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Highly Stereoselective Total Synthesis of Methynolide, the Aglycon of the 12-Membered Macrolide Antibiotic Methymycin. III. An Efficient Synthesis of Methynolide[1,2]

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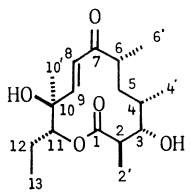
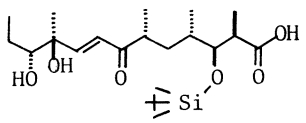
Methynolide (**1**), the aglycon of the 12-membered macrolide antibiotic methymycin, was synthesized highly stereoselectively and efficiently from D-glucose *via* two segments i (**3**: C-9—C-13) and ii (**4**: C-1—C-8). Esterification of the two segments proceeded smoothly by Yamaguchi's method. When the resulting ester (**10**) was treated with potassium carbonate in toluene in the presence of 18-crown-6 at 80 °C under Nicolaou's conditions, the intramolecular Wittig–Horner reaction occurred very smoothly, and the 12-membered cyclic enone (**11**) was isolated in excellent yield. Finally, silyl and benzyl protecting groups were removed with fluoride anion and 2,3-dichloro-5,6-dicyanobenzoquinone, respectively, to afford methynolide (**1**) in excellent yield. The overall stereoselectivity for the construction of four new chiral centers was very high (89%).

Keywords——macrolide antibiotic; methymycin; aglycon; methynolide; protecting group; esterification; macrocyclization; Wittig–Horner reaction; stereoselective synthesis

In the preceding papers,[1,3] we reported a highly stereoselective synthesis of the known seco-acid (**2**)[4] of methynolide (**1**) from D-glucose by means of some stereoselective reactions, *e.g.*, hydroboration and catalytic hydrogenation, and 4-methoxybenzyl (MPM)[5] and 4-methoxybenzylidene (MP acetal)[6] protections of hydroxy functions. The seco-acid (**2**) has already been converted to **1** by Masamune *et al. via* the macrolactonization, though the yield was unsatisfactory (20—30%).[4] Yamaguchi *et al.* also synthesized **1** using their macrolactoni-



1



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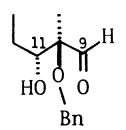
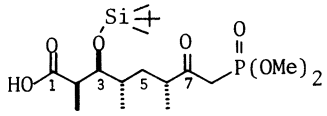


segment i

3



segment ii

4

Chart 1

zation method, which gave a better result (42% yield).[7] The seco-acid (**2**)[4] was also synthesized by Grieco *et al.*[8] and Ireland *et al.*,[9] but no conversion to **1** has been performed. Our highly stereoselective synthesis of **2**[1,3] has provided an additional example of the formal synthesis of **1**, but it was preferable to try to cyclize **2** into **1** after developing a superior macrolactonization method. Therefore, we decided to examine another synthetic route from D-glucose to **1**. In the present paper, we report an efficient synthesis of **1** *via* a key step of macrocyclization using the Wittig–Horner coupling[10] developed by Aristoff[11] and Nicolaou *et al.*[12]

Results and Discussion

We chose the aldehyde (**3**) and the carboxylic ketophosphonate (**4**) as segments i (C-9—C-13) and ii (C-1—C-8), respectively.[13]

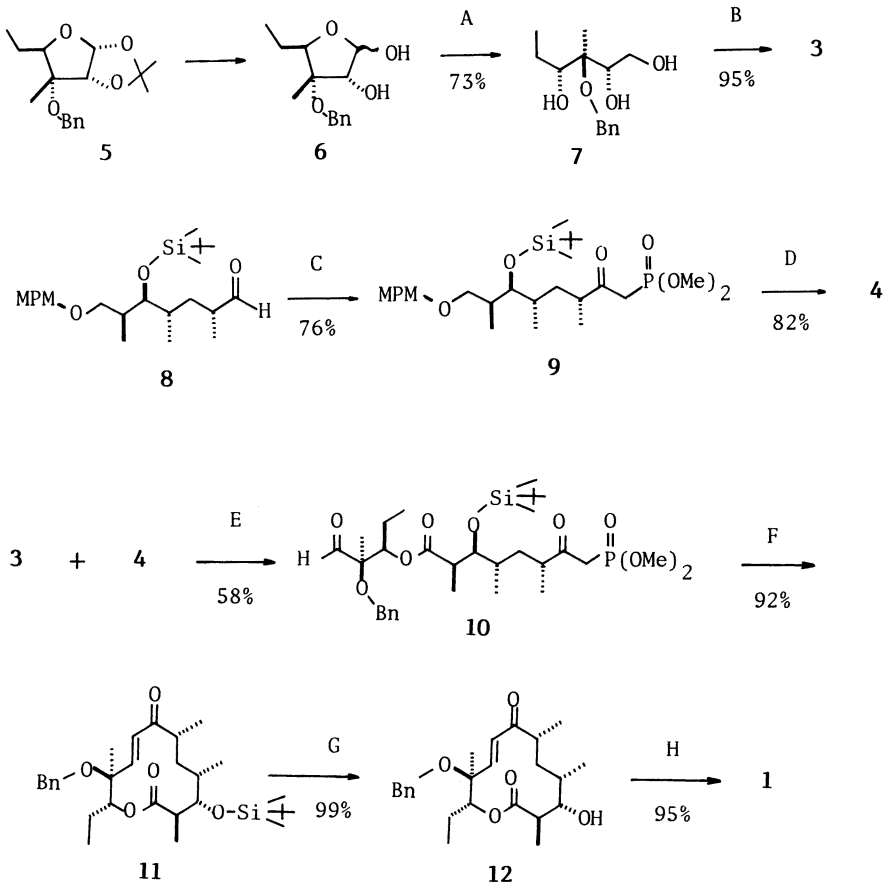
In our synthetic plan, the protecting group of the C-10 hydroxy group needed to be removed by a method other than reductive deprotection after construction of the enone structure at C-7—C-9. MPM protection, readily removable by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) oxidation,[5] was considered to be much more favorable than benzyl protection. Nevertheless, we chose the benzyl protection for the following two reasons: 1) many steps were required for the synthesis of segment i with MPM protection; 2) benzyl protection for tertiary hydroxy groups was found to be removable by prolonged treatment with DDQ.[14]

Actually, the aldehyde (**3**) bearing only two chiral centers was easily synthesized from **5**,[1,15] *via* the known hydroxy hemiacetal (**6**)[15a,c] and the acyclic triol (**7**) by only three-step conversion (acid hydrolysis, calcium borohydride reduction, and periodate oxidation) in 70% overall yield.

In the preceding paper,[1] we described the synthesis, as segment ii, of a diethyl phosphonate, whose structural confirmation was, however, somewhat troublesome because of its complex nuclear magnetic resonance (NMR) spectrum due to coupling with the phosphorus atom. Therefore, in this paper, we decided to synthesize the dimethyl analog (**4**) as segment ii from the aldehyde (**8**) by a method virtually identical with that described for the diethyl ketophosphonate in the preceding paper.[1]

Esterification of **3** and **4** with dicyclohexylcarbodiimide (DCC) in the presence of 4-dimethylaminopyridine (DMAP) proceeded rather smoothly to give the expected ester (**10**) in 70% yield, but it was very difficult to remove impurities. After examination of several esterification methods, we found that only the Yamaguchi method[16] gave an acceptable result, namely treatment of **3** and **4** with 2,4,6-trichlorobenzoyl chloride in the presence of DMAP in benzene gave pure **10**, though the reaction proceeded very slowly and over 20 h was required for disappearance of the starting materials. The ester (**10**) was then subjected to Nicolaou's macrocyclization,[12] namely when a 1 mM solution of **10** in toluene was treated with potassium carbonate (6 eq) in the presence of 18-crown-6 (12 eq) at 80 °C for 3 h,[12] a smooth cyclization proceeded to afford the expected 12-membered cyclic enone (**11**) in surprisingly high yield (92%).[17] The *tert*-butyldimethylsilyl (TBDMS) protection of **11** was first removed by treatment with fluoride anion to give **12**, and finally the benzyl group of **12** was removed; namely when **12** was treated with DDQ in dichloromethane containing a small amount of water at 40 °C, a very clean oxidative deprotection proceeded slowly, and after 9.5 h methynolide (**1**) was isolated in excellent yield. The structure of **1** was confirmed by careful examination of its 500 MHz NMR and mass spectra (MS) as well as by comparison of its physical data with those reported for an authentic sample.[4,7b]

Finally, it seems to be worth emphasizing two additional advantages of this approach, taken together with the results in the preceding two reports.[1,3] One is the very high



(A) $CaCl_2$, $NaBH_4$, EtOH (B) $NaIO_4$, MeOH–H_2O (C) 1) $MePO(OMe)_2$, *n*-BuLi, THF; 2) PDC, DMF (D) 1) DDQ, CH_2Cl_2–H_2O; 2) CrO_3, H_2SO_2, MeCOMe, 0 °C (E) 2,4,6-$Cl_3C_6H_2COCl$, Et_3N, DMAP, THF (F) K_2CO_3, 18-crown-6, toluene, 80 °C (G) *n*-Bu_4NF, THF (H) DDQ, CH_2Cl_2–H_2O, 40 °C

Chart 2

stereoselectivities throughout the synthesis of **1** from D-glucose, namely the stereoselectivities for the construction of the new chiral centers at C-2, C-4, C-6, and C-10 were 96, 97, 96, and 100%, respectively, and hence the overall stereoselectivity from D-glucose to methynolide (**1**) was 89%, which is the highest so far achieved. The other is that the methodology established here may be directly applicable to the synthesis of more complex natural products such as not only macrolides (tylonolide, pikronolide, 6-deoxyerythronolide B, erythronolide A, *etc.*) but also polyether ionophore antibiotics (salinomycin, isolasalocid A, *etc.*).

Experimental

Physical data were measured as described in the previous paper.[3]

(2*S*,3*R*,4*R*)-3-Benzyloxy-3-methyl-1,2,4-trihydroxyhexane (7)——An EtOH solution (20 ml) of sodium borohydride (300 mg, 7.8 mmol) was added dropwise to a chilled stirred EtOH solution (30 ml) of calcium chloride (840 mg, 7.6 mmol) at −20 °C. After 30 min, an EtOH solution of **6** (611 mg, 2.4 mmol) was added to the resulting calcium borohydride solution, stirring was continued for 1.5 h at room temperature, and then the excess reductant was decomposed with aqueous HCl. The mixture was neutralized with Na_2CO_3, and a white precipitate was removed by

filtration. The filtrate was concentrated *in vacuo*, and the residue was taken up in CH_2Cl_2 and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on a silica gel column with EtOAc to give **7** (450 mg, 73%). Leaflets, mp 69.5—70 °C (hexane–EtOAc). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550, 3400. ^{1}H-NMR ($CDCl_3$) δ: 1.04 (3H, t, J=7 Hz), 1.35 (3H, s), 1.45 (1H, ddq, J=14, 10.5, 7 Hz), 1.74 (1H, ddq, J=14, 2, 7 Hz), 2.75 (1H, d, J=4 Hz), 2.6—3.2 (1H, br s), 3.71 (1H, dd, J=10.5, 2 Hz), 3.75 (1H, dd, J=11, 4.5 Hz), 3.83 (1H, br q, J=4.5 Hz), 3.91 (1H, dd, J=11, 4.5 Hz), 4.53 (1H, d, J=12 Hz), 4.59 (1H, d, J=12 Hz), 7.25—7.4 (5H, m). MS m/z (relative intensity): 193 (M^+-61, 3.7), 91 (100), 43 (11). *Anal.* Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.11; H, 8.89.

(2*R*,3*R*)-2-Benzyloxy-3-hydroxy-2-methylpentanal (3)——An aqueous solution (1 ml) of sodium metaperiodate (50 mg, 0.23 mmol) was added to a stirred MeOH solution (2 ml) of **7** (40 mg, 0.16 mmol) at room temperature. After 1 h, the reaction mixture was filtered, and the filtrate was concentrated *in vacuo* to leave an oil, which was dissolved in CH_2Cl_2. The CH_2Cl_2 solution was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on a silica gel column with *n*-hexane–EtOAc to give **3** as a colorless oil (33.1 mg, 95%). ^{1}H-NMR ($CDCl_3$) δ: 1.03 (3H, t, J=7.5 Hz), 1.21—1.67 (2H, m), 1.36 (3H, s), 2.52 (1H, d, J=3.0 Hz), 3.70 (1H, dt, J=10.0, 3.0 Hz), 4.48 (1H, d, J=11.0 Hz), 4.56 (1H, d, J=11.0 Hz), 7.2—7.5 (5H, m), 9.79 (1H, s). IR ν_{max}^{neat} cm^{-1}: 3400, 1720. $[\alpha]_D^{12}+82°$ (c=1.4, $CHCl_3$). MS m/z (relative intensity): 221 (M^+-29, 3.5), 193 (1.8), 146 (1.6), 135 (2.3), 121 (3.9), 91 (100). Exact MS m/z Calcd for $C_{12}H_{17}O_2$ (M^+-29): 193.1229. Found: 193.1230.

(3*R*,5*S*,6*S*,7*S*)-6-*tert*-Butyldimethylsilyloxy-1-dimethylphosphono-8-(4-methoxybenzyl)oxy-3,5,7-trimethyloctan-2-one (9)——A 1.6 M hexane solution (1.6 ml) of *n*-butyllithium was added dropwise to a stirred tetrahydrofuran (THF) solution of dimethyl methylphosphonate (387 ng, 3.1 mmol) at −78 °C. After 30 min, a THF solution (2 ml) of **8** (532 mg, 1.26 mmol) was added dropwise, and the reaction mixture was allowed to warm gradually to room temperature then poured into aqueous NH_4Cl solution, and extracted with ether. The ether extract was washed with brine, dried over anhydrous Na_2SO_4, and evaporated *in vacuo* to leave an oil, which was dissolved in dimethylformamide (DMF) (5 ml). The solution was stirred with pyridinium dichromate (PDC) (1.8 g, 4.8 mmol) for 20 h at room temperature, then poured into H_2O (100 ml), and extracted with ether. The extract was washed with brine, dried over Na_2SO_4, and evaporated to leave an oil, which was chromatographed on a silica gel column with *n*-hexane–EtOAc (1 : 1) as the eluent to give **9** as a colorless oil (523 mg, 76%). ^{1}H-NMR ($CDCl_3$) δ: 0.06 (3H, s), 0.08 (3H, s), 0.84 (3H, d, J=7.0 Hz), 0.91 (9H, s), 0.96 (3H, d, J=7.0 Hz), 1.13 (3H, d, J=7.0 Hz), 1.13—1.29 (1H, m), 1.60—1.93 (3H, m), 2.95—3.15 (1H, m), 3.05 (1H, dd, J=23.0, 13.5 Hz), 3.21 (1H, dd, J=10, 6 Hz), 3.22 (1H, dd, J=23.0, 13.5 Hz), 3.31 (1H, dd, J=10, 8 Hz), 3.65 (1H, dd, J=5, 2.5 Hz), 3.76 (3H, d, J=11 Hz), 3.765 (3H, d, J=11 Hz), 3.80 (3H, s), 4.40 (2H, s), 6.86 (2H, d, J=9.0 Hz), 7.22 (2H, d, J=9.0 Hz). IR ν_{max}^{neat} cm^{-1}: 1710. MS m/z (relative intensity): 487 (M^+-57, 0.1), 294 (1.8), 233 (4.0), 121 (100). Exact MS m/z Calcd for $C_{23}H_{40}O_7PSi$ (M^+-57): 487.2280. Found: 487.2279. $[\alpha]_D^{12}+11°$ (c=1.0, $CHCl_3$).

(2*R*,3*S*,4*S*,6*R*)-3-*tert*-Butyldimethylsilyloxy-8-dimethoxyphosphono-7-oxo-2,4,6-trimethyloctanoic Acid (4)——DDQ (31 mg, 0.14 mmol) was added to a stirred CH_2Cl_2 (2 ml)–H_2O (0.1 ml) solution of **9** (50 mg, 0.092 mmol) at room temperature. After 1 h, the reaction mixture was poured into aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo* to leave an oil, which was chromatographed on a silica gel column with *n*-hexane–EtOAc (1 : 2) as the eluent to give (3*R*,5*S*,6*S*,7*S*)-6-*tert*-butyldimethylsilyloxy-1-dimethylphosphono-8-hydroxy-3,5,7-trimethyloctan-2-one as a colorless oil (33 mg, 85%). ^{1}H-NMR ($CDCl_3$) δ: 0.06 (3H, s), 0.08 (3H, s), 0.84 (3H, d, J=7.0 Hz), 0.91 (9H, s), 0.96 (3H, d, J=7.0 Hz), 1.13 (3H, d, J=7.0 Hz), 1.13—1.29 (1H, m), 1.60—1.93 (3H, m), 2.92 (1H, t, J=4.0 Hz), 2.95—3.15 (1H, m), 3.05 (1H, dd, J=23.0, 13.5 Hz), 3.22 (1H, dd, J=23.0, 13.5 Hz), 3.35—3.40 (2H, m), 3.77 (6H, d, J=12 Hz), 3.87 (1H, dd, J=3.5, 2.5 Hz). MS m/z (relative intensity): 425 (M^++1, 0.1), 409 (1.8), 367 (51), 337 (35), 233 (78), 151 (85), 147 (90), 73 (100). Exact MS m/z Calcd for $C_{15}H_{32}O_6PSi$ (M^+-57): 367.1705. Found: 367.1693. IR ν_{max}^{neat} cm^{-1}: 3400, 1710. $[\alpha]_D^{12}+39°$ (c=1.1, $CHCl_3$).

A stirred ice-cold acetone solution (0.5 ml) of the above 8-hydroxy compound (28.8 mg, 0.068 mmol) was treated dropwise with 2.67 M Jones reagent (0.07 ml). After 30 min, ether (30 ml) was added, and the mixture was washed with brine (3 times), dried over anhydrous $MgSO_4$, and evaporated *in vacuo* to leave **4** as an oil (28.6 mg, 96%). ^{1}H-NMR ($CDCl_3$) δ: 0.09 (3H, s), 0.10 (3H, s), 0.91 (9H, s), 0.99 (3H, d, J=6.5 Hz), 1.05—1.26 (1H, m), 1.11 (3H, d, J=7.0 Hz), 1.20 (3H, d, J=7.0 Hz), 1.64—1.84 (1H, m), 1.85 (1H, dt, J=13.5, 7.0 Hz), 2.63 (1H, dq, J=8.0, 7.0 Hz), 2.87 (1H, tq, J=7.5, 7.0 Hz), 3.19 (2H, d, J=23.0 Hz), 3.80 (3H, d, J=11.0 Hz), 3.81 (3H, d, J=11.0 Hz), 3.87 (1H, dd, J=7.5, 2.5 Hz), IR ν_{max}^{neat} cm^{-1}: 1710. MS m/z (relative intensity): 381 (M^+-57, 28), 363 (23), 233 (35), 180 (100), 151 (72). Exact MS m/z Calcd for $C_{15}H_{30}O_7PSi$ (M^+-57): 381.1497. Found: 381.1496.

(1*R*,2*R*)-2-Benzyloxy-1-ethyl-2-formylpropyl (2*R*,3*S*,4*S*,6*R*)-3-*tert*-Butyldimethylsilyloxy-8-dimethoxyphosphono-7-oxo-2,4,6-trimethyloctanoate (10)——2,4,6-Trichlorobenzoyl chloride (10 μl, 0.06 mmol) was added to a stirred THF solution of crude **4** (16.6 mg, 0.038 mmol) and Et_3N (10 μl, 0.07 mmol) at room temperature. After 1 h, the precipitate was filtered off, and the filtrate was evaporated *in vacuo* to leave an oil, which was taken up in benzene (2 ml). A solution of **3** (18 mg, 0.08 mmol) and DMAP (10 mg) in benzene (1 ml) was added to the above solution, and stirring was continued for 20 h at room temperature. The reaction mixture was diluted with ether, washed with brine and saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and evaporated *in vacuo* to leave an oil, which was chromatographed on a silica gel with *n*-hexane–EtOAc (1 : 1) as the eluent to give **10** as a colorless oil (14.1 mg, 58%).

^{1}H-NMR ($CDCl_3$) δ: 0.05 (3H, s), 0.06 (3H, s), 0.89 (9H, s), 0.92 (3H, t, J=7.5 Hz), 0.96 (3H, d, J=6.0 Hz), 1.00—2.00 (5H, m), 1.11 (3H, d, J=7.0 Hz), 1.16 (3H, d, J=7.0 Hz), 1.35 (3H, s), 2.60 (1H, quint, J=7 Hz), 2.87 (1H, m), 3.03 (1H, dd, J=23, 14 Hz), 3.17 (1H, dd, J=23, 14 Hz), 3.75 (3H, d, J=11 Hz), 3.78 (3H, d, J=11 Hz), 3.86 (1H, dd, J=7.0, 3.0 Hz), 4.39 (1H, d, J=12.0 Hz), 4.60 (1H, d, J=12.0 Hz), 5.15 (1H, dd, J=9.5, 4.0 Hz), 7.33 (5H, s), 9.60 (1H, s). FI-MS m/z (relative intensity): 643 (M^++1, 41), 585 (25), 91 (100). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1710.

10-*O*-Benzyl-3-*O*-*tert*-butyldimethylsilylmethynolide (11)——A toluene solution (10 ml) of **10** (23 mg, 0.036 mmol) was added gradually to a heated suspension of anhydrous K_2CO_3 (30 mg, 0.22 mmol) in toluene (36 ml) containing 18-crown-6 (114 mg, 0.43 mmol) at 80 °C over a period of 50 min. Stirring at the same temperature was continued for an additional 2.5 h, and then, after cooling, aqueous NH_4Cl (10 ml) was added. The mixture was extracted with ether, and the ether extract was washed with saturated KCl (4 times), dried over anhydrous Na_2SO_4, and evaporated *in vacuo* to leave an oil, which was chromatographed on a silica gel column with *n*-hexane–EtOAc (5 : 1) as the eluent to give **11** as a colorless oil (17 mg, 92%). ^{1}H-NMR ($CDCl_3$) δ: 0.07 (3H, s), 0.08 (3H, s), 0.87 (3H, t, J=7.5 Hz), 0.91 (9H, s), 0.94 (3H, d, J=7.0 Hz), 1.12—1.56 (3H, m), 1.23 (3H, d, J=7.0 Hz), 1.25 (3H, d, J=7.0 Hz), 1.44 (3H, s), 1.66 (1H, t, J=12.5 Hz), 2.00 (1H, ddq, J=14.0, 2.5, 7.5 Hz), 2.43—2.66 (1H, m), 2.63 (1H, dq, J=10.0, 7.0 Hz), 3.64 (1H, d, J=10.0 Hz), 4.43 (1H, d, J=11.5 Hz), 4.46 (1H, d, J=11.5 Hz), 4.87 (1H, dd, J=10.5, 2.5 Hz), 6.45 (1H, d, J=16.0 Hz), 6.75 (1H, d, J=16.0 Hz), 7.2—7.5 (5H, m). MS m/z (relative intensity): 459 (M^+−57, 3.4), 458 (2.0), 401 (1.9), 367 (3.7), 199 (10.5), 91 (100). FI-MS m/z (relative intensity): 517 (M^++1, 11), 461 (20), 459 (100). Exact MS m/z Calcd for $C_{26}H_{39}O_5Si$ (M^+−57): 459.2567. Found: 459.2587. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1690. $[\alpha]_D^{15}$+77° (c=0.7, $CHCl_3$).

10-*O*-Benzylmethynolide (12)——A 1 M THF solution (0.185 ml) of *n*-Bu_4NF was added to a stirred THF solution (0.5 ml) of **11** (19 mg, 0.037 mmol) at room temperature. After 24 h, the reaction mixture was evaporaed *in vacuo* to leave an oil, which was chromatographed on a silica gel column with *n*-hexane–EtOAc (3 : 1) as the eluent to give **12** as a colorless oil (14.6 mg, 99%). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=7.5 Hz), 1.01 (3H, d, J=4.5 Hz), 1.23 (3H, d, J=7.0 Hz), 1.26—2.20 (6H, m), 1.33 (3H, d, J=7.0 Hz), 1.45 (3H, s), 2.43—2.82 (2H, m), 3.59 (1H, dd, J=10.5, 5.5 Hz), 4.45 (2H, s), 4.88 (1H, dd, J=10.5, 2.0 Hz), 6.40 (1H, d, J=16.0 Hz), 6.72 (1H, d, J=16.0 Hz), 7.32 (5H, s). MS m/z (relative intensity): 344 (M^+−58, 13), 253 (18), 91 (100). Exact MS m/z Calcd for $C_{21}H_{28}O_4$ (M^+−58): 344.1987. Found: 344.1981. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1730, 1690. $[\alpha]_D^{16}$+61° (c=0.75, $CHCl_3$).

Methynolide (1)——A CH_2Cl_2 solution (1 ml) of **12** (5.6 mg, 0.014 mmol) and DDQ (10 mg, 0.044 mmol) containing H_2O (0.1 ml) was heated under reflux for 9.5 h. After cooling, the reaction mixture was diluted with CH_2Cl_2, washed with saturated $NaHCO_3$, dried over anhydrous Na_2SO_4, and then evaporated to leave an oil, which was chromatographed on a silica gel column with *n*-hexane–EtOAc (2 : 1) as the eluent to give **1** as colorless crystals (4.1 mg, 95%). Recrystallization from ether–hexane gave colorless needles, mp 162.5—163.5 °C. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 0.90 (3H, t, J=7.5 Hz, C-13), 1.01 (3H, d, J=6.0 Hz, C-4′), 1.15—1.40 (1H, m, C-5), 1.21 (3H, d, J=7.0 Hz, C-6′), 1.33 (3H, d, J=7.0 Hz, C-2′), 1.38 (3H, s, C-10′), 1.50—1.60 (1H, m, C-4), 1.52 (1H, ddq, J=11.0, 14.0, 7.5 Hz, C-12), 1.53 (1H, d, J=6.0 Hz, C-3 OH), 1.63 (1H, t, J=12.5 Hz, C-5), 1.94 (1H, ddq, J=2.0, 14.0, 7.5 Hz, C-12), 2.04 (1H, s, C-10 OH), 2.56 (1H, dq, J=3.0, 7.0 Hz, C-6), 2.62 (1H, dq, J=10.0, 7.0 Hz, C-2), 3.57 (1H, dd, J=6.0, 10.0 Hz, C-3), 4.78 (1H, dd, J=2,0, 11.0 Hz, C-11), 6.33 (1H, d, J=15.0 Hz, C-8), 6.59 (1H, d, J=15.0 Hz, C-9). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3450, 1730, 1690. $[\alpha]_D^{16}$+72° (c=0.45, $CHCl_3$); +56.4° (c=0.45, MeOH). MS m/z (relative intensity): 294 (M^+−18, 0.9), 254 (39), 236 (20), 198 (33), 127 (100). Exact MS m/z Calcd for $C_{17}H_{26}O_4$ (M^+−18): 294.1831. Found: 294.1844. Calcd for $C_{14}H_{22}O_4$ (M^+−58): 254.1518. Found: 254.1505.

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References and Notes

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