

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

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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.

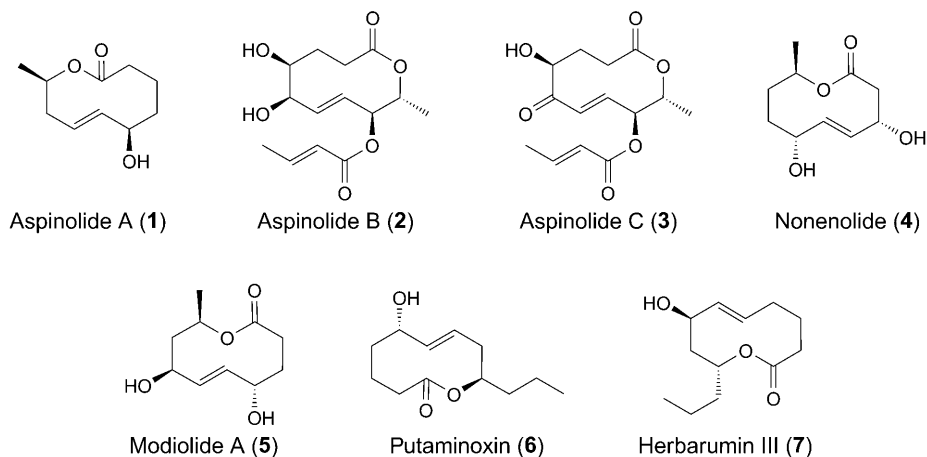
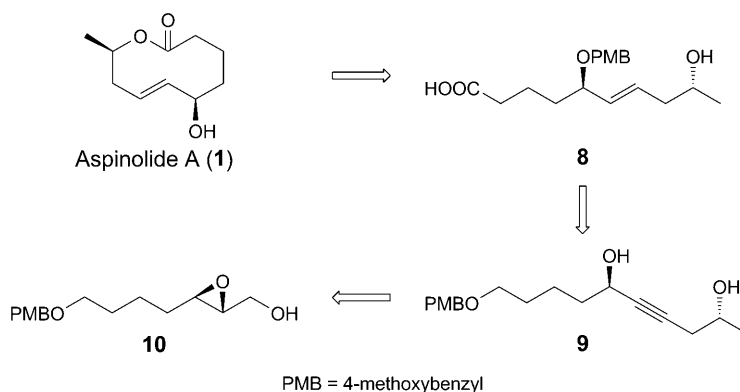


Figure. 10-Membered natural macrolides

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 homo-propargyl 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 NaHCO₃ in dry CCl₄ and refluxing for 4 h (*Scheme 2*). Accordingly, compound **11** was subjected to LiNH₂ in liquid NH₃ 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 LiAlH₄ 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 ('BuMe₂-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 CH₂Cl₂/H₂O 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 CH₂Cl₂ 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 'BuMe₂Si group with Bu₄NF provided the target molecule **1** in 90% yield. The ¹H- and ¹³C-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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a) TPP, NaHCO₃, reflux, CCl₄, 4 h; 87%. b) Li, liq. NH₃, Fe(NO₃)₃ (cat.), dry THF, 8 h; 80%. c) LiAlH₄, dry THF, 4 h; 85%. d) ^tBuMe₂SiCl, 1*H*-imidazole, dry CH₂Cl₂, 4 h; 86%. e) DDQ, CH₂Cl₂/H₂O, 1 h; 91%. f) 1. BAIB/TEMPO, CH₂Cl₂, 2 h; 2. NaClO₂, NaH₂PO₄, DMSO, 1 h; 83%. g) 2,4,6-Trichlorobenzoyl chloride, Et₃N, DMAP (= *N,N*-dimethylpyridin-4-amine), toluene, reflux, 12 h; 70%. h) Bu₃NF, dry THF, 6 h; 90%.

General. Reactions were conducted under N₂ in anh. solvents such as CH₂Cl₂, THF, and AcOEt. Yields refer to chromatographically and spectroscopically (¹H- and ¹³C-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. ¹H- and ¹³C-NMR Spectra: *Varian-FT-200 (Gemini)* and *Bruker-UXNMR-FT-300 (Avance)* spectrometers; in CDCl₃; δ in ppm rel. to Me₄Si 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. $^1\text{H-NMR}$ (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*, $J = 1.9, 5.8, 10.7, 1 \text{ H}$); $1.48\text{--}1.67$ (*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 ($[M + \text{Na}]^+$). HR-ESI-MS: 307.1809 ($[M + \text{Na}]^+$, $\text{C}_{15}\text{H}_{21}\text{ClNaO}_3^+$; calc. 307.1077).

(2R,6R)-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 $\text{Fe}(\text{NO}_3)_3$, 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 $\text{BF}_3 \cdot \text{Et}_2\text{O}$ followed by (2R)-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 ($3 \times 50 \text{ ml}$), 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. ^1H -NMR (500 MHz): 7.19 (*d*, $J = 8.3, 2 \text{ H}$); 6.81 (*d*, $J = 8.3, 2 \text{ H}$); 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*, $J = 6.2, 2 \text{ H}$); 2.35 (*ddq*, $J = 2.1, 4.2, 16.6, 1 \text{ H}$); 2.24 (*ddq*, $J = 2.1, 4.2, 16.6, 1 \text{ H}$); 1.57–1.67 (*m*, 4 H); 1.44–1.51 (*m*, 2 H); 1.20 (*d*, $J = 6.24, 3 \text{ H}$). ^{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 ($[M + \text{NH}_4]^+$), 307 ($[M + \text{H}]^+$). HR-ESI-MS: 329.1725 ($[M + \text{Na}]^+$, $\text{C}_{18}\text{H}_{26}\text{NaO}_4^+$; calc. 329.1729).

(2R,4E,6R)-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. ^1H -NMR (300 MHz): 7.19 (*d*, $J = 8.5, 2 \text{ H}$); 6.85 (*d*, $J = 8.5, 2 \text{ H}$); 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*, $J = 6.2, 2 \text{ H}$); 2.0–2.25 (*m*, 2 H); 1.36–1.64 (*m*, 6 H); 1.17 (*d*, $J = 6.3, 3 \text{ H}$). ^{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 ($[M + \text{Na}]^+$). HR-ESI-MS: 331.1880 ($[M + \text{Na}]^+$, $\text{C}_{18}\text{H}_{28}\text{NaO}_4^+$; calc. 331.1885).

(2R,4E,6R)-6-[(tert-Butyl)dimethylsilyloxy]-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 $\text{tBuMe}_2\text{SiCl}$ (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 ($3 \times 40 \text{ ml}$). The aq. layer was extracted with additional CH_2Cl_2 ($2 \times 30 \text{ ml}$), 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. ^1H -NMR (300 MHz): 7.20 (*d*, $J = 9.1, 2 \text{ H}$); 6.82 (*d*, $J = 9.1, 2 \text{ H}$); 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*, $J = 6.8, 2 \text{ H}$); 2.06–2.25 (*m*, 2 H); 1.54–1.65 (*m*, 2 H); 1.36–1.53 (*m*, 4 H); 1.17 (*d*, $J = 6.04, 3 \text{ H}$); 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 ($[M + \text{Na}]^+$). HR-ESI-MS: 445.2748 ($[M + \text{Na}]^+$, $\text{C}_{24}\text{H}_{42}\text{NaO}_4\text{Si}^+$; calc. 445.2750).

(5R,6E,9R)-5-[(tert-Butyl)dimethylsilyloxy]dec-6-ene-1,9-diol (**15**). To a soln. of **14** (1.6 g, 3.55 mmol) in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ 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. ^1H -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*, $J = 6.8, 2 \text{ H}$); 2.06–2.28 (*m*, 2 H); 1.46–1.61 (*m*, 4 H); 1.33–1.42 (*m*, 2 H); 1.19 (*d*, $J = 6.04, 3 \text{ H}$); 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).

(5R,6E,9R)-5-[[*tert*-Butyl]dimethylsilyl]oxy]-9-hydroxydec-6-enoic Acid (**8**). BAIB (0.847 g, 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. 1H -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 ($[M + Na]^+$, $C_{16}H_{32}NaO_3Si^+$; calc. 339.1968).

(6R,7E,10R)-6-[[*tert*-Butyl]dimethylsilyl]oxy]-3,4,5,6,9,10-hexahydro-10-methyl-2H-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. 1H -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).

(6R,7E,10R)-3,4,5,6,9,10-Hexahydro-6-hydroxy-10-methyl-2H-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. 1H -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).

REFERENCES

- [1] J. Fuchser, A. Zeeck, *Liebigs Ann. Recl.* **1997**, 87.
- [2] a) V. Rukachaisirikul, S. Pramjit, C. Pakawatchai, M. Isaka, S. Supothina, *J. Nat. Prod.* **2004**, 67, 1953; b) G. Sabitha, P. Padmaja, K. Sudhakar, J. S. Yadav, *Tetrahedron: Asymmetry* **2009**, 20, 1330; c) M. Tsuda, T. Mugishima, K. Komatsu, T. Sone, M. Tanaka, Y. Mikami, J. Kobayashi, *J. Nat. Prod.* **2003**, 66, 412; d) G. Sabitha, K. Yadagiri, R. Swapna, J. S. Yadav, *Tetrahedron Lett.* **2009**, 50, 5417; e) G. Sabitha, C. Srinivas, C. Maruthi, J. S. Yadav, *Helv. Chim. Acta* **2010**, 93, 1634.

- [3] P. S. Chowdhury, P. Gupta, P. Kumar, *Tetrahedron Lett.* **2009**, 50, 7018.
- [4] J. S. Yadav, P. K. Deshpande, C. V. M. Sharma, *Pure Appl. Chem.* **1990**, 62, 1333; G. Sabitha, E. Venkata Reddy, M. Bhikshapathi, J. S. Yadav, *Tetrahedron Lett.* **2007**, 48, 313; G. Sabitha, E. Venkata Reddy, K. Yadagiri, J. S. Yadav, *Synthesis* **2006**, 3270; G. Sabitha, N. Fatima, R. Swapna, J. S. Yadav, *Synthesis* **2006**, 2879.
- [5] D. K. Mohapatra, S. Nayak, S. Mohapatra, M. S. Chorghade, M. K. Gurjar, *Tetrahedron Lett.* **2007**, 48, 5197.
- [6] T. M. Hansen, G. J. Florence, P. Lugo-Mas, J. Chen, J. N. Abrams, C. J. Forsyth, *Tetrahedron Lett.* **2003**, 44, 57.
- [7] B. S. Bal, W. E. Childers Jr., H. W. Pinnick, *Tetrahedron* **1981**, 37, 2091.

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