An Iterative Acetylene–Epoxide Coupling Strategy for the Total Synthesis of Aspinolide A

by **Gowravaram Sabitha***, **Teega Rammohan Reddy**, **Chitti Srinivas**, and **Jhillu Singh Yadav**

Organic Division I, Indian Institute of Chemical Technology, Hyderabad 500007, India (phone: +91-40-27191629; fax: +91-40-27160512; e-mail: gowravaramsr@yahoo.com)

The total synthesis of aspinolide A (**1**) was successfully achieved by an iterative acetylene–epoxide coupling strategy and a *Yamaguchi* lactonization as the key steps.

Introduction. – Aspinolides A – C (**1** – **3**, *Fig.*), new 10-membered macrolides, were isolated by *Zeeck* and *Fuchser* [1] in 1997 from cultures of *Aspergillus ochraceus*. Their structures were established by detailed spectroscopic analysis. Other representative 10-membered natural lactones such as nonenolide (**4**) [2a][2b], modiolide A (**5**) [2c], putaminoxin (**6**) [2d], and herbarumin III (**7**) [2e] are shown in the *Figure*. The molecules containing medium-sized ring systems attracted the attention of synthetic organic chemists recently since they form the core of many natural products. The first total synthesis of aspinolide A (**1**) has been recently reported [3], which relied on a RCM (ring-closing metathesis) reaction for the macrolactonization.

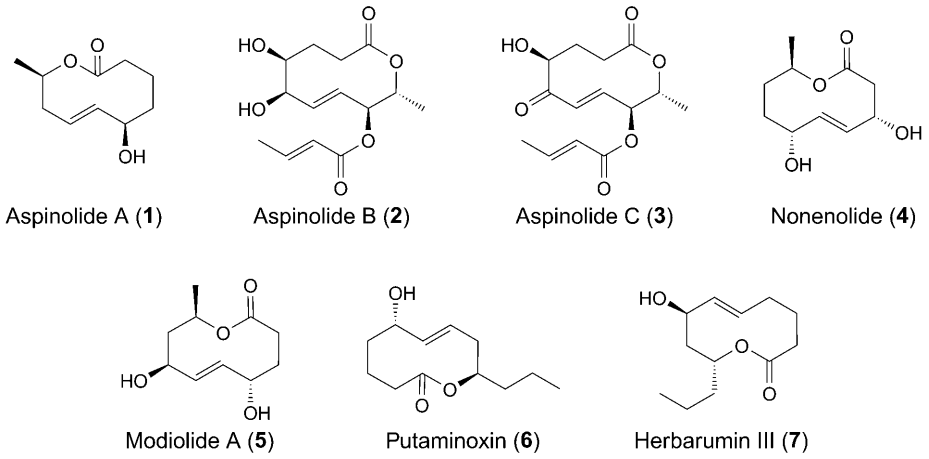
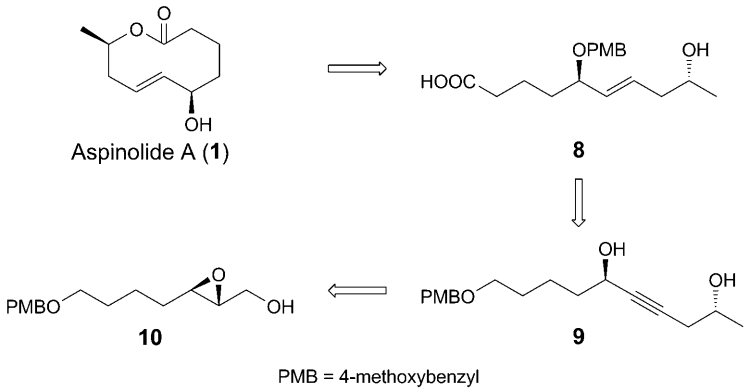


Figure. *10-Membered natural macrolides*

As a part of our current interest in naturally occurring pharmacologically active macrolides [2b][2d][2e], we report herein the second synthesis of aspinolide A through an iterative acetylene–epoxide opening and *Yamaguchi* lactonization. Our retrosynthetic analysis is outlined in *Scheme 1*. The macrolide **1** could be obtained by

Yamaguchi lactonization of **8**, which, in turn, could be made from **9**. The diol **9** could be prepared by iterative coupling of a triple-bond compound obtainable from **10** and (2*R*)-2-methyloxirane (**12**).

Scheme 1. *Retrosynthetic Analysis of Aspinolide A* (**1**)



Results and Discussion. – The known epoxy alcohol **10**, prepared from homopropargyl alcohol (= but-3-yn-1-ol), was converted to the corresponding epoxy chloride **11** in 87% yield by using TPP (= 5,10,15,20-tetraphenylporphyrin) and $NaHCO_3$ in dry CCl_4 and refluxing for 4 h (*Scheme 2*). Accordingly, compound **11** was subjected to $LiNH_2$ in liquid NH_3 to furnish the desired terminal acetylene [4], which was coupled *in situ* with 5 equiv. of (2*R*)-2-methyloxirane (**12**) to get the chiral propargyl alcohol **9** in a one-pot reaction in 80% yield. The triple bond in **9** was reduced with $LiAlH_4$ in THF providing (*E*)-allyl alcohol **13**. The differentiation of the two secondary OH groups of **13** relied on the discovery that the propargyl or the allyl alcohol function reacts selectively [5] with (*tert*-butyl)chlorodimethylsilane (^{t}BuMe$_2$SiCl). Accordingly, diol **13** was converted to alcohol **14** followed by removal of the 4-methoxybenzyl protecting group by using DDQ (= 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile), in CH_2Cl_2/H_2O 19 : 1, which resulted in diol **15** in 91% yield. Selective oxidation of the primary-alcohol group in diol **15** to an aldehyde function was achieved with BAIB/TEMPO (= [bis(acetyloxy)iodo]benzene/2,2,6,6-tetramethylpiperidin-1-yloxy) [6] in CH_2Cl_2 at room temperature, which, without isolation, was converted to the corresponding acid **8** by *Pinnick* oxidation [7] (83% yield over the two steps), followed by *Yamaguchi* lactonization (2,4,6-trichlorobenzoyl chloride in refluxing toluene) to provide macrolactone **16** (70% yield). Finally, removal of the ^{t}BuMe$_2$Si group with Bu_4NF provided the target molecule **1** in 90% yield. The ^{1}H- and ^{13}C-NMR data and optical-rotation value of synthetic **1** were in good accord with those of the natural product [1].

Conclusion. – An iterative acetylene–epoxide coupling and *Yamaguchi*'s protocols were successfully applied leading to the second synthesis of aspinolide A (**1**).

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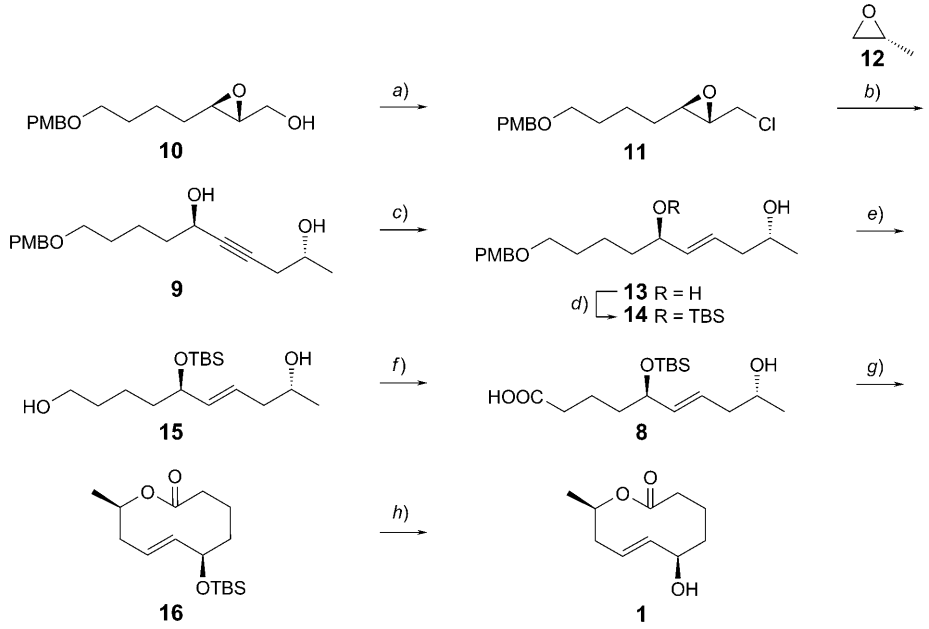
Scheme 2



PMB = 4-methoxybenzyl, TBS = (*tert*-butyl)dimethylsilyl

a) TPP, $NaHCO_3$, reflux, CCl_4, 4 h; 87%. *b*) Li, liq. NH_3, $Fe(NO_3)_3$ (cat.), dry THF, 8 h; 80%. *c*) $LiAlH_4$, dry THF, 4 h; 85%. *d*) ^{t}BuMe$_2$SiCl, 1*H*-imidazole, dry CH_2Cl_2, 4 h; 86%. *e*) DDQ, CH_2Cl_2/H_2O, 1 h; 91%. *f*) 1. BAIB/TEMPO, CH_2Cl_2, 2 h; 2. $NaClO_2$, NaH_2PO_4, DMSO, 1 h; 83%. *g*) 2,4,6-Trichlorobenzoyl chloride, Et_3N, DMAP (= *N*,*N*-dimethylpyridin-4-amine), toluene, reflux, 12 h; 70%. *h*) Bu_4NF, dry THF, 6 h; 90%.

Experimental Part

General. Reactions were conducted under N_2 in anh. solvents such as CH_2Cl_2, THF, and AcOEt. Yields refer to chromatographically and spectroscopically (^{1}H- and ^{13}C-NMR) homogeneous material. Air-sensitive reagents were transferred by syringe or double-ended needle. Column chromatography (CC): silica gel (60–120 mesh. *Acme Chemical Co.*, India). TLC: *Merck 60 F-254* silica gel plates and light petroleum ether (b.p. 60–80°) for reation monitoring; detection by UV light. Optical rotations: *Jasco-DIP-370* polarimeter; at 25°. IR Spectra: *Perkin-Elmer Infrared-683* spectrometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Varian-FT-200* (*Gemini*) and *Bruker-UXNMR-FT-300* (*Avance*) spectrometers; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. ESI-MS: *LC-MSD* (*Agilent Technologies*) spectrometers at 70 eV; in *m*/*z* (rel. %). HR-ESI-MS: *QSTAR-XL* hybrid ms/ms system (*Applied Biosystems*/*MDS Sciex*, Foster City, USA), equipped with an ESI source (*IICT*, Hyderabad); in *m*/*z*.

(2S,3R)-2-(Chloromethyl)-3-{4-[(4-methoxyphenyl)methoxy]butyl}oxirane (**11**). To a stirred soln. of alcohol **10** (3.2 g, 12.01 mmol) in dry CCl_4 (50 ml), TPP (3.78 g, 14.41 mmol) and $NaHCO_3$ (1.51 g, 18.02 mmol) were added. The mixture was heated to vigorous reflux for 4 h, and the resulting solid was filtered and washed with Et_2O. Concentration and purification by CC afforded **11** (2.97 g, 87%). Viscous liquid. $[\alpha]_D^{25} = +5.86$ (*c* = 3.4, $CHCl_3$). IR (neat): 3444, 2934, 2856, 1775, 1684, 1609, 1512, 1459, 1362, 1301, 1248, 1174, 1094, 1036. ^{1}H-NMR (500 MHz): 7.12 (*d*, *J* = 8.8, 2 H); 6.82 (*d*, *J* = 8.8, 2 H); 4.39 (*s*, 2 H); 3.79 (*s*, 3 H); 3.58 (*dd*, *J* = 4.2, 11.7, 1 H); 3.36–3.42 (*m*, 3 H); 2.92 (*ddd*, *J* = 1.9, 5.8, 10.7, 1 H); 2.79

(*ddd*, *J* = 1.9, 5.8, 10.7, 1 H); 1.48–1.67 (*m*, 6 H). ^{13}C-NMR (75 MHz): 159.2; 130.5; 129.2; 113.6; 72.5; 69.6; 58.9; 57.1; 55.2; 44.6; 31.1; 29.3; 22.5. ESI-MS: 307 ([*M* + Na]$^+$). HR-ESI-MS: 307.1809 ([*M* + Na]$^+$, $C_{15}H_{21}ClNaO_3^+$; calc. 307.1077).

*(2*R*,6*R*)-10-[(4-Methoxyphenyl)methoxy]dec-4-yne-2,6-diol* (**9**). To freshly dist. NH_3 (50 ml), in a two-necked round-bottomed flask fitted with a cold finger condenser, was added a cat. amount of $Fe(NO_3)_3$, followed by the portion-wise addition of Li metal (0.48 g, 68.82 mmol) at −33°. The resulting gray suspension was stirred for 30 min. Then **11** (2.8 g, 9.83 mmol) in dry THF (20 ml) was added within 20 min, and the mixture was stirred for 2 h at −33°. Then the addition of a cat. amount of $BF_3 \cdot Et_2O$ followed by (2*R*)-2-methyloxirane (**12**; 3.44 ml, 49.16 mmol) was carried out successively, the mixture stirred for 5 h at −33° and quenched by the addition of solid NH_4Cl (10 g), and NH_3 then allowed to evaporate. The mixture was diluted with H_2O (10 ml) and AcOEt (50 ml) and filtered over a small pad of *Celite*. The filtrate was extracted with AcOEt (3 × 50 ml), the combined org. layer dried (Na_2SO_4) and concentrated, and the residue purified by CC: **9** (2.41 g, 80%). Pale yellow viscous liquid. $[\alpha]_D^{25} = -5.4$ (*c* = 2.2, $CHCl_3$). IR (neat): 3383, 2928, 2860, 1774, 1611, 1572, 1457, 1371, 1300, 1248, 1173, 1089, 1033. ^{1}H-NMR (500 MHz): 7.19 (*d*, *J* = 8.3, 2 H); 6.81 (*d*, *J* = 8.3, 2 H); 4.38 (*s*, 2 H); 4.25–4.30 (*m*, 1 H); 3.76 (*s*, 3 H); 3.85–3.91 (*m*, 1 H); 3.41 (*t*, *J* = 6.2, 2 H); 2.35 (*ddq*, *J* = 2.1, 4.2, 16.6, 1 H); 2.24 (*ddq*, *J* = 2.1, 4.2, 16.6, 1 H); 1.57–1.67 (*m*, 4 H); 1.44–1.51 (*m*, 2 H); 1.20 (*d*, *J* = 6.24, 3 H). ^{13}C-NMR (75 MHz): 159.1; 130.5; 129.2; 113.7; 83.7; 81.6; 72.5; 69.8; 66.2; 62.3; 55.2; 37.6; 29.2; 29.1; 22.3; 21.9. ESI-MS: 324 ([*M* + NH_4]$^+$), 307 ([*M* + H]$^+$). HR-ESI-MS: 329.1725 ([*M* + Na]$^+$, $C_{18}H_{26}NaO_4^+$; calc. 329.1729).

*(2*R*,4*E*,6*R*)-10-[(4-Methoxyphenyl)methoxy]dec-4-ene-2,6-diol* (**13**). To a stirred suspension of $LiAlH_4$ (0.409 g, 10.77 mmol) in dry THF (30 ml) at 0° was added dropwise a soln. of **9** (2.2 g, 7.18 mmol) in dry THF (20 ml). The mixture was allowed to warm to r.t. and stirred for 4 h. After cooling to 0°, the mixture was diluted with Et_2O and quenched by dropwise addition of sat. aq. Na_2SO_4 soln. (10 ml). The solid material was filtered and washed thoroughly several times with hot AcOEt. The combined org. layer dried (Na_2SO_4), the solvent evaporated, and the residue purified by CC: **13** (1.88 g, 85%). Viscous liquid. $[\alpha]_D^{25} = -3.4$ (*c* = 2.6, $CHCl_3$). IR (neat): 3397, 2925, 2853, 1776, 1611, 1512, 1459, 1374, 1300, 1248, 1170, 1082, 1034. ^{1}H-NMR (300 MHz): 7.19 (*d*, *J* = 8.5, 2 H); 6.85 (*d*, *J* = 8.5, 2 H); 5.47–5.68 (*m*, 2 H); 4.39 (*s*, 2 H); 4.0–4.14 (*m*, 2 H); 3.79 (*s*, 3 H); 3.40 (*t*, *J* = 6.2, 2 H); 2.0–2.25 (*m*, 2 H); 1.36–1.64 (*m*, 6 H); 1.17 (*d*, *J* = 6.3, 3 H). ^{13}C-NMR (75 MHz): 159.1; 136.3; 130.5; 129.2; 127.2; 113.6; 72.4; 69.8; 67.0; 55.1; 41.7; 36.8; 29.9; 29.4; 22.6; 22.08. ESI-MS: 331 ([*M* + Na]$^+$). HR-ESI-MS: 331.1880 ([*M* + Na]$^+$, $C_{18}H_{28}NaO_4^+$; calc. 331.1885).

*(2*R*,4*E*,6*R*)-6-{[(*tert*-Butyl)dimethylsilyl]oxy}-10-[(4-methoxyphenyl)methoxy]dec-4-en-2-ol* (**14**). To a stirred soln. of **13** (1.6 g, 4.75 mmol) and 1*H*-imidazole (0.667 g, 9.51 mmol) in dry CH_2Cl_2 (20 ml) was added ^{t}BuMe$_2$SiCl (1.07 g, 7.13 mmol), portion-wise at 0°. The mixture was stirred at 0° for 4 h and then quenched with sat. aq. NH_4Cl soln. and extracted with CH_2Cl_2 (3 × 40 ml). The aq. layer was extracted with additional CH_2Cl_2 (2 × 30 ml), the combined org. layer washed with H_2O (30 ml) and brine (30 ml), dried (Na_2SO_4), and concentrated, and the residue purified by CC: **14** (1.84 g, 86%). Colorless liquid. $[\alpha]_D^{25} = -3.3$ (*c* = 2.4, $CHCl_3$). IR (neat): 3415, 2927, 2853, 1776, 1612, 1512, 1459, 1372, 1300, 1247, 1173, 1084, 1036, 972. ^{1}H-NMR (300 MHz): 7.20 (*d*, *J* = 9.1, 2 H); 6.82 (*d*, *J* = 9.1, 2 H); 5.40–5.66 (*m*, 2 H); 4.39 (*s*, 2 H); 4.00–4.09 (*m*, 1 H); 3.80 (*s*, 3 H); 3.74–3.83 (*m*, 1 H); 3.38 (*t*, *J* = 6.8, 2 H); 2.06–2.25 (*m*, 2 H); 1.54–1.65 (*m*, 2 H); 1.36–1.53 (*m*, 4 H); 1.17 (*d*, *J* = 6.04, 3 H); 0.88 (*s*, 9 H); 0.03 (*s*, 3 H); 0.01 (*s*, 3 H). ^{13}C-NMR (500 MHz): 159.0; 137.2; 130.7; 129.2; 125.7; 113.7; 73.2; 72.5; 70.0; 67.2; 55.2; 42.1; 38.1; 29.7; 25.9; 22.7; 22.0; 18.2; −4.3; −4.8. ESI-MS: 445 ([*M* + Na]$^+$). HR-ESI-MS: 445.2748 ([*M* + Na]$^+$, $C_{24}H_{42}NaO_4Si^+$; calc. 445.2750).

*(5*R*,6*E*,9*R*)-5-{[(*tert*-Butyl)dimethylsilyl]oxy}dec-6-ene-1,9-diol* (**15**). To a soln. of **14** (1.6 g, 3.55 mmol) in CH_2Cl_2/H_2O 19:1 (30 ml), DDQ (1.208 g, 5.32 mmol) was added, and the soln. was stirred for 1 h at r.t. The mixture was filtered, the filtrate washed with 5% $NaHCO_3$ soln. (30 ml) and brine (30 ml), dried (Na_2SO_4), and concentrated, and the residue purified by CC: **15** (1.06 g, 91%). $[\alpha]_D^{25} = -3.1$ (*c* = 1.4, $CHCl_3$). IR (neat): 3358, 2928, 2854, 1777, 1613, 1513, 1546, 1262, 1155, 1080, 1040, 973. ^{1}H-NMR (500 MHz): 5.45–5.66 (*m*, 2 H); 4.01–4.12 (*m*, 1 H); 3.74–3.86 (*m*, 1 H); 3.62 (*t*, *J* = 6.8, 2 H); 2.06–2.28 (*m*, 2 H); 1.46–1.61 (*m*, 4 H); 1.33–1.42 (*m*, 2 H); 1.19 (*d*, *J* = 6.04, 3 H); 0.89 (*s*, 9 H); 0.04 (*s*, 3 H); 0.01 (*s*, 3 H). ^{13}C-NMR (75 MHz): 137.2; 125.9; 73.2; 67.2; 62.8; 42.1; 37.9; 32.6; 25.9; 22.7;

21.4; 18.2; −4.3; −4.7. ESI-MS: 325 ([M+Na]$^+$). HR-ESI-MS: 325.2175 ([M+Na]$^+$, $C_{16}H_{34}NaO_3Si^+$; calc. 325.5272).

*(5*R*,6*E*,9*R*)-5-{[(*tert*-Butyl)dimethylsilyl]oxy}-9-hydroxydec-6-enoic Acid* (**8**). BAIB (0.847g, 2.66 mmol) was added to a soln. of **15** (0.8 g, 2.42 mmol) and TEMPO (0.038 g 0.242 mmol) in CH_2Cl_2 (1 ml). The mixture was stirred until **15** was no longer detectable (TLC), and then it was diluted with CH_2Cl_2 (20 ml). The mixture was washed with sat. aq. $Na_2S_2O_3$ soln. (20 ml) and extracted with CH_2Cl_2 (4 × 20 ml). The combined org. extract was washed with aq. $NaHCO_3$ soln. (30 ml) and brine (30 ml), dried (Na_2SO_4), and concentrated. The unstable crude aldehyde was immediately used for the next reaction.

A soln. of $NaClO_2$ (0.33 g, 3.65 mmol) in H_2O (2 ml) was added dropwise within 5 min at r.t. to a stirred soln. of the above crude aldehyde (0.8 g, 2.43 mmol) in DMSO (5 ml) and NaH_2PO_4 (0.759 g, 4.869 mmol) in H_2O (5 ml). The mixture was left overnight at r.t., and then 5% aq. $NaHCO_3$ soln. was added. The aq. phase was extracted (3 × 30 ml) with CH_2Cl_2 (3 × 30 ml), the extract washed with brine (30 ml), dried (Na_2SO_4), and concentrated, and the residue purified by CC: **8** (0.692 g; 83% yield over the two steps). Yellowish liquid. $[\alpha]_D^{25} = +1.2$ ($c = 2.5$, $CHCl_3$). IR (neat): 3424, 2926, 2856, 1774, 1724, 1377, 1246, 1170, 1059, 972, 838. ^{1}H-NMR (400 MHz): 5.45–5.61 (*m*, 2 H); 4.06–4.13 (*m*, 1 H); 3.75–3.83 (*m*, 1 H); 2.94 (*s*, 1 H); 2.33 (*t*, $J = 6.8$, 2 H); 2.07–2.25 (*m*, 2 H); 1.59–1.73 (*m*, 2 H); 1.46–1.56 (*m*, 2 H); 1.18 (*d*, $J = 6.8$, 3 H); 0.88 (*s*, 9 H); 0.04 (*s*, 3 H); 0.01 (*s*, 3 H). ^{13}C-NMR (50 MHz): 179.2; 136.8; 126.1; 72.9; 67.4; 41.9; 37.5; 33.9; 25.9; 22.7; 20.5; 18.2; −4.3; −4.8. ESI-MS: 339 ([M+Na]$^+$). HR-ESI-MS: 339.1978 ([M+Na]$^+$, $C_{16}H_{32}NaO_4Si^+$; calc. 339.1968).

*(6*R*,7*E*,10*R*)-6-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,4,5,6,9,10-hexahydro-10-methyl-2*H*-oxecin-2-one* (**16**). To a soln. of **8** (0.4 g, 1.16 mmol) and Et_3N (0.245 mg, 1.74 mmol) in THF (3 ml), 2,4,6-trichlorobenzoyl chloride (0.272 ml, 1.74 mmol) was added at r.t. The soln. was stirred at r.t. for 3 h, diluted with toluene (6 ml), and added into a refluxing soln. of DMAP (0.709 g, 5.80 mmol) and toluene (50 ml). The mixture was refluxed for 6 h and then cooled to r.t. Sat. aq. $NaHCO_3$ soln. was added, the aq. layer further extracted with AcOEt (3 × 20 ml), the combined org. layer washed with H_2O (20 ml) and brine (20 ml), dried (Na_2SO_4), and concentrated and the crude product purified by CC: **16** (0.265 g, 70%). Colorless oil. $[\alpha]_D^{25} = -3.4$ ($c = 0.7$, $CHCl_3$). IR (neat): 3446, 2923, 2853, 1733, 1641, 1462, 1365, 1254, 1220, 1186, 1159, 1062, 972, 942. ^{1}H-NMR (300 MHz): 5.37 (*ddd*, $J = 15.3$, 10.0, 4.3, 1 H); 5.27 (*dd*, $J = 15.5$, 9.0, 1 H); 5.09–5.20 (*m*, 1 H); 3.90–4.01 (*m*, 1 H); 2.29–2.49 (*m*, 2 H); 1.71–2.07 (*m*, 5 H); 1.43–1.65 (*m*, 1 H); 1.3 (*d*, $J = 6.4$, 3 H); 0.86 (*s*, 9 H); 0.03 (*s*, 3 H); 0.02 (*s*, 3 H). ^{13}C-NMR (75 MHz): 175.7; 138.5; 129.5; 74.6; 71.7; 42.2; 39.9; 35.7; 29.7; 25.9; 22.2; 18.1; −4.3; −4.7. ESI-MS: 321 ([M+Na]$^+$). HR-ESI-MS: 321.1876 ([M+Na]$^+$, $C_{16}H_{30}NaO_3Si^+$; calc. 321.1862).

*(6*R*,7*E*,10*R*)-3,4,5,6,9,10-Hexahydro-6-hydroxy-10-methyl-2*H*-oxecin-2-one* (= *Aspinolide A*; **1**). To a soln. of **16** (0.15 g, 0.459 mmol) in THF (10 ml) was added 1M Bu_4NF in THF (0.689 ml, 0.689 mmol) at 0°. The mixture was stirred for 6 h and then diluted with H_2O and extracted with AcOEt (3 × 10 ml). The org. layer was washed with H_2O (20 ml) and brine (20 ml), dried (Na_2SO_4), and concentrated. The crude product was purified by CC: **1** (0.087 g, 90%). Colorless oil. $[\alpha]_D^{25} = -41.8$ ($c = 0.6$, MeOH). IR (neat): 3442, 2926, 2855, 1728, 1448, 1270, 1187, 1054, 977. ^{1}H-NMR (500 MHz): 5.51 (*ddd*, $J = 15.8$, 10.6, 4.5, 1 H); 5.30 (*dd*, $J = 15.8$, 9.8, 1 H); 5.09–5.20 (*m*, 1 H); 3.98 (*ddd*, $J = 3.0$, 3.7, 9.8, 1 H); 2.26–2.45 (*m*, 2 H); 1.98–2.06 (*m*, 2 H); 1.86–1.93 (*m*, 2 H); 1.42–1.70 (*m*, 2 H); 1.32 (*d*, $J = 6.8$, 3 H). ^{13}C-NMR (75 MHz): 176.6; 137.1; 131.8; 74.1; 71.7; 42.1; 38.7; 35.6; 22.3; 19.8. ESI-MS: 207 ([M+Na]$^+$). HR-ESI-MS: 207.099 ([M+Na]$^+$, $C_{10}H_{16}NaO_3^+$; calc. 207.0997).

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