New Chromane Derivatives Isolated from the Brown Alga, *Sargassum micracanthum*

Makoto IWASHIMA,*[,a] Natsuko TAKO,[b] Tomoyo HAYAKAWA,[b] Takayuki MATSUNAGA,[c] Jun MORI,[d] and Haruo SAITO[d]

[a] *Graduate School of Medicine and Pharmaceutical Sciences, University of Toyama;* [b] *Faculty of Pharmaceutical Sciences, University of Toyama; 2630 Sugitani, Toyama 930–0194, Japan:* [c] *Toyama Prefectural Institute for Pharmaceutical Research; 17–1 Nakataikoyama, Imizu, Toyama 939–0363, Japan: and* [d] *Department of Pharmaceutical Research, Lead Chemical Co., Ltd.; 77–3 Himata, Toyama 930–0912, Japan.*

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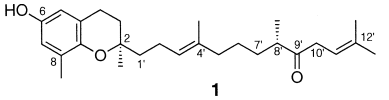
Two new chromane type meroterpenoids were isolated from the methanolic extract of the brown alga, *Sargassum micracanthum*. Their structures were elucidated based on spectroscopic analysis and chemical conversion. The absolute stereochemistry of the methyl group at C-8′ in 1 and related compounds were determined by modified Mosher's method.

Key words plastoquinone; chromane; tocotorienol; modified Mosher's method; *Sargassum micracanthum*

From the many species belonging to the brown algae of the genus *Sargassum* (Sargassaceae, Fucales), structurally unique secondary metabolites with various biological activities have been found.[1—3] Concerning these bioactive metabolites, the structure–activity-relationship towards the development of new drugs or supplements, and the biological functions in the algae themselves were yet unclear. In the course of our investigations[1,2] on biologically active constituents from algae, two new chromane derivatives **1** and **2** were isolated from the brown alga, *Sargassum micracanthum* (KUETZING) ENDLICHER (togemoku in Japanese). In this paper, we wish to report the isolation and structural elucidation of the new chromanes from this alga.

The chloroform–methanol (3 : 1) soluble portion of the methanol extract of *S. micracanthum*, collected at the Toyama Bay coast, was fractionated by silica gel column chromatography, using chloroform–methanol (99 : 1, 9 : 1 and 0 : 1) to obtain three fractions. The second fraction, eluted with chloroform–methanol (9 : 1), was chromatographed with ODS silica gel column (methanol–H_2O=3 : 1, 9 : 1, then methanol) to remove chlorophylls and carotenoids. Further separation of the fraction eluted with methanol was carried out using silica gel flash column and medium-pressure liquid chromatography (MPLC) gave the mixture of compounds **1** and **2**. HPLC purification of the mixture afforded **1** (a colorless oil, 17.3 mg, $[\alpha]_D^{25}$ −9.9°), and **2** (a colorless oil, 11.3 mg, $[\alpha]_D^{25}$ −7.0°).



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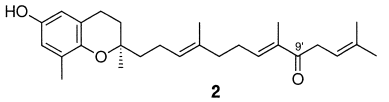

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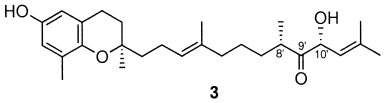

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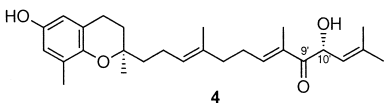

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The molecular formula of **1**, $C_{27}H_{40}O_3$, was determined by high-resolution EI-MS (HR-EI-MS). The IR spectrum of **1** showed absorptions due to a hydroxyl (br, 3418 cm^{-1}) and a carbonyl group (1709 cm^{-1}). UV absorption maxima at 296 (log ε 2.1) nm suggested that the presence of an aromatic ring system. All of the carbons appeared in the ^{13}C-NMR spectrum (Table 1). Distortionless enhancement by polariza-

Table 1. ^1H- and ^{13}C-NMR Data of the New Chromanes **1** and **2**[a)]

No.	**1**		**2**	
	^{13}C	^1H	^{13}C	^1H
2	75.3 (C)		75.2	
3	31.3 (CH_2)	1.73 (m), 1.78 (m)	31.4 (CH_2)	1.73 (m), 1.78 (m)
4	22.4 (CH_2)	2.69 (2H, m)	22.4 (CH_2)	2.70 (2H, m)
4a	121.2 (C)		121.2 (C)	
5	112.6 (CH)	6.38 (d, 3.0)	112.6 (CH)	6.38 (d, 3.0)
6	147.8 (C)		147.8 (C)	
7	115.6 (CH)	6.47 (d, 3.0)	115.6 (CH)	6.48 (d, 3.0)
8	127.3 (C)		127.3 (C)	
8a	145.9 (C)		145.9 (C)	
1′	39.6 (CH_2)	1.52 (m), 1.62 (m)	39.6 (CH_2)	1.52 (m), 1.62 (m)
2′	22.1 (CH_2)	2.10 (2H, m)	22.1 (CH_2)	2.10 (2H, m)
3′	124.5 (CH)	5.10 (br t, 6.8)	125.4 (CH)	5.19 (br t, 6.9)
4′	134.8 (C)		133.9 (C)	
5′	39.5 (CH_2)	1.93 (2H, m)	38.2 (CH_2)	2.11 (2H, m)
6′	25.4 (CH_2)	1.30 (2H, m)	27.5 (CH_2)	2.33 (2H, m)
7′	32.5 (CH_2)	1.29 (m), 1.57 (m)	142.6 (CH)	6.60 (dt, 1.3, 6.9)
8′	45.6 (CH)	2.56 (br q, 7.3)	136.9 (C)	
9′	213.4 (C)		200.5 (C)	
10′	41.0 (CH_2)	3.13 (2H, m)	37.2 (CH_2)	3.34 (2H, m)
11′	116.0 (CH)	5.29 (br t, 6.8)	116.0 (CH)	5.28 (br t, 6.9)
12′	135.4 (C)		135.4 (C)	
2-Me	24.0 (CH_3)	1.25 (3H, s)	24.0 (CH_3)	1.25 (3H, s)
8-Me	16.0 (CH_3)	2.12 (3H, s)	16.0 (CH_3)	2.12 (3H, s)
4′-Me	15.7 (CH_3)	1.56 (3H, br s)	15.7 (CH_3)	1.61 (3H, br s)
8′-Me	16.4 (CH_3)	1.03 (3H, d, 7.3)	11.4 (CH_3)	1.76 (3H, br s)
12′-Me	18.1 (CH_3)	1.62 (3H, br s)	18.0 (CH_3)	1.63 (3H, br s)
12′-Me	25.7 (CH_3)	1.74 (3H, br s)	25.8 (CH_3)	1.72 (3H, br s)

a) Measured in $CDCl_3$, ^{13}C; 125 MHz, ^1H; 500 MHz, δ ppm, J in Hz. Assignments were made based on HMQC analysis.

* To whom correspondence should be addressed. e-mail: iwashi@pha.u-toyama.ac.jp

tion transfer (DEPT) spectrum indicated six methyls, eight sp^3 methylenes, one sp^3 methine, four sp^2 methines, one sp^3 quaternary carbon, six sp^2 quaternary carbons, and one carbonyl carbon. The ^{1}H-NMR data of **1** (Table 1) was similar to that of **3**[3] simultaneously obtained from *S. micracanthum*, with the exception of one oxymethine group in the side chain at C-10′. Two-dimensional (2D) NMR (COSY, HMQC, HMBC) analysis confirmed the gross structure of **1**. *E* stereochemistry of olefin was determined by the chemical shift value of olefinic methyl carbon connecting to C-4′ (δ_C 15.7 ppm), which is observed in the higher field region in the ^{13}C-NMR spectrum. The absolute configuration at C-2 bearing the side chain was established as *R* by Crabbe's rule with the circular dichroism (CD) data.[3,4]

On the other hand, the absolute stereochemistry at C-8′ was still unclear and the reference did not describe it.[3] We decided to determine the chiral center at C-8′ by an alternative modified Mosher's method with methoxy-(2-naphtyl)acetic acid (2-NMA),[5] which can demonstrate the stereochemistry of both the α-carbon with secondary hydroxyl and the adjacent β-carbon with a methyl group in the case of acyclic compounds. Some 2-NMA esters of **3** were prepared first, and assigned the stereochemistry at C-8′ by NMR analysis. After that, the physical properties of **1** would be compared to those of the synthetic **1** obtained from **3** by chemical conversion.

Because the di-2-NMA esters of **3** could not be obtained in one step with normal condition using *N*,*N*′-dicyclohexylcarbodiimide (DCC), we prepared two series of 2-NMA esters using **6** and **7** as show in Chart 1. Two hydroxyl groups in **3** were both protected as methoxymethyl (MOM) ether to give **5**, followed by C-9′ carbonyl reduction with $NaBH_4$ to provide a 4 : 3 mixture of secondary alcohols. After separation of the diastereomeric mixture by HPLC, these secondary alcohols were independently treated with (±)-2-NMA, DCC and catalytic 4-(dimethylamino)pyridine (DMAP) to prepare totally four 2-NMA esters (**8**—**11**). HPLC (recycle) purification for the former mixture of **8** and **9** and the later **10** and **11**was carried out, and then the CD spectra were measured for each 2-NMA ester. The cotton effect in CD spectrum around 240 nm based on the orientation of the naphthalene ring was revealed their chiralities in 2-NMA. These observations led to the compounds **8**, showing an early retention time (t_R), and **9**, a late t_R, to possess (*S*)- and (*R*)-2-NMA esters, respectively, as well as **10** having an early t_R, and **11**, a late t_R, to be also determined as (*R*)- and (*S*)-2-NMA esters, respectively. In order to evaluate the $\Delta\delta_H$ values ($\delta_{(R)\text{-2-NMA}} - \delta_{(S)\text{-2-NMA}}$), NMR spectra including ^{13}C, COSY and HMQC afforded complete assignment for all protons of four 2-NMA esters. Figure 1 shows $\Delta\delta_H$ values of two series. The positive and negative areas of $\Delta\delta_H$ values for the C-9′ secondary hydroxyl group were suitably arranged. Both the absolute configurations at C-9′ of compounds **6** and **7** were confirmed as (*S*) and (*R*), respectively, by modified Mosher's method.

The stereochemistry of the adjacent C-8′ carbon with a methyl group was also determined above $\Delta\delta_H$ values. Focused on $|\Delta\delta_H|$ values (numerical number) of γ- and δ-positions, corresponding to the C-7′ and C-6′, respectively, *anti* configuration of the secondary hydroxyl with 2-NMA and the methyl group gave smaller $|\Delta\delta_H|$ value [below $|\Delta\delta_H|$ 0.35 ppm for γ-position (C-7′) and 0.25 ppm for δ-position (C-6′)], while *syn* configuration showed larger number (over $|\Delta\delta_H|$ 0.35 and 0.25 ppm, respectively).[5] Figure 1 obviously showed the series of **6** to be observed smaller $|\Delta\delta_H|$ values at C-6′ and C-7′ such as 0.24 and 0.35 ppm, respectively, however, those of **7** to be found larger values such as 0.41 and 0.43 ppm at C-7′ and 0.34 ppm at C-6′. These findings concluded the configuration of **6** to be assigned as *anti* and that of **7** to be *syn*, thus the absolute stereochemistry at C-8′ of **3** to be determined as (*S*) configuration.

The chemical conversion of compound **3** to **1** was depicted in Chart 2. The diacetate analog **12** was reduced with SmI_2 in the presence of acetic acid as a proton source at 0 °C in THF to give mostly **13** and a small amount of the conjugated isomer **14** in good yield. Hydrolysis under weak basic condi-

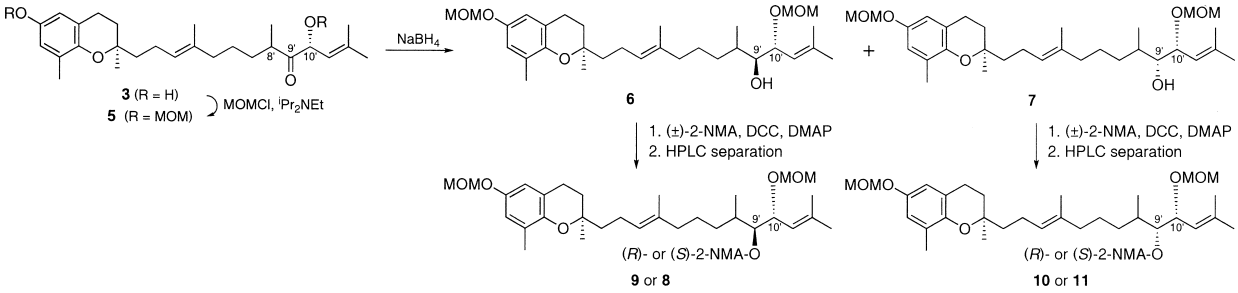

Chart 1

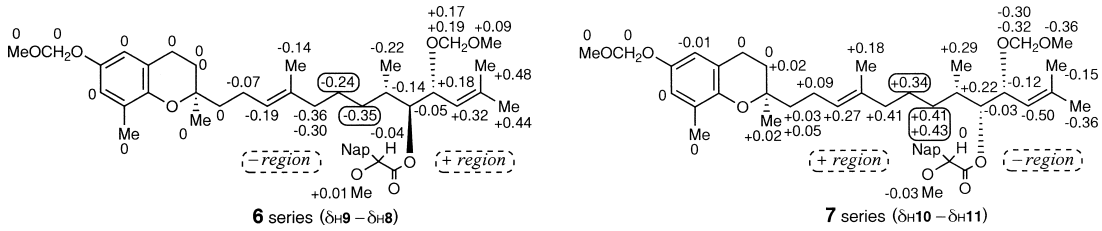

Fig. 1. $\Delta\delta$ Values and the Absolute Configuration of Compounds **6** and **7**

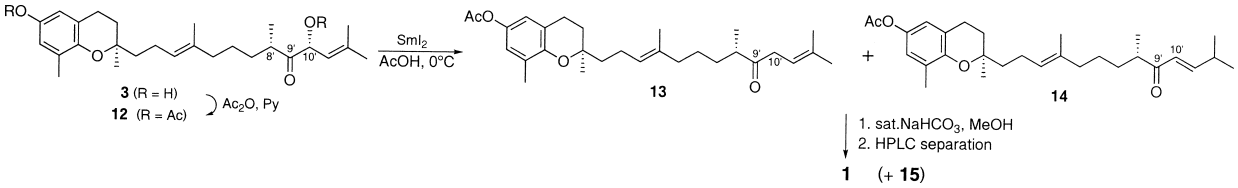

Chart 2

tion, followed by HPLC separation provided the synthetic compound **1**. The spectral data of the synthetic **1** involving the optical rotation value ($[\alpha]_D^{25}$ −6.4°) were identical to those of naturally occurring **1**. These results gave the chromane derivative **1** to be determined as (2*R*,8′*S*)-7′,8′-dihydro-9′-oxo-δ-tocotrienol.

Compound **2** showed the molecular formula $C_{27}H_{38}O_3$ by HR-EI-MS analysis, missing two protons compared to **1**. The ^{1}H- and ^{13}C-NMR spectra of **2** indicated a lot of similarities to those of **1** (Table 1), however, some exceptions were found. For example, the IR absorption due to an additional conjugated carbonyl moiety was observed at 1716 and 1659 cm^{-1}, and the UV absorption maxima (225 nm) were also newly detected. Two new signals corresponding to the conjugated sp^2 carbons appeared in the ^{13}C-NMR spectrum (δ_C 136.9, 142.6 ppm) in **2**, instead of the two signals at δ_C 32.5 (CH_2) and 45.6 (CH) ppm in the higher field area in **1**. ^{1}H-NMR and COSY analysis also supported a partial structure of an α,β-unsaturated carbonyl group from H-7′ to H-9′ in the side chain. The gross structure of **2** was elucidated by HMBC analysis. *E* stereochemistry of two olefins at C-3′ to C-4′, and C-7′ to C-8′ were determined by NOESY analysis. NOEs were observed between H-2′ and methyl protons at 4′-Me, and between H-6′ and methyl protons at 8′-Me. The absolute configuration of C-2 was assigned as *R* configuration based on the cotton effects in CD spectrum. These results concluded another new chromane derivative **2** to be assigned as (2*R*)-9′-oxo-δ-tocotrienol.

The biological activity of above mentioned compounds including some chemically modified derivatives are also under investigation.

Experimental

CD spectra were measured with a JASCO J-805. Medium-pressure liquid chromatography (MPLC) was carried out with a Tosoh SC-8020 apparatus using a CIG prepack column (silica gel, CPS-HS-221-05, for normal phase). HPLC with a recycling loop was conducted with a YMC-Pack SIL-06 column (silica gel, SH-043-5-06, normal phase). The other spectral measurements were carried out with the instruments described in the previous paper.[2)]

Material The brown alga, *Sargassum micracanthum* (KUETZING) ENDLICHER (order Sargassaceae, family Fucales), was collected off the coast of Toyama Bay, Toyama Prefecture, Japan, in September 2003, at a depth of 2—8 m. A voucher specimen (No. SM-0307) has been deposited at our laboratory in University of Toyama.

Extraction and Isolation Wet specimens (3.8 kg) were immersed in methanol (3×3 l). After filtration, the combined extracts were concentrated under reduced pressure. The methanol extract (386 g) was dissolved into a mixture of chloroform–methanol (3 : 1, 0.6 l), and then the precipitate was filtered with a sintered glass filter to remove highly polar compounds and salts. The precipitate on the glass filter was rinsed with a small amount of a 3 : 1 mixture of chloroform–methanol. The combined filtrate was concentrated under reduced pressure to give a chloroform–methanol (3 : 1) soluble portion (105 g). An aliquot of this portion (14.0 g) was chromatographed on a silica gel column (300 g). Stepwise elution with chloroform–methanol (99 : 1, 9 : 1 and 1 : 1, 400 ml of each) gave three fractions. The second fraction (3.0 g out of 4.4 g) eluted with chloroform–methanol (9 : 1) was subjected to a silica gel flash column chromatography [hexane–acetone (5 : 1)] followed by ODS silica gel flash column chromatography [H_2O–methanol (1 : 9, 1 : 19), and methanol] to obtain fractions of chromanes, fatty acids, fucosterol and colors such as chlorophylls and carotenoids. The second fraction (0.42 g) eluted with H_2O–methanol (1 : 19) was purified with MPLC [hexane–ethyl acetate (5 : 1)] followed by HPLC separation [hexane–ethyl acetate (7 : 1)] to afford new compounds **1** (17.3 mg), **2** (11.3 mg). The first fraction (1.97 g) eluted with H_2O–methanol (1 : 9) was purified with MPLC [hexane–ethyl acetate (2 : 1)] to give compounds **3** (286 mg) and **4** (234 mg), whose data were identical to those in the reference.[3)]

Compound 1 Colorless oil. $[\alpha]_D^{25}$ −9.9° (*c*=0.87, $CHCl_3$), $[\alpha]_D^{25}$ −10.2° (*c*=0.87, MeOH). UV λ_{max} (EtOH) nm (log ε): 296 (2.06). IR (dry film) cm^{-1}: 3418 (br), 1705, 1627. ^{1}H- and ^{13}C-NMR, see Table 1. HMBC (H→C): H-3→C-2, C-4, C-4a, C-1′, 2-Me; H-4→C-2, C-3, C-4a, C-8a; H-5→C-4, C-6, C-8a; H-7→C-5, C-6, C-8a; 2-Me→C-2, C-3, C-1′; 8-Me→C-7, C-8, C-8a; H-1′→C-2, C-3, 2-Me; H-2′→C-1′, C-3′, C-4′; H-3′→C-2′, C-4′, 4′-Me; H-5′→C-3′, C-4′, C-6′; H-6′→C-4′, C-5′, C-7′; H-7′→C-5′, C-8′, C-9′, 8′-Me; H-8′→C-9′, C-10′, 8′-Me; H-10′→C-8′, C-9′, C-11′, C-12′; H-11′→C-9′, C-10′, C-12′, 12′*E*-Me, 12′*Z*-Me; 4′-Me→C-3′, C-4′, C-5′; 8′-Me→C-7′, C-8′, C-9′; 12′*E*-Me→C-11′, C-12′, 12′*Z*-Me; 12′*Z*-Me→C-11′, C-12′, 12′*E*-Me. HR-EI-MS *m*/*z*: 412.2942 [Calcd for $C_{27}H_{40}O_3$: 412.2978 $(M)^+$]. CD λ_{max} (MeOH) $\Delta\varepsilon_{217}$ +25.3, $\Delta\varepsilon_{296}$ −10.1 (*c*=0.12 mM).

Compound 2 Colorless oil. $[\alpha]_D^{25}$ −7.0° (*c*=0.57, $CHCl_3$), $[\alpha]_D^{25}$ −4.2° (*c*=0.57, MeOH), UV λ_{max} (EtOH) nm (log ε): 225 (2.62), 296 (2.18). IR (dry film) cm^{-1}: 3390 (br), 1716, 1659, 1614. ^{1}H- and ^{13}C-NMR, see Table 1. HMBC (H→C): H-3→C-2, C-4, C-4a, C-1′, 2-Me; H-4→C-2, C-3, C-4a, C-8a; H-5→C-4, C-6, C-8a; H-7→C-5, C-6, C-8a; 2-Me→C-2, C-3, C-1′; 8-Me→C-7, C-8, C-8a; H-1′→C-2, C-3, 2-Me; H-2′→C-1′, C-3′, C-4′; H-3′→C-2′, C-4′, 4′-Me; H-5′→C-3′, C-4′, C-6′; H-6′→C-4′, C-5′, C-7′, C-8′; H-7′→C-5′, C-8′, C-9′, 8′-Me; H-10′→C-8′, C-9′, C-12′; H-11′→C-9′, C-10′, C-12′, 12′*E*-Me, 12′*Z*-Me; 4′-Me→C-3′, C-4′, C-5′; 8′-Me→C-7′, C-8′, C-9′; 12′*E*-Me→C-11′, C-12′, 12′*Z*-Me; 12′*Z*-Me→C-11′, C-12′, 12′*E*-Me. HR-EI-MS *m*/*z*: 410.2782 [Calcd for $C_{27}H_{38}O_3$: 410.2821 $(M)^+$]. CD λ_{max} (MeOH) $\Delta\varepsilon_{224}$ +3.8, $\Delta\varepsilon_{295}$ −10.6 (*c*=0.12 mM).

Preparation of Dimethoxymethyl Ether 5 To a solution of **3** (60 mg, 0.14 mmol) in dichroloethane (0.6 ml) was added *N*,*N*-diisopropylethylamine (0.10 ml, 0.56 mmol) and chloromethyl methyl ether (0.03 ml, 0.42 mmol) stirred at 40 °C for 8 h. The reaction mixture was diluted with a mixture of hexane and ethyl acetate (2 : 1, 40 ml), and then washed twice with water and brine. The organic layer was dried and concentrated under reduced pressure. The residue was purified by silica gel column chromatography [hexane–ethyl acetate (5 : 1)] to give **5** (69 mg, 95% yield).

Compound 5 Colorless oil. ^{1}H-NMR ($CDCl_3$) δ ppm: 1.03 (3H, d, *J*=6.8 Hz, 8′-Me), 1.26 (3H, s, 2-Me), 1.28 (1H, m, one of H-7′), 1.30 (1H, m, one of H-6′), 1.36 (1H, m, one of H-7′), 1.53 (1H, m, one of H-1′), 1.57 (3H, s, 4′-Me), 1.58 (1H, m, one of H-6′), 1.60 (1H, m, one of H-1′), 1.73 (1H, m, one of H-3), 1.76 (1H, m, one of H-3), 1.79 (3H, br s, 12′*E*-Me), 1.81 (3H, br s, 12′*Z*-Me), 1.94 (2H, dd, *J*=6.8, 7.3 Hz, H-5′), 2.11 (2H, dt, *J*=7.3, 8.1 Hz, H-2′), 2.14 (3H, s, 8-Me), 2.72 (1H, m, H-8′), 2.73 (2H, m, H-4), 3.35 (3H, s, Me protons in C-10′ MOM), 3.47 (3H, s, Me protons in C-6 MOM), 4.57 (1H, d, *J*=6.8 Hz, one of the CH_2 in C-10′ MOM), 4.67 (1H, d, *J*=6.8 Hz, one of the CH_2 in C-10′ MOM), 4.92 (1H, d, *J*=9.4 Hz, H-10′), 5.02 (1H, br d, *J*=9.4 Hz, H-11′), 5.07 (2H, s, CH_2 protons in C-6 MOM), 5.11 (1H, dt, *J*=1.3, 7.3 Hz, H-3′), 6.59 (1H, d, *J*=3.0 Hz, H-5), 6.67 (1H, d, *J*=3.0 Hz, H-7). ^{13}C-NMR ($CDCl_3$) δ ppm: 15.7 (4′-Me), 16.1 (8′-Me), 16.4 (8-Me), 18.7 (12′*Z*-Me), 22.1 (C-2′), 22.5 (C-4), 24.0 (2-Me), 25.5 (C-6′), 26.0 (12′*E*-Me), 31.2 (C-3), 33.1 (C-7′), 39.5 (C-5′), 39.8 (C-1′), 42.1 (C-8′), 55.6 (Me carbon in C-10′ MOM), 55.8 (Me carbon in C-6 MOM), 75.3 (C-2), 77.2 (C-10′), 93.6 (CH_2 carbon in C-10′ MOM), 95.3 (CH_2 carbon in C-6 MOM), 114.1 (C-5), 117.2 (C-7), 118.9 (C-11′), 120.9 (C-5a), 124.5 (C-3′), 127.2 (C-8), 134.7 (C-4′), 141.6 (C-12′), 147.1 (C-8a), 149.7 (C-6), 211.6 (C-9′). EI-MS *m*/*z*: 471 $[M-MeOCH_2]^+$.

Conversion to 6 and 7 Compound **5** (69 mg, 0.13 mmol) was treated with sodium borohydride (5 mg, 0.13 mmol) in MeOH (1.0 ml) at 0 °C under N_2 atmosphere. After stirred for 1 h at 0 °C, saturated ammonium chloride solution (0.01 ml) was added to terminate the reaction. The mixture was concentrated under reduced pressure. The residue was poured into a separation funnel containing a mixture of hexane and ethyl acetate (2 : 1, 40 ml), and then the combined mixture was washed twice with water and brine. The organic layer was dried and concentrated under reduced pressure. The residue was separated by silica gel column chromatography [hexane–ethyl acetate (4 : 1)] to give a diastereomer mixture of **6** and **7** (67 mg, 97% yield). ^{1}H-NMR analysis suggested the ratio to be 4 : 3. These products were purified by HPLC [hexane–ethyl acetate (5 : 1), flow rate: 3 ml/min] to give the pure alcohols **6** (34 mg, t_R: 32.8 min) and **7** (26 mg, t_R: 35.4 min).

Compound 6 Colorless oil. IR (dry film) cm^{-1}: 3430 (br), 1651. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.96 (3H, d, J=7.2 Hz, 8′-Me), 1.15 (1H, m, one of H-7′), 1.26 (3H, s, 2-Me), 1.31 (1H, m, one of H-7′), 1.34 (1H, m, one of H-6′), 1.42 (1H, m, one of H-6′), 1.54 (1H, m, one of H-1′), 1.58 (3H, s, 4′-Me), 1.63 (1H, m, one of H-1′), 1.65 (1H, m, H-8′), 1.72 (3H, s, 12′*E*-Me), 1.73 (1H, m, one of H-3), 1.78 (1H, m, one of H-3), 1.80 (3H, s, 12′*Z*-Me), 1.93 (2H, m, H-5′), 2.11 (2H, dt, J=7.7, 8.0 Hz, H-2′), 2.14 (3H, s, 8-Me), 2.73 (2H, m, H-4), 3.36 (3H, s, Me protons in C-10′ MOM), 3.48 (3H, s, Me protons in C-6 MOM), 3.49 (1H, dd, J=5.6, 7.3 Hz, H-9′), 4.37 (1H, dd, J=5.6, 9.8 Hz, H-10′), 4.48 (1H, d, J=6.4 Hz, one of the CH_2 in C-10′ MOM), 4.66 (1H, d, J=6.4 Hz, one of the CH_2 in C-10′ MOM), 5.07 (2H, s, CH_2 protons in C-6 MOM), 5.11 (1H, dt, J=1.3, 8.0 Hz, H-3′), 5.16 (1H, br d, J=9.8 Hz, H-11′), 6.59 (1H, d, J=3.0 Hz, H-5), 6.68 (1H, d, J=3.0 Hz, H-7). ^{13}C-NMR ($CDCl_3$) δ ppm: 14.0 (8′-Me), 15.8 (4′-Me), 16.2 (8-Me), 18.5 (12′*Z*-Me), 22.1 (C-2′), 22.5 (C-4), 24.0 (2-Me), 25.2 (C-6′), 26.1 (12′*E*-Me), 31.2 (C-3), 33.0 (C-7′), 34.0 (C-8′), 39.8 (C-1′), 39.9 (C-5′), 55.4 (Me carbon in C-10′ MOM), 55.8 (Me carbon in C-6 MOM), 72.6 (C-9′), 75.4 (C-2), 76.3 (C-10′), 93.0 (CH_2 carbon in C-10′ MOM), 95.3 (CH_2 carbon in C-6 MOM), 114.1 (C-5), 117.2 (C-7), 120.6 (C-11′), 120.9 (C-5a), 124.1 (C-3′), 127.2 (C-8), 135.3 (C-4′), 140.3 (C-12′), 147.1 (C-8a), 149.6 (C-6).

Compound 7 Colorless oil. IR (dry film) cm^{-1}: 3445 (br), 1645. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.98 (3H, d, J=6.8 Hz, 8′-Me), 1.20 (1H, m, one of H-7′), 1.22 (1H, m, one of H-6′), 1.26 (3H,s, 2-Me), 1.39 (1H, m, one of H-7′), 1.49 (1H, m, one of H-6′), 1.55 (1H, m, one of H-1′), 1.57 (3H, s, 4′-Me), 1.60 (1H, m, H-8′), 1.65 (1H, m, one of H-1′), 1.70 (3H, s, 12′*E*-Me), 1.74 (1H, m, one of H-3), 1.77 (3H, s, 12′*Z*-Me), 1.79 (1H, m, one of H-3), 1.92 (2H, m, H-5′), 2.11 (2H, dt, J=7.7, 8.1 Hz, H-2′), 2.14 (3H, s, 8-Me), 2.73 (2H, m, H-4), 3.35 (1H, dd, J=5.6, 7.0 Hz, H-9′), 3.38 (3H, s, Me protons in C-10′ MOM), 3.48 (3H, s, Me protons in C-6 MOM), 4.33 (1H, dd, J=5.6, 9.8 Hz, H-10′), 4.50 (1H, d, J=6.4 Hz, one of the CH_2 in C-10′ MOM), 4.69 (1H, d, J=6.4 Hz, one of the CH_2 in C-10′ MOM), 5.03 (1H, br d, J=9.8 Hz, H-11′), 5.08 (2H, s, CH_2 protons in C-6 MOM), 5.11 (1H, dt, J=1.3, 8.1 Hz, H-3′), 6.59 (1H, d, J=3.0 Hz, H-5), 6.67 (1H, d, J=3.0 Hz, H-7). ^{13}C-NMR ($CDCl_3$) δ ppm: 15.8 (4′-Me), 16.2 (8-Me), 16.9 (8′-Me), 18.4 (12′*Z*-Me), 22.1 (C-2′), 22.5 (C-4), 24.0 (2-Me), 25.8 (C-6′), 26.0 (12′*E*-Me), 30.4 (C-7′), 31.2 (C-3), 34.7 (C-8′), 39.8 (C-1′), 40.0 (C-5′), 55.6 (Me carbon in C-10′ MOM), 55.8 (Me carbon in C-6 MOM), 73.4 (C-9′), 75.4 (C-2), 78.4 (C-10′), 93.0 (CH_2 carbon in C-10′ MOM), 95.3 (CH_2 carbon in C-6 MOM), 114.1 (C-5), 117.2 (C-7), 120.9 (C-5a), 121.6 (C-11′), 124.0 (C-3′), 127.2 (C-8), 135.4 (C-4′), 138.9 (C-12′), 147.1 (C-8a), 149.6 (C-6).

Preparation of 2-NMA Esters 8 and 9 To a mixture of **6** (20 mg, 0.039 mmol), (±)-2-NMA (15 mg, 0.070 mmol) and DMAP (5 mg) in dichloromethane (0.7 ml) was added DCC (16 mg, 0.078 mmol) at room temperature under N_2 atmosphere. After stirred for 1 h, the reaction mixture was diluted with ethyl acetate (2 ml), followed by filtration through a small plug of silica gel. The filtrate was concentrated under reduced pressure. The residue was separated by silica gel column chromatography [hexane–ethyl acetate (4 : 1)] to give 2-NMA esters **8** and **9** (25 mg, 90% yield). The mixture of 2-NMA esters was subjected to a recycled HPLC [hexane–ethyl acetate (7 : 1), flow rate: 3 ml/min, recycle: six times] to provide **8** [9 mg, with (*S*)-2-NMA, t_R: 271 min] and **9** [10 mg, with (*R*)-2-NMA, t_R: 276 min].

Compound 8 Colorless oil. CD λ_{max} (MeOH) $\Delta_{\varepsilon 239}$ +38.2 (c=0.33 mM). ^{1}H-NMR ($CDCl_3$) δ ppm: 0.92 (3H, d, J=6.8 Hz, 8′-Me), 1.05 (1H, m, one of H-7′), 1.19 (1H, m, one of H-7′), 1.20 (3H, s, 12′*Z*-Me), 1.24 (3H, s, 12′*E*-Me), 1.26 (3H, s, 2-Me), 1.38 (2H, m, H-6′), 1.53 (1H, m, one of H-1′), 1.57 (3H, s, 4′-Me), 1.63 (1H, m, one of H-1′), 1.73 (1H, m, one of H-3), 1.82 (1H, m, one of H-3), 1.86 (2H, m, H-5′), 1.92 (1H, m, H-8′), 2.10 (2H, dt, J=7.7, 8.1 Hz, H-2′), 2.15 (3H, s, 8-Me), 2.73 (2H, m, H-4), 3.24 (3H, s, Me protons in C-10′ MOM), 3.44 (3H, s, Me protons in 2-NMA), 3.48 (3H, s, Me protons in C-6 MOM), 4.26 (1H, d, J=6.4 Hz, one of the CH_2 in C-10′ MOM), 4.27 (1H, dd, J=7.3, 9.8 Hz, H-10′), 4.42 (1H, d, J=6.4 Hz, one of the CH_2 in C-10′ MOM), 4.75 (1H, br d, J=9.8 Hz, H-11′), 4.88 (1H, s, α-proton in 2-NMA), 5.03 (1H, dd, J=3.9, 7.3 Hz, H-9′), 5.08 (1H, br t, J=8.1 Hz, H-3′), 5.08 (2H, s, CH_2 protons in C-6 MOM), 6.59 (1H, d, J=3.0 Hz, H-5), 6.68 (1H, d, J=3.0 Hz, H-7), naphthalene protons appeared at δ: 7.48 (2H, m), 7.53 (1H, dd, J=1.7, 8.5 Hz), 7.82 (3H, m), 7.88 (1H, d, J=1.7 Hz). ^{13}C-NMR ($CDCl_3$) δ ppm: 13.6 (8′-Me), 15.7 (4′-Me), 16.2 (8-Me), 17.6 (12′*Z*-Me), 22.1 (C-2′), 22.5 (C-4), 24.0 (2-Me), 25.3 (C-6′), 25.4 (12′*E*-Me), 31.2 (C-3), 33.1 (C-7′), 33.3 (C-8′), 39.68 (C-5′), 39.74 (C-1′), 55.4 (Me carbon in C-10′ MOM), 55.8 (Me carbon in C-6 MOM), 57.3 (Me in 2-NMA), 69.9 (C-10′), 75.4 (C-2), 77.7 (C-9′), 82.8 (α-carbon in 2-NMA), 92.5 (CH_2 carbon in C-10′ MOM), 95.3 (CH_2 carbon in C-6 MOM), 114.2 (C-5), 117.2 (C-7), 120.7 (C-11′), 120.9 (C-5a), 124.2 (C-3′), 127.2 (C-8), 135.1 (C-4′), 139.8 (C-12′), 147.1 (C-8a), 149.6 (C-6), naphthalene carbons appeared at δ 124.7, 126.2, 126.3, 126.7, 127.6, 128.0, 128.2, 133.1, 133.4, 133.8.

Compound 9 Colorless oil. CD λ_{max} (MeOH) $\Delta_{\varepsilon 241}$ −46.8 (c=0.47 mM). ^{1}H-NMR ($CDCl_3$) δ ppm: 0.70 (1H, m, one of H-7′), 0.70 (3H, d, J=6.8 Hz, 8′-Me), 0.84 (1H, m, one of H-7′), 1.14 (2H, m, H-6′), 1.26 (3H, s, 2-Me), 1.43 (3H, s, 4′-Me), 1.50 (1H, m, one of H-5′), 1.53 (1H, m, one of H-1′), 1.56 (1H, m, one of H-5′), 1.63 (1H, m, one of H-1′), 1.68 (3H, s, 12′*Z*-Me), 1.68 (3H, s, 12′*E*-Me), 1.73 (1H, m, one of H-3), 1.78 (1H, m, H-8′), 1.82 (1H, m, one of H-3), 2.03 (2H, dt, J=7.7, 8.1 Hz, H-2′), 2.15 (3H, s, 8-Me), 2.73 (2H, m, H-4), 3.33 (3H, s, Me protons in C-10′ MOM), 3.45 (3H, s, Me protons in 2-NMA), 3.48 (3H, s, Me protons in C-6 MOM), 4.43 (1H, d, J=6.8 Hz, one of the CH_2 in C-10′ MOM), 4.45 (1H, dd, J=7.3, 9.8 Hz, H-10′), 4.61 (1H, d, J=6.8 Hz, one of the CH_2 in C-10′ MOM), 4.84 (1H, s, α-proton in 2-NMA), 4.89 (1H, dt, J=1.3, 8.1 Hz, H-3′), 4.98 (1H, dd, J=3.9, 7.3 Hz, H-9′), 5.07 (1H, br d, J=9.8 Hz, H-11′), 5.08 (2H, s, CH_2 protons in C-6 MOM), 6.60 (1H, d, J=3.0 Hz, H-5), 6.68 (1H, d, J=3.0 Hz, H-7), naphthalene protons appeared at δ: 7.47 (2H, m), 7.54 (1H, dd, J=1.7, 8.5 Hz), 7.83 (3H, m), 7.91 (1H, br s). ^{13}C-NMR ($CDCl_3$) δ ppm: 13.3 (8′-Me), 15.6 (4′-Me), 16.2 (8-Me), 18.3 (12′*Z*-Me), 22.0 (C-2′), 22.5 (C-4), 24.0 (2-Me), 25.0 (C-6′), 25.9 (12′*E*-Me), 31.2 (C-3), 32.9 (C-7′), 33.0 (C-8′), 39.4 (C-5′), 39.7 (C-1′), 55.5 (Me carbon in C-10′ MOM), 55.7 (Me carbon in C-6 MOM), 57.4 (Me in 2-NMA), 70.3 (C-10′), 75.4 (C-2), 77.4 (C-9′), 82.7 (α-carbon in 2-NMA), 93.0 (CH_2 carbon in C-10′ MOM), 95.3 (CH_2 carbon in C-6 MOM), 114.2 (C-5), 117.2 (C-7), 120.9 (C-5a), 121.7 (C-11′), 123.9 (C-3′), 127.2 (C-8), 135.0 (C-4′), 139.2 (C-12′), 147.1 (C-8a), 149.6 (C-6), naphthalene carbons appeared at δ 124.6, 126.2, 126.3, 126.6, 127.7, 128.0, 128.3, 133.1, 133.3, 134.0.

Preparation of 2-NMA Esters 10 and 11 The same procedure as described above. From **7** (20 mg, 0.039 mmol) with (±)-2-NMA (15 mg, 0.070 mmol), DCC (16 mg, 0.078 mmol) and DMAP (5 mg) in dichloromethane (0.7 ml) were obtained 2-NMA esters **8** and **9** (26 mg, 94% yield). Recycled HPLC separation [hexane–ethyl acetate (7 : 1), flow rate: 3 ml/min, recycle: nine times] gave **10** [11 mg, with (*R*)-2-NMA, t_R: 487 min] and **11** [10 mg, with (*S*)-2-NMA, t_R: 493 min].

Compound 10 Colorless oil. CD λ_{max} (MeOH) $\Delta_{\varepsilon 240}$ −39.2 (c=0.46 mM). ^{1}H-NMR ($CDCl_3$) δ ppm: 0.90 (3H, d, J=6.8 Hz, 8′-Me), 1.08 (1H, m, one of H-7′), 1.21 (1H, m, one of H-6′), 1.27 (3H, s, 2-Me), 1.32 (1H, m, one of H-7′), 1.34 (3H, s, 12′*E*-Me), 1.45 (1H, m, one of H-6′), 1.53 (3H, s, 12′*Z*-Me), 1.53 (1H, m, one of H-1′), 1.56 (3H, s, 4′-Me), 1.63 (1H, m, one of H-1′), 1.73 (1H, m, one of H-3), 1.82 (1H, m, one of H-3), 1.84 (2H, m, H-5′), 1.90 (1H, m, H-8′), 2.12 (2H, m, H-2′), 2.15 (3H, s, 8-Me), 2.73 (2H, m, H-4), 2.97 (3H, s, Me protons in C-10′ MOM), 3.45 (3H, s, Me protons in 2-NMA), 3.48 (3H, s, Me protons in C-6 MOM), 4.15 (1H, d, J=6.4 Hz, one of the CH_2 in C-10′ MOM), 4.28 (1H, d, J=6.4 Hz, one of the CH_2 in C-10′ MOM), 4.35 (1H, dd, J=5.6, 9.8 Hz, H-10′), 4.42 (1H, br d, J=9.8 Hz, H-11′), 4.87 (1H, dd, J=5.6, 7.4 Hz, H-9′), 4.96 (1H, s, α-proton in 2-NMA), 5.07 (2H, s, CH_2 protons in C-6 MOM), 5.08 (1H, br t, J=8.1 Hz, H-3′), 6.60 (1H, d, J=3.0 Hz, H-5), 6.68 (1H, d, J=3.0 Hz, H-7), naphthalene protons appeared at δ: 7.48 (2H, m), 7.53 (1H, dd, J=1.7, 8.5 Hz), 7.82 (3H, m), 7.88 (1H, d, J=1.7 Hz). ^{13}C-NMR ($CDCl_3$) δ ppm: 15.8 (8′-Me), 15.9 (4′-Me), 16.2 (8-Me), 18.1 (12′*Z*-Me), 22.1 (C-2′), 22.5 (C-4), 24.0 (2-Me), 25.3 (12′*E*-Me), 25.5 (C-6′), 31.1 (C-7′), 31.3 (C-3), 33.6 (C-8′), 39.8 (C-1′), 39.9 (C-5′), 55.1 (Me carbon in C-10′ MOM), 55.8 (Me carbon in C-6 MOM), 57.3 (Me in 2-NMA), 70.8 (C-10′), 75.4 (C-2), 80.4 (C-9′), 82.9 (α-carbon in 2-NMA), 92.9 (CH_2 carbon in C-10′ MOM), 95.3 (CH_2 carbon in C-6 MOM), 114.2 (C-5), 117.2 (C-7), 120.6 (C-11′), 120.9 (C-5a), 124.1 (C-3′), 127.2 (C-8), 135.2 (C-4′), 138.5 (C-12′), 147.1 (C-8a), 149.6 (C-6), naphthalene carbons appeared at δ 124.9, 126.2, 126.3, 127.1, 127.6, 128.1, 128.3, 133.1, 133.5 , 133.8.

Compound 11 Colorless oil. CD λ_{max} (MeOH) $\Delta_{\varepsilon 239}$ +66.8 (c=0.44 mM). ^{1}H-NMR ($CDCl_3$) δ ppm: 0.61 (3H, d, J=6.8 Hz, 8′-Me), 0.65 (1H, m, one of H-7′), 0.87 (1H, m, one of H-6′), 0.91 (1H, m, one of H-7′), 1.11 (1H, m, one of H-6′), 1.25 (3H, s, 2-Me), 1.38 (3H, s, 4′-Me), 1.43 (2H, m, H-5′), 1.50 (1H, m, one of H-1′), 1.58 (1H, m, one of H-1′), 1.68 (1H, m, H-8′), 1.68 (3H, s, 12′*Z*-Me), 1.70 (3H, s, 12′*E*-Me), 1.73 (1H, m, one of H-3), 1.80 (1H, m, one of H-3), 2.03 (2H, dt, J=7.7, 8.1 Hz, H-2′), 2.15 (3H, s, 8-Me), 2.73 (2H, m, H-4), 3.33 (3H, s, Me protons in C-10′ MOM), 3.475 (3H, s, Me protons in C-6 MOM), 3.482 (3H, s, Me protons in 2-NMA), 4.45 (1H, d, J=6.8 Hz, one of the CH_2 in C-10′ MOM), 4.47 (1H, dd, J=6.0, 9.8 Hz, H-10′), 4.60 (1H, d, J=6.8 Hz, one of the CH_2 in C-10′ MOM), 4.84 (1H, br t, J=8.1 Hz, H-3′), 4.90 (1H, br t, J=6.0 Hz, H-9′), 4.92 (1H, br d, J=9.8 Hz, H-11′), 4.96 (1H, s, α-proton in 2-NMA), 5.08 (2H, s, CH_2 protons in C-6 MOM), 6.61 (1H, d, J=3.0 Hz, H-5), 6.68 (1H, d, J=3.0 Hz, H-7), naphthalene protons appeared at δ: 7.46 (2H, m), 7.60 (1H, dd, J=1.7, 8.6 Hz), 7.81 (3H, m), 7.95 (1H, d, J=1.7 Hz). ^{13}C-NMR ($CDCl_3$) δ ppm: 15.6 (8′-Me), 15.8 (4′-Me), 16.2 (8-Me), 18.3 (12′*Z*-Me), 22.0 (C-2′), 22.5 (C-4), 24.1 (2-Me), 25.0 (C-6′), 25.9 (12′*E*-Me), 30.3 (C-7′), 31.2 (C-3), 33.6 (C-8′), 39.5 (C-5′), 39.7 (C-1′), 55.4 (Me carbon in C-10′ MOM), 55.8 (Me carbon in C-6 MOM), 57.4 (Me in 2-NMA), 71.0 (C-10′), 75.4 (C-2), 80.1 (C-9′), 82.7 (α-carbon in 2-NMA), 92.9 (CH_2 carbon in C-10′ MOM), 95.3 (CH_2 carbon in C-6 MOM), 114.2 (C-5), 117.2 (C-7), 120.8 (C-11′), 120.9 (C-5a), 123.8 (C-3′), 127.2 (C-8), 135.1 (C-4′), 139.0 (C-12′), 147.1 (C-8a), 149.6 (C-6), naphthalene carbons appeared at δ 124.7, 126.2, 126.3, 126.8, 127.7, 128.0, 128.3, 133.1, 133.4, 134.0.

Esterification of 3 To a solution of **3** (60 mg, 0.14 mmol) in pyridine (0.4 ml) and acetic anhydride (0.3 ml) was stirred at room temperature for 5 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography [hexane–ethyl acetate (6 : 1)] to give **12** (74 mg, 96% yield).

Compound 12 Colorless oil. IR (dry film) cm^{-1}: 1735, 1716, 1659, 1614, 1240. ^{1}H-NMR ($CDCl_3$) δ ppm: 1.01 (3H, d, J=6.8 Hz, 8′-Me), 1.27 (3H, s, 2-Me), 1.30 (1H, m, one of H-7′), 1.39 (2H, m, H-6′), 1.57 (3H, s, 4′-Me), 1.58 (1H, m, one of H-1′), 1.65 (1H, m, one of H-1′), 1.67 (1H, m, one of H-7′), 1.73 (1H, m, one of H-3), 1.80 (1H, m, one of H-3), 1.81 (3H, br s, 12′*E*-Me), 1.85 (3H, br s, 12′*Z*-Me), 1.95 (2H, m, H-5′), 2.11 (2H, m, H-2′), 2.12 (3H, s, protons in C-10′ Ac), 2.14 (3H, s, 8-Me), 2.24 (3H, s, protons in C-6 Ac), 2.62 (1H, m, H-8′), 2.73 (2H, m, H-4), 5.13 (1H, br d, J=9.8 Hz, H-11′), 5.13 (1H, m, H-3′), 5.80 (1H, d, J=9.8 Hz, H-10′), 6.61 (1H, d, J=2.6 Hz, H-5), 6.66 (1H, d, J=2.6 Hz, H-7). ^{13}C-NMR ($CDCl_3$) δ ppm: 15.6 (4′-Me), 16.0 (8′-Me), 16.1 (8-Me), 18.7 (12′*Z*-Me), 22.0 (C-2′), 22.3 (C-4), 24.0 (2-Me), 25.2 (C-6′), 25.9 (12′*E*-Me), 30.9 (C-3), 33.0 (C-7′), 39.4 (C-5′), 39.8 (C-1′), 42.0 (C-8′), 75.77 (C-2), 77.79 (C-10′), 116.7 (C-11′), 119.0 (C-5), 120.8 (C-5a), 121.1 (C-7), 124.4 (C-3′), 127.2 (C-8), 134.8 (C-4′), 142.4 (C-12′), 142.5 (C-8a), 149.6 (C-6), 170.1 (Ac), 170.2 (Ac), 208.5 (C-9′). EI-MS m/z: 452 [M−AcOH]$^+$.

Conversion of 12 to 13 To a mixture of **12** (70 mg, 0.14 mmol) and acetic acid (0.1 ml) in THF at 0 °C under N_2 atmosphere was added 0.1 M solution of SmI_2 (0.31 ml, 0.031 mmol). After stirred for 30 min, saturated $Na_2S_2O_4$ solution (0.1 ml) was added to quench the reaction. The reaction mixture was diluted with a mixture of hexane and ethyl acetate (3 : 1, 40 ml), and then washed twice with water and brine. The organic layer was dried and concentrated under reduced pressure. The residue was purified by silica gel column chromatography [hexane–ethyl acetate (6 : 1)] to give a 9 : 1 mixture (60 mg, 94% yield) of **13** and **14**. Further purification of the mixture was not carried out due to the difficulty of separation. The mixture was directly used for the next reaction. To obtain the NMR data, a small amount of the product was purified by HPLC [hexane–ethyl acetate (7 : 1), flow rate: 2 ml/min] to give **13** (t_R: 36.9 min).

Compound 13 Colorless oil. ^{1}H-NMR ($CDCl_3$) δ ppm: 1.06 (3H, d, J=6.8 Hz, 8′-Me), 1.27 (3H, s, 2-Me), 1.31 (1H, m, one of H-7′), 1.35 (2H, m, H-6′), 1.57 (3H, s, 4′-Me), 1.58 (1H, m, one of H-1′), 1.63 (3H, br s, 12′*E*-Me), 1.65 (1H, m, one of H-1′), 1.67 (1H, m, one of H-7′), 1.73 (1H, m, one of H-3), 1.75 (3H, br s, 12′*Z*-Me), 1.80 (1H, m, one of H-3), 1.94 (2H, m, H-5′), 2.11 (2H, m, H-2′), 2.14 (3H, s, 8-Me), 2.25 (3H, s, protons in C-6 Ac), 2.56 (1H, m, H-8′), 2.73 (2H, m, H-4), 3.13 (2H, m, H-10′), 5.11 (1H, br t, J=7.3 Hz, H-3′), 5.29 (1H, br t, J=7.3 Hz, H-10′), 6.61 (1H, d, J=2.6 Hz, H-5), 6.66 (1H, d, J=2.6 Hz, H-7). EI-MS m/z: 454 [M]$^+$.

Conversion of 13 (and 14) to 1 To a mixture of **13** and **14** (46 mg, 0.010 mmol) was treated with saturated $NaHCO_3$ solution (0.3 ml) in MeOH (1 ml) at room temperature. After stirring for 2 h, saturated NH_4Cl solution (0.3 ml) was added, and the mixture was concentrated. The residue was extracted trice with ethyl acetate (30 ml), and combined organic layer was dried and concentrated. Obtained oil residue was subject to a silica gel column chromatography [hexane–ethyl acetate (5 : 1)] to provide compound **1** involving minor isomer **15** (36 mg). HPLC purification [hexane–ethyl acetate (7 : 1), flow rate: 2.8 ml/min] gave pure compounds **1** (32 mg, 77% yield, t_R: 44.5 min) and **15** (3 mg, 7% yield, t_R: 45.3 min), respectively. The spectral data of the obtained synthetic compound **1** were identical to those of the naturally occurring **1** {colorless oil. $[\alpha]_D^{25}$ −6.4° (c=0.29, $CHCl_3$), $[\alpha]_D^{25}$ −8.5° (c=0.29, MeOH)}.

Compound 15 Colorless oil. ^{1}H-NMR ($CDCl_3$) δ ppm: 1.07 (3H, d, J=6.8 Hz, one of 12′-Me), 1.07 (3H, d, J=6.8 Hz, one of 12′-Me), 1.08 (3H, d, J=6.8 Hz, one of 8′-Me), 1.26 (3H, s, 2-Me), 1.31 (1H, m, one of H-7′), 1.35 (1H, m, one of H-6′), 1.50 (1H, m, one of H-6′), 1.55 (3H, s, 4′-Me), 1.58 (1H, m, one of H-1′), 1.60 (1H, m, one of H-7′), 1.63 (1H, m, one of H-1′), 1.73 (1H, m, one of H-3), 1.78 (1H, m, one of H-3), 1.94 (2H, m, H-5′), 2.11 (2H, m, H-2′), 2.12 (3H, s, 8-Me), 2.46 (1H, m, H-12′), 2.70 (2H, m, H-4), 2.73 (1H, m, H-8′), 4.30 (1H, br s, C-6 OH), 5.11 (1H, dt, J=1.3, 7.3 Hz, H-3′), 6.10 (1H, dd, J=1.7, 15.8 Hz, H-10′), 6.61 (1H, d, J=2.6 Hz, H-5), 6.66 (1H, d, J=2.6 Hz, H-7), 6.83 (1H, dd, J=6.8, 15.8 Hz, H-10′).

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References and Notes

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