**An Effective Use of Benzoic Anhydride and Its Derivatives for the
Synthesis of Carboxylic Esters and Lactones.
A Powerful and Convenient Mixed-anhydride Method
Promoted by Basic Catalysts**

Isamu Shiina,* Mari Kubota, Hiromi Oshiumi, Minako Hashizume

*Contribution from the Department of Applied Chemistry, Faculty of Science,
Tokyo University of Science, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*

Supporting Information

General Information. All melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS), chloroform (in chloroform-*d*) or benzene (in benzene-*d*₆) as internal standard. Column chromatography was performed on Silica gel 60 (Merck) or Wakogel B5F. Thin layer chromatography was performed on Wakogel B5F.

All reactions were carried out under argon atmosphere in dried glassware, unless otherwise noted. Dichloromethane was distilled from diphosphorus pentoxide, then calcium hydride, and dried over MS 4 Å, toluene was distilled from diphosphorus pentoxide, and dried over MS 4 Å, and DMF was distilled from calcium hydride, and dried over MS 4 Å. All reagents were purchased from Tokyo Kasei Kogyo Co., Ltd., Kanto Chemical Co., Inc. or Aldrich Chemical Co., Inc., and used without further purification unless otherwise noted.

2-Methyl-6-nitrobenzoic anhydride (NMBA).

2-Methyl-6-nitrobenzoic anhydride was purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI, M1439) or synthesized from 2-methyl-6-nitrobenzoic acid. 2-Methyl-6-nitrobenzoic acid was also purchased from TCI. A solution of 2-methyl-6-nitrobenzoic acid (5.00 g, 27.6 mmol) and thionyl chloride (20.1 mL, 276 mmol) in dichloromethane (50 mL) was stirred for 15 h at room temperature. The solvent and thionyl chloride were distilled under reduced pressure at 50 °C and then dichloromethane (40 mL), 2-methyl-6-nitrobenzoic acid (5.00 g, 27.6 mmol) and pyridine (2.40 mL, 30.4 mmol) were successively added at 0 °C. After the reaction mixture had been stirred for 24 h at room temperature, cooled water (100 mL) was added at 0 °C. The mixture was extracted with dichloromethane, and the organic layer was washed with saturated aqueous copper(II) sulfate, saturated aqueous sodium hydrogencarbonate, cold water and brine, dried over

sodium sulfate. Filtration of the mixture and evaporation of the solvent under reduced pressure produced 8.80 g of the crude MNBA. First recrystallization of the crude product from dichloromethane (*ca.* 90 mL) at 0 °C gave 7.70 g (81%) of pure MNBA as a white solid: Mp. 178-180 °C; IR (KBr): 1759, 1820 cm^{-1} ; ^1H NMR (CDCl_3): δ 2.57 (6H, s), 7.53 (2H, dd, $J = 7.6, 8.1$ Hz), 7.64 (2H, d, $J = 7.6$ Hz), 8.06 (2H, d, $J = 8.1$ Hz); ^{13}C NMR (CDCl_3) δ 19.1, 121.7, 127.5, 130.5, 136.6, 137.9, 145.1, 160.3; Anal: calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_7$: C, 55.82; H, 3.51; N, 8.14, found: C, 55.81; H, 3.39; N, 8.07.

Typical Experimental Procedure for the Esterification Reaction

A typical experimental procedure is described for the reaction of 3-phenylpropanoic acid with 4-phenyl-2-butanol; to a solution of triethylamine (66.1 mg, 0.653 mmol) in dichloromethane (1.5 mL) were added DMAP (2.5 mg, 0.020 mmol), MNBA (82.9 mg, 0.241 mmol) and 3-phenylpropanoic acid (36.3 mg, 0.242 mmol). After having been stirred for 10 min, a solution of 4-phenyl-2-butanol (30.1 mg, 0.200 mmol) in dichloromethane (2.0 mL) was added. The reaction mixture was stirred for 20 h at room temperature and then saturated aqueous ammonium chloride was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford 53.9 mg (95%) of 1-methyl-3-phenylpropyl 3-phenylpropanoate.

3-Phenylpropyl 3-phenylpropanoate¹ (1). IR (neat) 1735 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.91 (2 H, m), 2.62 (4H, m), 2.95 (2H, t, $J = 7.8$ Hz), 4.08 (2H, t, $J = 6.6$ Hz), 7.13-7.31 (10H, m); Found: C, 80.35; H, 7.77%. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2$: C, 80.56; H, 7.51%.

Benzyl 3-phenylpropanoate² (3). IR (neat) 1736 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.67 (2H, t, $J = 7.8$ Hz), 2.96 (2H, t, $J = 7.8$ Hz), 5.10 (2H, s), 7.12-7.40 (10H, m).

Allyl 3-phenylpropanoate (4). IR (neat) 1736 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.66 (2H, t, $J = 7.8$ Hz), 2.97 (2H, t, $J = 7.8$ Hz), 4.57 (2H, td, $J = 1.3, 5.6$ Hz), 5.21 (1H, tdd, $J = 1.3, 1.7, 10.6$ Hz), 5.28 (1H, tdd, $J = 1.3, 1.7, 17.2$ Hz), 5.89 (1H, tdd, $J = 5.6, 10.6, 17.2$ Hz), 7.10-7.35 (5H, m); HR MS: calcd for $\text{C}_{12}\text{H}_{15}\text{O}_2$ ($\text{M} + \text{H}^+$) 191.1072, found 191.1073.

1-Methyl-3-phenylpropyl 3-phenylpropanoate¹ (5). IR (neat) 1730 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.21 (3H, d, $J = 6.3$ Hz), 1.72-1.96 (2H, m), 2.51-2.69 (4H, m), 2.95 (2H, t, $J = 7.6$ Hz), 4.94 (1H, m), 7.11-7.31 (10H, m); Found: C, 80.74; H, 7.99%. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_2$: C, 80.82; H, 7.85%.

Cyclohexyl 3-phenylpropanoate³ (6). IR (neat) 1730 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.10-1.19 (8H, m), 1.80 (2H, td, $J = 5.4, 9.1$ Hz), 2.60 (2H, t, $J = 7.8$ Hz), 2.95 (2H, t, $J = 7.8$ Hz), 4.75 (1H, tt, $J = 4.4, 9.1$ Hz), 7.09-7.38 (5H, m).

(-)-Mentyl 3-phenylpropanoate (7). $[\alpha]_{\text{D}}^{28} = -58.0^\circ$ (c 1.67, CHCl_3); IR (neat) 1730 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.62 (3H, d, $J = 6.9$ Hz), 0.68-1.75 (14H, m), 1.78-1.93 (1H, m), 2.53 (2H, t, $J = 7.8$ Hz), 2.87 (2H, t, $J = 7.8$ Hz), 4.59 (1H, dt, $J = 4.6, 10.9$ Hz), 7.05-7.26 (5H, m); HR MS: calcd for $\text{C}_{19}\text{H}_{29}\text{O}_2$ ($\text{M} + \text{H}^+$) 289.2167, found 289.2177.

(+)-5 α -Cholestan-3 β -yl 3-phenylpropanoate (8). Mp. 96-98 $^\circ\text{C}$; $[\alpha]_{\text{D}}^{28} = +13.2^\circ$ (c 1.00, CHCl_3); IR (neat) 1730 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.52-2.02 (46H, m), 2.58 (2H, t, $J = 7.8$ Hz), 2.93 (2H, t, $J = 7.8$ Hz), 4.69 (1H, tt, $J = 5.6, 11.2$ Hz), 7.07-7.36 (5H, m); ^{13}C NMR (CDCl_3) δ 12.06, 12.20, 18.65, 21.19, 22.55, 22.81, 23.83, 24.19, 27.44, 28.00, 28.23, 28.59, 31.05, 31.97, 33.98, 35.44, 35.78, 36.16, 36.26, 36.73, 39.50, 39.97, 42.57, 44.62, 54.20, 56.25, 56.39, 73.77, 126.15, 128.30, 128.41, 140.61, 172.42; HR MS: calcd for $\text{C}_{36}\text{H}_{57}\text{O}_2$ ($\text{M} + \text{H}^+$) 521.4358, found 521.4360.

1,1-Dimethyldecyl 3-phenylpropanoate (9). IR (neat) 1728 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.88 (3H, t, $J = 6.7$ Hz), 1.21-1.31 (14H, m), 1.39 (6H, s), 1.66-1.72 (2H, m), 2.54 (2H, dd, $J = 6.8, 9.1$ Hz), 2.91 (2H, dd, $J = 6.8, 9.1$ Hz), 7.16-7.31 (5H, m); HR MS: calcd for $\text{C}_{21}\text{H}_{35}\text{O}_2$ ($\text{M} + \text{H}^+$) 319.2637, found 319.2639.

6-Tetrahydropyranyloxyhexyl 3-phenylpropanoate (10). IR (neat) 1736 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.33-1.43 (4H, m), 1.51-1.87 (10H, m), 2.62 (2H, dd, $J = 6.8, 9.1$ Hz), 2.95 (2H, dd, $J = 6.8, 9.1$ Hz), 3.34-3.42 (1H, m), 3.46-3.54 (1H, m), 3.69-3.77 (1H, m), 3.82-3.90 (1H, m), 4.06 (2H, t, $J = 6.6$ Hz), 4.57 (1H, dd, $J = 2.8, 4.1$ Hz), 7.17-7.31 (5H, m); HR MS: calcd for $\text{C}_{20}\text{H}_{31}\text{O}_4$ ($\text{M} + \text{H}^+$) 335.2223, found 335.2227.

3-Phenylpropyl 3-(*t*-butyldimethylsiloxy)-3-phenylpropanoate (11). IR (neat) 1736 cm^{-1} ; ^1H NMR (CDCl_3) δ -0.17 (3H, s), 0.02 (3H, s), 0.84 (9H, s), 1.94

(2H, dddd, $J = 6.6, 7.4, 8.1, 10.9$ Hz), 2.56 (1H, dd, $J = 4.3, 14.6$ Hz), 2.66 (2H, dd, $J = 7.4, 8.1$ Hz), 2.75 (1H, dd, $J = 9.1, 14.6$ Hz), 4.08 (1H, ddd, $J = 6.6, 10.9, 14.8$ Hz), 4.10 (1H, ddd, $J = 6.6, 10.9, 14.8$ Hz), 5.14 (1H, dd, $J = 4.3, 9.1$ Hz), 7.15-7.37 (10H, m); HR MS: calcd for $C_{24}H_{35}O_3Si$ ($M + H^+$) 399.2355, found 399.2353.

3-Phenylpropyl cyclohexanecarboxylate¹ (12). IR (neat) 1732 cm^{-1} ; ^1H NMR (CCl_4) δ 1.05-2.40 (13H, m), 2.65 (2H, t, $J = 8.0$ Hz), 4.00 (2H, t, $J = 6.0$ Hz), 7.15 (5H, s); Found: C, 77.89; H, 8.90%. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00%.

1-Methyl-3-phenylpropyl cyclohexanecarboxylate¹ (13). IR (neat) 1728 cm^{-1} ; ^1H NMR (CCl_4) δ 1.15 (3H, d, $J = 6.0$ Hz), 1.25-2.25 (13H, m), 2.25-2.80 (2H, m), 4.85 (1H, m), 7.15 (5H, s); Found: C, 78.18; H, 9.07%. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29%.

Cyclohexyl cyclohexanecarboxylate (14) IR (neat) 1728 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.14-1.91 (20H, m), 2.20-2.31 (1H, m), 4.70-4.78 (1H, m); HR MS: calcd for $C_{13}H_{23}O_2$ ($M + H^+$) 211.1698, found 211.1699.

3-Phenylpropyl 2,2-dimethylpropanoate¹ (15). IR (neat) 1728 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.26 (9H, s), 1.97-2.03 (2H, m), 2.74 (2H, t, $J = 7.6$ Hz), 4.12 (2H, t, $J = 6.3$ Hz), 7.21-7.34 (5H, m); Found: C, 76.06; H, 9.21%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

1-Methyl-3-phenylpropyl 2,2-dimethylpropanoate¹ (16). IR (neat) 1726 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.22 (9H, s), 1.25 (3H, d, $J = 6.3$ Hz), 1.73-2.00 (2H, m), 2.54-2.74 (2H, m), 4.91 (1H, m), 7.15-7.31 (5H, m); Found: C, 76.70; H, 9.52%. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46%.

3-Phenylpropyl benzoate¹ (17). IR (neat) 1718 cm^{-1} ; ^1H NMR (CCl_4) δ 2.23 (2H, m), 2.77 (2H, t, $J = 8$ Hz), 4.27 (2H, t, $J = 6$ Hz), 7.05-7.54 (8H, m), 7.85-8.10 (2H, m); Found: C, 79.69; H, 6.97%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

1-Methyl-3-phenylpropyl benzoate¹ (18). IR (neat) 1716 cm^{-1} ; ^1H NMR (CCl_4) δ 1.44 (3H, d, $J = 6$ Hz), 1.74-2.23 (2H, m), 2.55-2.90 (2H, m), 5.15 (1H, m), 7.05-7.54 (8H, m), 7.98 (2H, dd, $J = 8, 2$ Hz); Found: C, 80.47; H, 7.22%. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%.

3-Phenylpropyl (*E*)-crotonate¹ (19). IR (neat) 1722 cm⁻¹; ¹H NMR (CDCl₃) δ 1.87 (3H, dd, *J* = 6.9, 1.7 Hz), 1.99 (2H, tt, *J* = 7.6, 6.6 Hz), 2.70 (2H, t, *J* = 7.6 Hz), 4.14 (2H, t, *J* = 6.6 Hz), 5.85 (1H, dq, *J* = 15.0, 1.7 Hz), 6.96 (1H, dq, *J* = 15.0, 6.9 Hz), 7.15-7.31 (5H, m); Found: C, 76.21; H, 8.00%. Calcd for C₁₃H₁₆O₂: C, 76.44; H, 7.90%.

1-Methyl-3-phenylpropyl (*E*)-crotonate (20). IR (neat) 1730 cm⁻¹; ¹H NMR (CDCl₃) δ 1.27 (3H, d, *J* = 6.3 Hz), 1.70-2.06 (2H, m), 1.87 (3H, dd, *J* = 1.8, 6.9 Hz), 2.50-2.76 (2H, m), 4.99 (1H, tq, *J* = 6.3, 6.3 Hz), 5.84 (1H, qd, *J* = 1.8, 15.4 Hz), 6.96 (1H, qd, *J* = 6.9, 15.4 Hz), 7.10-7.34 (5H, m); HR MS: calcd for C₁₄H₁₉O₂ (M + H⁺) 219.1385, found 219.1387.

3-Phenylpropyl (*E*)-3-phenyl-2-propenoate⁴ (21). IR (neat): 1712 cm⁻¹; ¹H NMR (CDCl₃) δ 2.04 (2H, tdd, *J* = 6.4, 7.4, 7.9 Hz), 2.75 (2H, dd, *J* = 7.4, 7.9 Hz), 4.23 (2H, t, *J* = 6.4 Hz), 6.45 (1H, d, *J* = 16.0 Hz), 7.17-7.32 (5H, m), 7.35-7.43 (3H, m), 7.50-7.54 (2H, m), 7.68 (1H, d, *J* = 16.0 Hz); HR MS: calcd for C₁₈H₁₉O₂ (M + H⁺) 267.1385, found 267.1376.

1-Methyl-3-phenylpropyl (*E*)-3-phenyl-2-propenoate (22). IR (neat): 1712 cm⁻¹; ¹H NMR (CDCl₃) δ 1.33 (3H, d, *J* = 6.3 Hz), 1.81-1.96 (1H, m), 1.98-2.07 (1H, m), 2.65 (1H, ddd, *J* = 6.8, 9.2, 13.9 Hz), 2.75 (1H, ddd, *J* = 6.3, 9.7, 13.9 Hz), 5.08 (1H, dqd, *J* = 1.2, 6.3, 12.5 Hz), 6.43 (1H, d, *J* = 16.0 Hz), 7.15-7.32 (5H, m), 7.36-7.43 (3H, m), 7.50-7.55 (2H, m), 7.67 (1H, d, *J* = 16.0 Hz); HR MS: calcd for C₁₉H₂₁O₂ (M + H⁺) 281.1541, found 281.1541.

Ethyl 3-phenylpropyl fumarate (23). IR (neat): 1720 cm⁻¹; ¹H NMR (CDCl₃) δ 1.33 (3H, t, *J* = 7.2 Hz), 2.02 (2H, tdd, *J* = 6.4, 7.3, 8.1 Hz), 2.72 (2H, dd, *J* = 7.3, 8.1 Hz), 4.22 (2H, t, *J* = 6.4 Hz), 4.27 (2H, q, *J* = 7.2 Hz), 6.82 (1H, d, *J* = 15.8 Hz), 6.88 (1H, d, *J* = 15.8 Hz), 7.17-7.38 (5H, m); HR MS: calcd for C₁₅H₁₉O₄ (M + H⁺) 263.1284, found 263.1283.

Typical Experimental Procedure for the Synthesis of Lactones

A typical experimental procedure is described for the reaction of protected *erythro*-aleuritic acid **24**; (Method A) to a solution of MNBA (157.8 mg, 0.458 mmol) and DMAP (111.4 mg, 0.912 mmol) in dichloromethane (135.8 mL) at room temperature was slowly added a solution of **24** (149.2 mg, 0.380 mmol) in dichloromethane (84.6 mL) with a mechanically driven syringe over a 16-h period. After addition of the

solution, the reaction mixture was additionally stirred for 1 h at room temperature. The reaction mixture was concentrated to ca. 20 mL by evaporation of the solvent under reduced pressure and then saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin layer chromatography to afford 128.2 mg (90%) of **25**, 4.4 mg (1.5%) of diolide and 1.8 mg (0.4%) of triolide.

(Method B) to a solution of MNBA (148.7 mg, 0.432 mmol), triethylamine (80.1 mg, 0.792 mmol) and DMAPO (9.9 mg, 0.072 mmol) in dichloromethane (151.0 mL) at room temperature was slowly added a solution of **24** (141.3 mg, 0.360 mmol) in dichloromethane (108.0 mL) with a mechanically driven syringe over a 16 h period. After addition of the solution, the reaction mixture was additionally stirred for 1 h at room temperature. Same treatment of the reaction mixture as mentioned above afforded 120.8 mg (90%) of **25**, 4.9 mg (1.8%) of diolide and 0.7 mg (0.2%) of triolide.

Dodecan-12-olide⁵ (13-Membered ring lactone). IR (neat) 1734 cm⁻¹; ¹H NMR (CDCl₃) δ 1.23-1.48 (14H, m), 1.60-1.73 (4H, m), 2.33-2.38 (2H, m), 4.15 (2H, dd, *J* = 4.0, 5.1 Hz); EI MS: calcd for C₁₂H₂₂O₂ (M⁺) 198, found 198.

Octadecan-12-olide^{6,7} (12-Hydroxystearic acid lactone). IR (neat) 1730 cm⁻¹; ¹H NMR (CDCl₃) δ 0.87 (3H, t, *J* = 6.7 Hz), 1.17-1.80 (28H, m), 2.24 (1H, ddd, *J* = 3.9, 9.0, 12.3 Hz), 2.43 (1H, ddd, *J* = 3.6, 8.1, 12.3 Hz), 4.92 (1H, dddd, *J* = 2.2, 4.3, 6.5, 8.9 Hz); EI MS: calcd for C₁₈H₃₄O₂ (M⁺) 282, found 282.

Tridecan-13-olide⁵ (14-Membered ring Lactone). IR (neat) 1736 cm⁻¹; ¹H NMR (CDCl₃) δ 1.19-1.50 (16H, m), 1.58-1.72 (4H, m), 2.35-2.39 (2H, m), 4.14 (2H, dd, *J* = 4.5, 5.3 Hz); EI MS: calcd for C₁₃H₂₄O₂ (M⁺) 212, found 212.

Tetradecan-14-olide⁵ (15-Membered ring Lactone). IR (neat) 1728 cm⁻¹; ¹H NMR (CDCl₃) δ 1.19-1.48 (18H, m), 1.56-1.73 (4H, m), 2.32-2.37 (2H, m), 4.13 (2H, t, *J* = 4.1, 5.3 Hz); EI MS: calcd for C₁₄H₂₆O₂ (M⁺) 226, found 226.

Pentadecan-15-olide⁵ (16-Membered ring Lactone). IR (neat) 1740 cm⁻¹; ¹H NMR (CDCl₃) δ 1.24-1.49 (20H, m), 1.56-1.72 (4H, m), 2.33 (2H, dd, *J* = 6.6, 7.1 Hz), 4.13 (2H, dd, *J* = 5.4, 5.6 Hz); EI MS: calcd for C₁₅H₂₈O₂ (M⁺) 240, found 240.

Hexadecan-16-olide⁵ (17-Membered ring Lactone). IR (neat) 1736 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.22-1.45 (22H, m), 1.55-1.71 (4H, m), 2.32 (2H, dd, $J = 6.6, 6.9$ Hz), 4.12 (2H, t, $J = 5.6$ Hz); EI MS: calcd for $\text{C}_{16}\text{H}_{30}\text{O}_2$ (M^+) 254, found 254.

***erythro*-16-Hydroxy-9,10-benzylidenedioxyhexadecanoic acid (24).** *erythro*-Aleuritic acid was purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI). To a mixture of *erythro*-aleuritic acid (3.00 g, 9.85 mmol) and benzaldehyde dimethyl acetal (1.65 g, 10.8 mmol) in DMF (9.85 mL) at room temperature was added CSA (458 mg, 1.97 mmol). After the reaction mixture had been stirred for 5 h at 60 °C and for 10 h at room temperature, triethylamine (1 mL) was added. The reaction mixture was concentrated by evaporation of the solvent. The crude product was purified by column chromatography ($\text{MeOH} / \text{CH}_2\text{Cl}_2 = 1 / 20$) to afford 2.68 g (70%) of **24** (a mixture of stereoisomeric benzylidene acetals) as a colorless oil; IR (neat) 1666, 1720, 3456 cm^{-1} ; ^1H NMR (C_6D_6) δ 1.21-1.66 (22H, m), 2.19 (2H, dt, $J = 3.0, 7.5$ Hz), 3.45-3.51 (2H, m), 3.73-3.81 (2H, m), 5.24 (2H, br s), 6.05 (1H, s), 7.15-7.28 (3H, m), 7.68-7.71 (2H, m); HR MS: calcd for $\text{C}_{23}\text{H}_{37}\text{O}_5$ ($\text{M} + \text{H}^+$) 393.2641, found 393.2650.

***erythro*-9,10-Benzylidenedioxyhexadecan-16-olide (25).** IR (neat) 1728 cm^{-1} ; ^1H NMR (C_6D_6 , a mixture of stereoisomeric benzylidene acetals) δ 1.05-1.95 (22H, m), 2.19 (2H, dd, $J = 5.8, 7.1$ Hz), 3.72-3.85 (2H, m), 4.03-4.08 (2H, m), 6.04 (1H, s), 7.10-7.28 (3H, m), 7.70-7.73 (2H, m); HR MS: calcd for $\text{C}_{23}\text{H}_{35}\text{O}_4$ ($\text{M} + \text{H}^+$) 375.2535, found 375.2536.

***erythro*-Aleuritic acid lactone.⁸** The protected *erythro*-aleuritic acid lactone **25** (9.9 mg, 0.026 mmol) was dissolved in water (0.19 mL) and acetic acid (0.76 mL). After having been stirred for 24 h at room temperature, solid sodium hydrogencarbonate was added to the reaction mixture at 0 °C. Water, ethyl acetate and solid sodium hydrogencarbonate were added to the reaction mixture and then it was further stirred for 10 h at 0 °C. The mixture was extracted with ethyl acetate, and the organic layer was washed with brine, dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by silica gel chromatography ($\text{AcOEt} / \text{hexane} = 1 / 1$) to afford 7.0 mg (93%) of *erythro*-aleuritic acid lactone as a white solid; Mp. 53-54 °C; IR (neat) 1728, 3456 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.22-1.73 (22H, m), 1.73-1.98 (2H, br m), 2.33 (2H, t, $J = 6.6$ Hz), 3.42-3.51 (2H, m), 4.11-4.15 (2H, m); ^{13}C NMR (CDCl_3) δ 23.1, 23.9, 25.1, 25.4, 27.6, 27.8, 28.1, 28.2, 28.7, 31.4, 32.5, 34.6, 64.2, 73.4, 74.2, 174.0; HR MS: calcd for $\text{C}_{16}\text{H}_{31}\text{O}_4$ ($\text{M} + \text{H}^+$) 287.2222, found 287.2221.

Experimental Procedure for the Synthesis of the 8-Membered Ring Lactone Moiety of Octalactins A and B

To a solution of MNBA (6.9 mg, 0.020 mmol) and DMAP (11.3 mg, 0.092 mmol) in toluene (5.3 mL) at room temperature was added a solution of the seco acid **26** (8.7 mg, 0.015 mmol) in toluene (2.4 mL). After the reaction mixture had been stirred for 13 h at room temperature, saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was extracted with ethyl acetate, and the organic layer was washed with brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by preparative thin layer chromatography (AcOEt / hexane = 1 / 5) to afford 7.1 mg (84%) of (3*R*,4*S*,7*S*,8*R*)-3-benzyloxy-9-(*t*-butyldimethylsiloxy)-4,8-dimethylnonan-7-olide (**28**) as a colorless oil.

(3*R*,4*S*,7*S*,8*R*)-3-Benzyloxy-9-(*t*-butyldiphenylsiloxy)-4,8-dimethyl-7-hydroxynonanoic acid (26**).** IR (neat): 1712, 3448 cm⁻¹; ¹H NMR (CDCl₃): δ 0.79 (3H, d, *J* = 6.9 Hz), 0.94 (3H, d, *J* = 6.9 Hz), 1.05 (9H, s), 1.32-1.60 (2H, m), 1.71-1.84 (1H, m), 1.85-1.97 (1H, m), 2.51-2.57 (2H, m), 3.57-3.64 (2H, m), 3.76 (1H, dd, *J* = 4.0, 10.2 Hz), 3.82-3.87 (1H, m), 4.54 (1H, d, *J* = 11.2 Hz), 4.62 (1H, d, *J* = 11.2 Hz), 7.28-7.48 (11H, m), 7.60-7.69 (4H, m); ¹³C NMR(CDCl₃): δ 13.5, 14.1, 19.0, 21.2, 26.8, 28.2, 32.6, 35.6, 39.6, 69.0, 71.8, 76.3, 80.0, 127.5, 127.7, 127.8, 128.3, 129.9, 132.7, 135.5, 138.3, 175.5; HR MS: calcd for C₃₄H₄₇O₅Si (M + H⁺) 563.3193, found 563.3191.

(3*R*,4*S*,7*S*,8*R*)-3-Benzyloxy-9-(*t*-butyldiphenylsiloxy)-4,8-dimethylnonan-7-olide (28**).** IR (neat): 1728 cm⁻¹; ¹H NMR (CDCl₃): δ 0.98 (3H, d, *J* = 7.1 Hz), 1.06 (9H, s), 1.10 (3H, d, *J* = 7.1 Hz), 1.15-1.24 (1H, m), 1.50-1.75 (3H, m), 1.86-2.06 (2H, m), 2.67 (1H, d, *J* = 13.3 Hz), 3.03 (1H, dd, *J* = 6.4, 13.3 Hz), 3.52 (1H, dd, *J* = 4.3, 10.1 Hz), 3.63 (1H, br d, *J* = 6.4 Hz), 3.87 (1H, dd, *J* = 4.0, 10.1 Hz), 4.44 (1H, d, *J* = 11.5 Hz), 4.55-4.63 (1H, m), 4.95 (1H, d, *J* = 11.5 Hz), 7.25-7.46 (11H, m), 7.60-7.66 (4H, m); ¹³C NMR(CDCl₃): δ 13.3, 19.3, 21.6, 23.9, 26.9, 31.3, 34.8, 37.9, 40.3, 65.0, 70.7, 78.1, 78.2, 127.5, 127.7, 127.7, 128.0, 128.2, 129.7, 129.7, 133.3, 133.4, 135.4, 135.6, 138.3, 171.7; HR MS: calcd for C₃₄H₄₅O₄Si (M + H⁺) 545.3087, found 545.3095.

References and Notes

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