 208.5, and 90.0, respectively, in compound **3**, and this was confirmed by the correlations observed in the HMBC experiment between H₂-4 (δ_H 2.83 and 2.93) and C-3 (δ_C 75.5), C-5 (δ_C 208.5) and between H-6 (δ_H 4.13) and C-5, C-7 (δ_C 53.0), C-8 (δ_C 38.7). These data suggested the presence of a carbonyl group at C-5 and a tetrahydrofuran ring instead of the enol-ether from the classical dihydropyran system. Meanwhile correlations between H₃-18 (δ_H 0.93) and C-7, C-10 (δ_C 40.7), C-11 (δ_C 56.3), and C-12 (δ_C 115.2) and between H₃-19 (δ_H 1.22) and C-6, C-7, and C-8 situated the cyclopentane ring in the molecule. Correlation of H₂-13 (δ_H 2.07 and 2.66) with C-12, C-14 (δ_C 78.6) and C-15 (δ_C 83.2), and H₃-16 and H₃-17 with C-15, confirmed the structure proposed for compound **3**.

Once the planar structure had been established, the biogenetic origin of compound **3** could be attributed to oxidation of the enol-ether system in compound **2** and subsequent rearrangement. On the basis of this hypothesis, a chemical correlation was achieved by treating compound **2** with MCPBA in dichloromethane to afford two isomers,

one of which was identical to **3**, and the other was given the name isocystoseirone diacetate (**7**).

The relative stereochemistries of carbons C-3, C-7, C-11, and C-14 in compounds **3** and **7** were established by ROESY correlations as identical to those observed for compound **2**. The chirality at C-6 was proposed as R^* according to the correlations with methyl groups H₃-18 and H₃-19, while that at C-12 was established as follows. In compound **3**, the methyl group H₃-18 was correlated with H-10β, while H-10α was correlated with H-13β, which, in turn, was correlated with the methyl group H₃-16. Taking into account that the acetate methine H-14 showed correlations with H₃-17, it was concluded that H-13β and H₃-16 must be on the same face of the acetate group. These results allowed us to assign the relative configuration at C-12 as S^*. However, in compound **7**, H-10β still correlated with H₃-18, while H-13α showed correlations to both H₃-18 and H₃-19. These correlations could be accounted for only if **7** is an epimer of **3** at C-12, with a relative configuration $12R^*$ (Figure 2).

Following these results, a plausible mechanism for the conversion of compound **2** into **3** and **7** is present in Scheme 1. Compound **3** is the first example of a meroditerpene possessing this new rearranged structure with an unusual
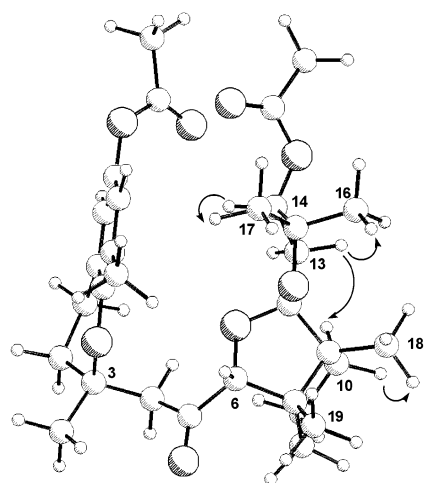
Cystoseirone diacetate (3)
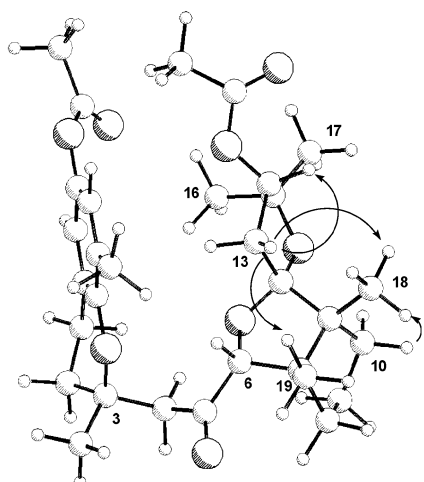
Isocystoseirone diacetate (7)

Figure 2. Lowest energy conformation and significant NOE for cystoseirone diacetate (**3**) and isocystoseirone diacetate (**7**).

ether linkage between the C-6 and C-12 to the diterpene side chain.

Compound **4**, preamentol triacetate, oil $[\alpha]^{25}_D$ +4.1 (*c* 0.04, CHCl₃), was assigned a molecular formula of $C_{33}H_{44}O_8$ by HREIMS (*m/z* 568.3037). The IR spectrum presented bands at 1764 and 1717 cm^{-1}, indicating two carbonyl groups, while UV absorptions at 270 and 202 suggested a hydroquinol chromophore. The NMR data of this compound were very similar to those observed for bifurcarenone,[7] the difference being the absence of the α,β-conjugated ketone system, which was replaced by an isolated ketone and a double bond. The ketone was located at C-12 by HMBC correlations to the quaternary center (δ_C 212.3) from H₃-19 (δ_H 1.14) and H₂-13 (δ_H 2.65 and 2.94), while the double bond was placed at C-15 by the correlations between the ^{13}C signal at δ_C 143.5 and H-14 (δ_H 5.60), H₂-16 (δ_H 4.99 and 4.90), and H₃-17 (δ_H 1.67), establishing a double bond between C-15 and C-16.

The relative configurations of the stereocenters in **4** proved identical to those of the other meroditerpenes, 7*R**, 11*R**, and 14*S**, respectively, according to the correlations observed in the ROESY experiment.

Compound **5**, 14-*epi*-amentol triacetate, was also isolated from this alga, together with its isomer amentol triacetate (**8**). Interpretation of COSY, HMQC, and HMBC data led

to assignments of ^{1}H and ^{13}C NMR signals, which readily demonstrated that the only differences between **5** and **8** were those observed in the carbons C-13 and C-14. In compound **8**, the ^{1}H NMR chemical shifts for this fragment were centered at δ_H 2.46 (H-13α, dd, $J_{13\alpha,14}$ = 7.0 Hz, $J_{13\alpha-13\beta}$ = 14.4 Hz), 2.10 (H-13β, dd, $J_{13\beta,14}$ = 4.4 Hz, $J_{13\alpha-13\beta}$ = 14.4 Hz), and 5.12 (H-14, dd, $J_{13\alpha-14}$ = 7, $J_{13\beta-14}$ = 4.4 Hz), while in compound **5** they were centered at δ_H 2.08 (H-13α, dd, $J_{13\alpha,14}$ = 1.4 Hz, $J_{13\alpha-13\beta}$ = 14.4 Hz), 2.49 (H-13β, dd, $J_{13\beta,14}$ = 7.3 Hz, $J_{13\alpha-13\beta}$ = 14.4 Hz), and 5.00 (H-14, dd, $J_{13\alpha-14}$ = 1.8, $J_{13\beta-14}$ = 7.3 Hz). These data clearly established compound **5** as an epimer of compound **8** at the chiral center C-14, in agreement with the strong ROESY correlation observed in compound **5** between H-14 and H₃-17 (δ_H 1.36) and H-13β, which established the relative configuration at C-14 as *R**.

Finally, nonacetylated fractions of this alga yielded 14-methoxyamentol chromane (**6**) as a colorless oil, $[\alpha]^{25}_D$ +17.6 (*c* 0.15, CHCl₃). Its spectral data showed that the chemical structure was closely related to that observed for compound **2**, the main difference being the methoxy group at C-14 in compound **6** (δ_H 3.36, s; δ_C 58.1). This was corroborated by HMBC correlations between the methoxy protons and C-14 (δ_C 82.0). The relative configuration at this center was proposed as *S** on the basis of ROESY correlations and the coupling constants being equivalent to those found in amentol chromane diacetate (**2**).

Experimental Section

General Experimental Procedures. Optical rotations were determined on a Perkin-Elmer 241 polarimeter. IR spectra were measured on a Bruker IFS55 spectrometer. The NMR spectra were obtained with a Bruker Avance 400 instrument. Chemical shifts are reported relative to TMS, and coupling constants are given in Hz. HREIMS were taken on a VG AutoSpec FISON spectrometer. HPLC was carried out with a LKB 2248 system equipped with a differential diffractometer detector. Silica gel CC and TLC were performed on silica gel Merck 60 G. TLC plates were visualized by spraying with $H_2SO_4-H_2O-HOAc$ (1:4:20) and heating.

Plant Material. Specimens of *Cystoseira* sp. were collected by scuba at −10 m at Montaña Clara Island (Canary Islands). Dried material of sterile plants was deposited in the TFC Phyc 5640 (Herbario de La Universidad de La Laguna, Departamento de Biología Vegetal, Botánica, Tenerife).

Extraction and Isolation. The dried algae were extracted with acetone and dichloromethane at room temperature, and the combined extracts were evaporated in vacuo to leave a dark green viscous oil. The crude residue was chromatographed on a silica gel column eluted with increasing concentrations of EtOAc in *n*-hexane. Fractions of 100 mL were collected, and those exhibiting similar TLC were combined. Fractions eluted with *n*-hexane−EtOAc (7:3) contained crude amentol (**1**) and 14-methoxyamentol chromane (**6**), which were purified by chromatography on Sephadex LH-20 with *n*-hexane−CHCl₃−MeOH (2:1:1), and a final purification with HPLC on a *μ*-Porasil column eluted with a mixture of *n*-hexane−EtOAc (7:3) was achieved, yielding **1** (300 mg) and **6** (9 mg). The attempts to purify the other metabolites failed due to their instability. These fractions from the silica gel column were combined, the solvent was evaporated, and the crude extract was acetylated with Ac₂O−Py (1:1) followed by the usual workup. The crude extract (10 g) was chromatographed on a silica gel column eluted with *n*-hexane−EtOAc (8:2) and purified by HPLC on a *μ*-Porasil column, affording the pure acetylated compounds amentol chromane diacetate **2** (21 mg), cystoseirone diacetate **3** (23 mg), preamentol triacetate **4** (6 mg), and 14-*epi*-amentol chromane diacetate **5** (2 mg). From the nonacetylated fractions an equivalent chomatography process eluted with *n*-hexane−EtOAc (7:3) yielded 14-methoxyamentol **6** (9 mg).

Scheme 1. Chemical Transformation of Compound **2** to Compounds **3** and **7**
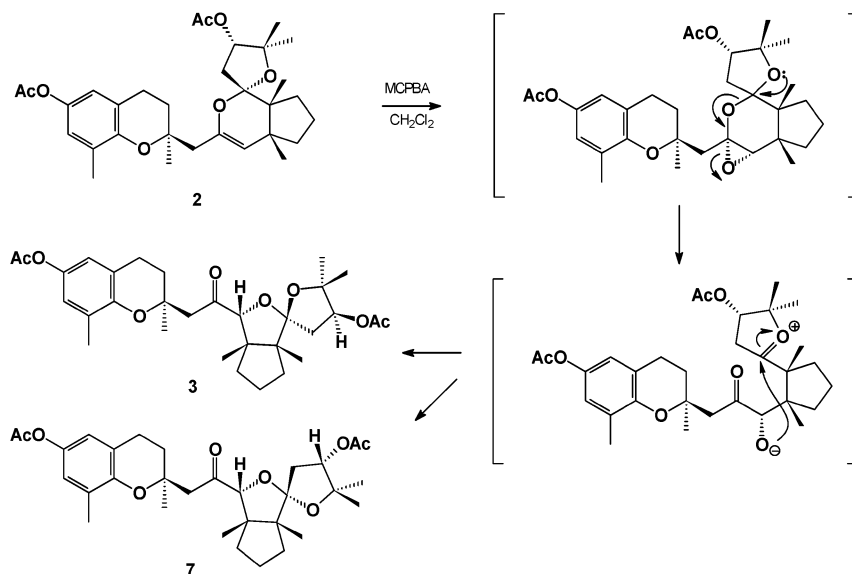
Table 2. ^{13}C NMR Data for Compounds **2**−**6**

carbon	2	3	4	5	6
1′	149.6	142.8	145.5	147.3	147.7
2′	120.8	120.9	134.6	133.6	121.4
3′	119.0	119.1	120.4	119.6	112.5
4′	142.5	149.1	147.9	148.3	145.8
5′	121.7	121.3	121.7	115.2	115.2
6′	127.3	127.4	131.5	131.5	127.2
7′	16.2	16.2	16.5	16.5	16.0
1	22.5	22.4	28.9	28.3	24.9
2	30.5	30.0	126.1	124.5	31.5
3	76.0	75.5	134.6	133.5	75.1
4	44.7	49.1	55.4	44.6	44.0
5	144.5	208.5	208.9	144.0	145.6
6	111.7	90.0	47.8	106.1	106.5
7	46.4	53.0	47.0	44.4	43.0
8	40.4	38.7	37.3	37.6	40.4
9	20.5	24.3	19.8	20.9	20.4
10	36.0	40.7	34.8	35.7	36.2
11	43.3	56.3	60.4	47.0	47.0
12	109.1	115.2	212.3	110.0	111.2
13	41.1	38.7	43.6	40.2	40.7
14	78.8	78.6	72.9	79.9	82.0
15	83.7	83.2	143.5	84.1	86.6
16	21.0	22.9	112.7	27.7	29.6
17	28.0	28.2	18.6	21.1	22.2
18	19.6	18.0	20.2	20.6	19.6
19	20.9	24.1	21.6	19.6	22.7
20	25.3	24.9	16.6	15.6	27.9
*C*OOCH$_3$-1′			169.0	172.7	
COO*C*H$_3$-1′			20.5	23.6	
*C*OOCH$_3$-4′	170.5	170.4	170.0	171.5	
COO*C*H$_3$-4′	22.7	20.1	20.1	23.0	
*C*OOCH$_3$-14	170.2	170.2	170.0	170.4	
COO*C*H$_3$-14	21.1	21.0	20.1	22.6	
H$_3$CO-14					58.1

Compound 2: colorless oil; $[\alpha]^{25}_D$ +6.0° (*c* 0.19, CHCl$_3$); UV (MeOH) λ_{max} (log ϵ) 280 (3.36) and 220 (ϵ 3.97) nm; IR (CHCl$_3$) ν_{max} 2960, 2932, 2872, 1764, 1739, 1683, and 1472 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz), Table 1; ^{13}C NMR (CDCl$_3$, 100 MHz), Table 2; EIMS *m/z* 526 (12), 466 (11), 316 (16), 233 (13), 220 (15), and 219 (100); HREIMS *m/z* 526.2935 (calcd for C$_{31}$H$_{42}$O$_7$, 526.2930).

Compound 3: colorless oil; $[\alpha]^{25}_D$ +26.9° (*c* 0.0125, CHCl$_3$); UV (MeOH) λ_{max} (log ϵ) 280 (3.38) and 205 (4.05) nm; IR (CHCl$_3$) ν_{max} 2954, 2358, 1759, 1745, 1715, and 1474 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz), Table 1; ^{13}C NMR (CDCl$_3$, 100 MHz), Table 2; HREIMS *m/z* 542.2875 (calcd for C$_{31}$H$_{42}$O$_8$, 542.2880).

Compound 4: colorless oil; $[\alpha]^{25}_D$ +4.1° (*c* 0.004, CHCl$_3$); UV (MeOH) λ_{max} (log ϵ) 270 (3.46) and 202 (4.08) nm; IR

(CHCl$_3$) ν_{max} 2962, 2873, 1764, 1717, 1474, and 1368 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz), Table 1; ^{13}C NMR (CDCl$_3$, 100 MHz), Table 2; HREIMS *m/z* 568.3037 (calcd for C$_{33}$H$_{44}$O$_8$, 568.3036).

Compound 5: colorless oil; $[\alpha]^{25}_D$ −15.2° (*c* 0.023, CHCl$_3$); UV (MeOH) λ_{max} (log ϵ) 285 (3.40) and 208 (4.08) nm; IR (CHCl$_3$) ν_{max} 2961, 2933, 2872, 1760, 1743, 1685, and 1475 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz), Table 1; ^{13}C NMR (CDCl$_3$, 100 MHz), Table 2; EIMS *m/z* 568 (6), 508 (10), 538 (14), 303 (13), and 233 (61); HREIMS *m/z* 568.3033 (calcd for C$_{33}$H$_{44}$O$_8$, 568.3036).

Compound 6: colorless oil; $[\alpha]^{25}_D$ +17.6° (*c* 0.015, CHCl$_3$); UV (MeOH) λ_{max} (log ϵ) 280 (3.40) and 220 (3.97) nm; IR (CHCl$_3$) ν_{max} 2958, 2931, 2867, 1784, 1733, 1684, and 1471 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz), Table 1; ^{13}C NMR (CDCl$_3$, 100 MHz), Table 2; EIMS *m/z* 456 (18), 424 (9), 287 (3), 274 (100), and 190 (54); HREIMS *m/z* 456.2867 (calcd for C$_{38}$H$_{40}$O$_5$, 456.2876).

Compound 7: colorless oil; $[\alpha]^{25}_D$ +46.0° (*c* 0.0141, CHCl$_3$); UV (MeOH) λ_{max} (log ϵ) 280 (3.41) and 220 (4.01) nm; IR (CHCl$_3$) ν_{max} 2932, 1744, 1473, 1369, 1204, and 1023 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.63 (H-3′), 6.69 (H-5′); 2.15 (H$_3$-7′), 2.74 (H$_2$-1); 1.94 (H-2), 2.07 (H-2), 2.74 (H-4), 2.84 (H-4), 4.25 (H-6), 1.35 (H-8), 1.45 (H-8), 1.20 (H-9), 1.60 (H-9), 1.40 (H-10), 1.65 (H-10), 2.09 (H-13), 2.68 (H-13), 5.18 (H-14), 1.12 (H$_3$-16), 1.33 (H$_3$-17), 0.92 (H$_3$-18), 1.14 (H$_3$-19), 1.40 (H$_3$-20), 2.07 (COOC*H*$_3$-4′), and 2.25 (COOC*H*$_3$-14); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 142.9 (C, C-1′), 120.7 (C, C-2′), 119.1 (CH, C-3′), 150.0 (C, C-4′), 121.4 (CH, C-5′), 127.5 (C, C-6′), 16.3 (CH$_3$, C-7′), 22.2 (CH$_2$, C-1), 31.4 (CH$_2$, C-2), 75.4 (C, C-3), 49.1 (CH$_2$, C-4), 207.8 (C, C-5), 89.7 (CH, C-6), 54.2 (C, C-7), 38.7 (CH$_2$, C-8), 24.2 (CH$_2$, C-9), 40.6 (CH$_2$, C-10), 56.6 (C, C-11), 115.3 (C, C-12), 38.7 (CH$_2$, C-13), 78.6 (CH, C-14), 83.3 (C, C-15), 22.8 (CH$_3$, C-16), 28.1 (CH$_3$, C-17), 17.9 (CH$_3$, C-18), 24.1 (CH$_3$, C-19), 24.4 (CH$_3$, C-20), 170.1 (*C*OOCH$_3$-4′), 21.1 (COO*C*H$_3$-4′), 170.0 (*C*OOCH$_3$-14), and 21.0 (COO*C*H$_3$-14); HREIMS *m/z* 542.2881 (calcd for C$_{31}$H$_{42}$O$_8$, 542.2880).

Compound 8: oil; $[\alpha]^{25}_D$ +21.9° (*c* 0.019, CHCl$_3$); IR (CHCl$_3$) ν_{max} 2960, 2935, 2872, 1764, 1739, 1683, and 1472 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.81 (H-3′), 6.78 (H-5′); 2.14 (H$_3$-7′), 3.18 (H$_2$-1); 5.30 (H-2), 2.65 (H$_2$-4), 4.26 (H-6), 1.80−1.30 (H$_2$-8, H$_2$-9, H$_2$-10), 2.10 (H-13), 2.46 (H-13), 5.12 (H-14), 1.31 (H$_3$-16), 1.14 (H$_3$-17), 1.09 (H$_3$-18), 1.00 (H$_3$-19), 1.64 (H$_3$-20), 2.32 (COOC*H*$_3$-1′), 2.26 (COOC*H*$_3$-4′), and 2.06 (COOC*H*$_3$-14); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 146.2 (C, C-1′), 134.6 (C, C-2′), 119.9 (CH, C-3′), 148.0 (C, C-4′), 121.5 (CH, C-5′), 131.5 (C, C-6′), 16.5 (CH$_3$, C-7′), 28.5 (CH$_2$, C-1), 122.9 (CH, C-2), 134.7 (C, C-3), 44.7 (CH$_2$, C-4), 145.0 (C, C-5), 109.0 (CH, C-6), 43.3 (C, C-7), 40.4 (CH$_2$, C-8), 24.6 (CH$_2$, C-9), 36.1 (CH$_2$, C-10), 46.6 (C, C-11), 110.0 (C, C-12), 41.2 (CH$_2$, C-13), 79.0 (CH, C-14), 83.7 (C, C-15), 27.9 (CH$_3$, C-16), 21.0 (CH$_3$, C-17), 20.5

(CH$_3$, C-18), 19.6 (CH$_3$, C-19), 15.8 (CH$_3$, C-20), 170.4 (COOCH$_3$-1′), 22.8 (COOCH$_3$-1′), 169.4 (COOCH$_3$-4′), 22.6 (COOCH$_3$-4′), 168.7 (COOCH$_3$-14), and 21.1 (COOCH$_3$-14); EIMS *m/z* 568 (13), 508 (12), 358 (9), 234 (11), and 210 (53).

Chemical Transformation of Compound 2 to Compound 3. Amentol chromane diacetate (**2**) (9.2 mg, 0.0175 mmol) was dissolved in dichloromethane (1 mL) and the solution stirred at 0 °C. A solution of MCPBA (4.6 mg, 0.27 mmol) in dichloromethane (0.5 mL) was added dropwise, and the mixture was stirred at 25 °C for 2 h. The mixture was poured onto ice, extracted with dicloromethane, and worked up as usual. The reaction crude was chromatographed on a silica gel column eluted with a mixture of *n*-hexane−AcOEt (7:3), yielding 1.9 mg of **3** (21%) and 2.8 mg of **7** (31%).

Supporting Information Available: Photo of the brown alga *Cystoseira*. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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