A Stereoselective Synthesis of (±)-Pestalotin

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(±)-Pestalotin (1) was synthesized by employing a stereoselective reduction of a 5-alkyltetronate derivative (3) and a two-carbon elongation reaction of the aldehyde (13) with ethyl diazoacetate in the presence of stannous chloride as key steps.

Keywords (±)-pestalotin; tetronate; *syn*-glycol; stereoselective reduction; ethyl diazoacetate

Pestalotin (**1**) was isolated from culture filtrate of a phytopathogenic fungus, *Pestalotia cryptomeriaecola*, as an active principle showing gibberellin-synergistic activity.[1] Pestalotin has been the target of several syntheses owing to its interesting biological activity and *syn*-glycol structural feature.[2] We describe here a stereoselective synthesis of (±)-pestalotin using a catalytic reduction of a 5-alkyltetronate to construct the *syn*-glycol system as a key reaction.

Since the alkylation of tetronate has been established to afford the 5-alkylated product site-selectively,[3] methoxymethyl tetronate (**2**) was reacted with crotyl bromide in the presence of lithium cyclohexyl isopropylamide to give the desired compound (**3**) in 61% yield. In contrast, similar alkylation of **2** with *n*-butyl bromide yielded a trace amount of alkylated product. Catalytic reduction of the tetronate (**3**) over 5% rhodium on alumina under medium pressure (7 atm) of hydrogen provided the lactones (**4** and **5**) in 76 and 22% yields, respectively, where the reduction occurred predominantly from the opposite side to the substituent at the 5-position.[4]

Thus, the desired *syn*-glycol system was constructed stereoselectively, and we next attempted the conversion of **4** into (±)-pestalotin as follows.

Reduction of **4** with lithium aluminum hydride gave the diol (**6**) whose mono-silylation with *tert*-butyldimethylsilyl chloride and triethylamine afforded the silyl ether (**7**) in 78% yield from **4**. The secondary hydroxyl group of **7** was then benzylated in a usual manner with benzyl bromide and sodium hydride to give the benzyl ether, which (without

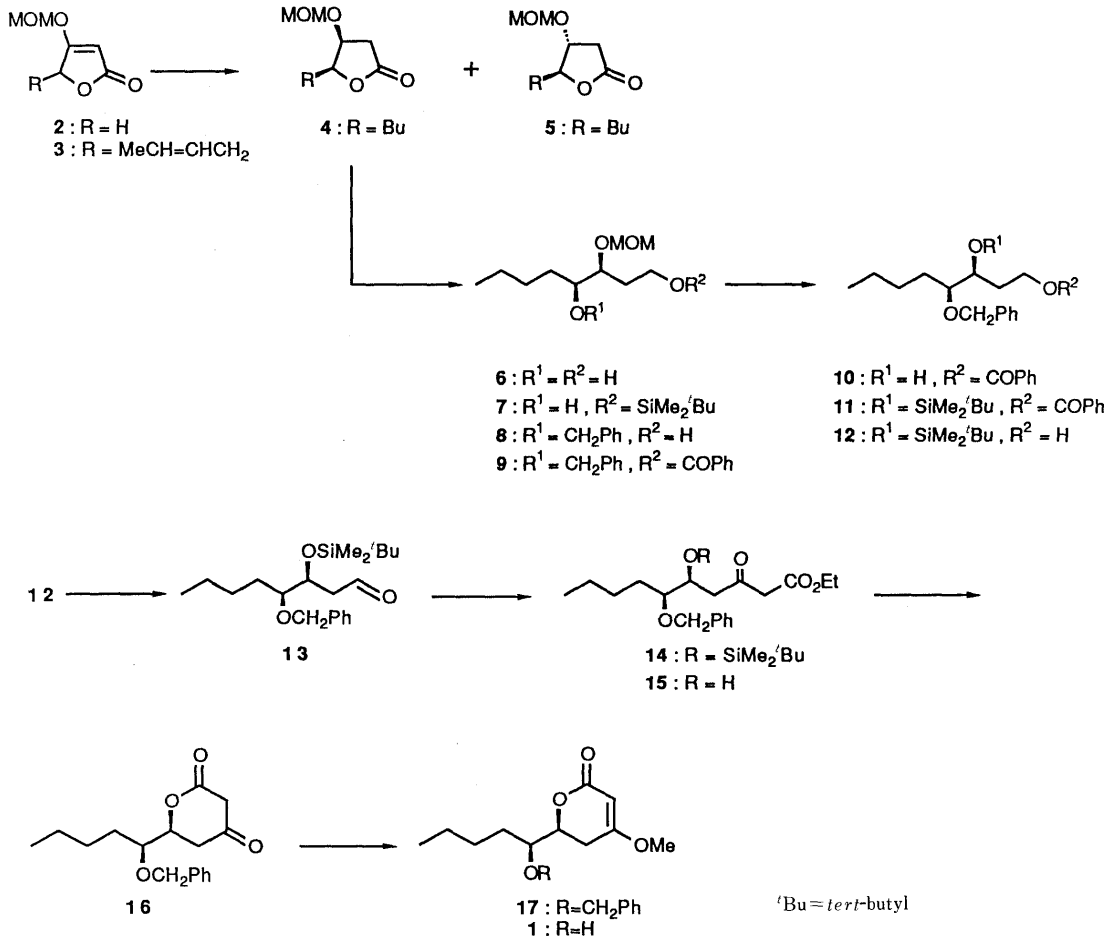

Chart 1

further purification) was subjected to desilylation with tetrabutylammonium fluoride to afford the alcohol (**8**) in 80% yield in two steps. Although we first employed **8** as a starting material, difficulties were encountered in removal of the methoxymethyl protecting group in the later stage of this synthesis. Compound **8** was, therefore, treated with benzoyl chloride in pyridine to give the benzoate (**9**), which, on treatment with aqueous hydrochloric acid, followed by silylation of the resulting alcohol (**10**) with *tert*-butyldimethylsilyl chloride and imidazole, gave the silyl ether (**11**) in 67% yield from **8**. Alkaline hydrolysis of **11** afforded the primary alcohol (**12**), which was subjected to oxidation with pyridinium chlorochromate (PCC) to provide the aldehyde (**13**). Two-carbon elongation reaction was achieved by treatment of **13** with ethyl diazoacetate in the presence of a catalytic amount of stannous chloride[5] to form the β-keto ester (**14**) in 94% yield. The silyl group of **14** was deprotected with aqueous hydrochloric acid, furnishing the alcohol (**15**), which on hydrolysis with 10% sodium hydroxide, followed by neutralization with 10% hydrochloric acid, brought about δ-lactone formation to give **16** in 72% yield from **14**. Finally, methylation of **16** with dimethyl sulfate and potassium carbonate in acetone gave benzyl pestalotin (**17**) whose spectroscopic data were identical with those reported.[2i] Since compound **17** has already been transformed into (±)-pestalotin,[2i] this synthesis constitutes a formal total synthesis of **1**.

The stereoselective reduction of a tetronate derivative yielding a *syn*-glycol system was thus applied successfully to the synthesis of (±)-pestalotin.

Experimental

Infrared (IR) spectra were measured in $CHCl_3$ solution and recorded with a Hitachi 260-10 spectrophotometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were determined with a JEOL PMX GSX 270 spectrometer and δ values are quoted relative to tetramethylsilane. Mass spectra (MS) were measured with a JEOL JMS D300.

Methoxymethyl 5-Crotyltetronate (3) A solution of methoxymethyl tetronate (**2**) (5 g, 34.72 mmol) in dry tetrahydrofuran (THF) (10 ml) was added to a stirred solution of lithium cyclohexyl isopropylamide (1.2 eq) [prepared from cyclohexyl isopropylamine and *n*-butyllithium in dry THF (50 ml)] at −78 °C and the mixture was stirred for 2 h at −20 °C. After addition of crotyl bromide (4.46 ml, 45.09 mmol) at −78 °C, this solution was further stirred for 3 h at −20 °C. The reaction mixture was treated with aqueous NH_4Cl and extracted with $CHCl_3$. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel using hexane–AcOEt (4 : 1) as the eluant to afford **3** (4.2 g, 61.1%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 1720, 1610. ^{1}H-NMR ($CDCl_3$) δ: 1.60 (3H, d, J=5.5 Hz, Me), 2.26—2.63 (2H, m, 6-H_2), 3.45 (3H, s, OMe), 4.74—4.81 (1H, m, 5-H), 5.09 (1H, d, J=6.1 Hz, OCH_2O), 5.11 (1H, d, J=6.1 Hz, OCH_2O), 5.30—5.38 (1H, m, 7-H), 5.50—5.61 (1H, m, 8-H). MS m/z: 198 (M^+).

(3*S,4*S**)-4-Butyl-3-methoxymethoxy-γ-butyrolactone (4) and (3*R**,4*S**)-4-Butyl-3-methoxymethoxy-γ-butyrolactone (5)** A solution of **3** (2.2 g, 11.1 mmol) in AcOEt (20 ml) containing 5% rhodium on alumina (0.45 g) was stirred under medium pressure (7 atm) of hydrogen for 4 h and an insoluble material was filtered off. The filtrate was concentrated to give a residue, which was subjected to column chromatography on silica gel. Elution with hexane–AcOEt (10 : 1) afforded **4** (1.7 g, 75.9%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 1760. ^{1}H-NMR ($CDCl_3$) δ: 0.90—1.85 (9H, m, *n*-Bu), 2.62 (1H, dd, J=1.8, 17.7 Hz, 3-H), 2.72 (1H, dd, J=4.9, 17.7 Hz, 3-H), 3.38 (3H, s, OMe), 4.33—4.47 (2H, m, 4-H, 5-H), 4.62, 4.67 (each 1H, each d, J=6.7 Hz, OCH_2O). MS m/z: 141 (M^+ − OMOM). Further elution with the same solvent gave **5** (0.51 g, 22.3%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 1765. ^{1}H-NMR ($CDCl_3$) δ: 0.90—1.69 (9H, m, *n*-Bu), 2.57 (1H, dd, J=4.3, 18.3 Hz, 3-H), 2.83 (1H, dd, J=6.7, 18.3 Hz, 3-H), 3.38 (3H, s, OMe), 4.10—4.46 (2H, m, 4-H, 5-H), 4.66 (2H, s, OCH_2O). MS m/z: 141 (M^+ − OMOM).

(3*S,4*S**)-1,4-Dihydroxy-3-methoxymethoxyoctane (6)** A solution of the lactone (**4**) (1.3 g, 6.44 mmol) in dry ether (20 ml) was added to a stirred suspension of lithium aluminum hydride in dry ether (30 ml) at 0 °C and the mixture was stirred at ambient temperature for 2 h. After quenching of the reaction by addition of 10% aqueous NaOH, the mixture was filtered through a Celite pad and the filtrate was concentrated to give a residue, which was purified by column chromatography on silica gel using hexane–AcOEt (1 : 1) as the eluant to afford **6** (1.3 g, 97.7%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 3300. ^{1}H-NMR ($CDCl_3$) δ: 0.88—1.92 (11H, m, *n*-Bu, 2-H_2), 3.41 (3H, s, OMe), 3.55—3.76 (4H, m, 1-H_2, 3-H, 4-H), 4.71 (2H, s, OCH_2O). MS m/z: 172 ($M^+ - 2\times$OH).

(3*S,4*S**)-1-*tert*-Butyldimethylsilyloxy-4-hydroxy-3-methoxymethoxyoctane (7)** A solution of **6** (2 g, 9.7 mmol), *tert*-butyldimethylsilyl chloride (1.54 g, 10.7 mmol) and triethylamine (1.49 ml, 10.7 mmol) in dry benzene (30 ml) was stirred at ambient temperature for 6 h and poured into brine. The mixture was extracted with AcOEt and the organic layer was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel using hexane–AcOEt (20 : 1) as the eluant to afford **7** (2.43 g, 78.3%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 3300. ^{1}H-NMR ($CDCl_3$) δ: 0.06, 0.07 (each 3H, each s, $SiMe_2$), 0.89 (9H, s, *tert*-Bu), 1.26—1.85 (11H, m, *n*-Bu, 2-H_2), 3.41 (3H, s, OMe), 3.54—3.77 (4H, m, 1-H_2, 3-H, 4-H). MS m/z: 259 (M^+ − OMOM).

(3*S,4*S**)-4-Benzyloxy-3-methoxymethoxyoctan-1-ol (8)** Sodium hydride (0.36 g, 60% oil dispersion, 9 mmol) and benzyl bromide (1.78 ml, 14.97 mmol) were added to a stirred solution of **7** (2.43 g, 7.59 mmol) in dry THF (20 ml) and the mixture was further stirred at ambient temperature for 6 h, then poured into aqueous NH_4Cl and extracted with AcOEt. The organic layer was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was subjected to column chromatography on silica gel. Elution with hexane–AcOEt (40 : 1) gave the silyl ether (2.82 g, 90.6%) as a colorless oil, which (without further purification) was used in the next step. A mixture of the silyl ether (2.29 g, 5.59 mmol) and a 1 M solution of tetrabutylammonium fluoride (5.57 ml, 5.57 mmol) in THF was stirred at room temperature for 6 h. After evaporation of the solvent, the residue was extracted with AcOEt and the organic layer was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel using hexane–AcOEt (5 : 1) as the eluant to give **8** (1.80 g, 80.2%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 3300. ^{1}H-NMR ($CDCl_3$) δ: 0.86—1.92 (11H, m, *n*-Bu, 2-H_2), 2.60 (1H, br s, OH), 3.39 (3H, s, Me), 3.44—3.87 (4H, m, 1-H_2, 3-H, 4-H), 4.56, 4.61 (each 1H, each d, J=11.0 Hz, C$\underline{H}_2$Ph), 4.66, 4.72 (each 1H, each d, J=6.7 Hz, OCH_2O), 7.28—7.35 (5H, m, aromatic protons). MS m/z: 251 (M^+ − MOM).

(3*S,4*S**)-1-Benzoyloxy-4-benzyloxy-3-methoxymethoxyoctane (9)** A solution of **8** (550 mg, 1.86 mmol), benzoyl chloride (0.35 ml, 3.02 mmol) and pyridine (0.35 ml, 3.02 mmol) in THF (10 ml) was stirred at ambient temperature for 2 h and then poured into aqueous NH_4Cl. The aqueous layer was extracted with AcOEt and the organic layer was washed with aqueous $KHSO_4$ and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was subjected to column chromatography on silica gel. Elution with hexane–AcOEt (15 : 1) afforded **9** (707 mg, 95.1%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 1720. ^{1}H-NMR ($CDCl_3$) δ: 0.83—2.21 (11H, m, *n*-Bu, 2-H_2), 3.37 (3H, s, OMe), 3.49—3.91 (2H, m, 3-H, 4-H), 4.41—4.58 (2H, m, 1-H_2), 4.56, 4.61 (each 1H, each d, J=11.6 Hz, C$\underline{H}_2$Ph), 4.65, 4.71 (each 1H, each d, J=6.7 Hz, OCH_2O), 7.23—8.18 (10H, m, aromatic protons). MS m/z: 356 (M^+ − MOM).

(3*S,4*S**)-1-Benzoyloxy-4-benzyloxy-3-hydroxyoctane (10)** A solution of **9** (70 mg, 0.18 mmol) and 10% HCl in THF (5 ml) was heated at reflux for 2 h, and then diluted with AcOEt. The combined organic layer was washed with aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel using hexane–AcOEt (8 : 1) as the eluant to afford **10** (51 mg, 81.9%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 1710. ^{1}H-NMR ($CDCl_3$) δ: 0.87—2.02 (11H, m, *n*-Bu and 2-H_2), 2.50 (1H, br s, OH), 3.33 (1H, dt, J=5.5, 10.5 Hz, 4-H), 3.79 (1H, m, 3-H), 4.47—4.69 (4H, m, 1-H_2, OC$\underline{H}_2$Ph), 7.25—8.04 (10H, m, aromatic protons). MS m/z: 339 (M^+ − OH).

(3*S,4*S**)-1-Benzoyloxy-4-benzyloxy-3-*tert*-butyldimethylsilyloxyoctane (11)** A solution of **10** (90 mg, 0.25 mmol), *tert*-butyldimethylsilyl chloride (114 mg, 0.76 mmol) and imidazole (52 mg, 0.76 mmol) in dry THF (5 ml) was stirred at room temperature for 6 h, then the mixture was poured into ice-cooled water and extracted with AcOEt. The extract was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave a residue,

which was subjected to column chromatography on silica gel. Elution with hexane–AcOEt (30 : 1) afforded **11** (102 mg, 85.9%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 1710. ^{1}H-NMR ($CDCl_3$) δ: 0.01 (6H, s, $SiMe_2$), 0.89 (9H, s, *tert*-Bu), 0.93—2.14 (11H, m, *n*-Bu, 2-H_2), 3.37 (1H, ddd, J=2.4, 4.9, 9.2 Hz, 4-H), 4.01—4.08 (1H, m, 3-H), 4.28—4.53 (2H, m, 1-H_2), 4.55, 4.61 (each 1H, each d, J=11.6 Hz, CH_2Ph), 7.24—8.05 (10H, m, aromatic protons). MS *m/z*: 413 ($M^+ - tert$-Bu).

(3*S,4*S**)-4-Benzyloxy-3-*tert*-butyldimethylsilyloxyoctan-1-ol (12)** A solution of **11** (120 mg, 0.26 mmol) and 10% aqueous NaOH (0.5 ml) in MeOH (5 ml) was stirred at room temperature for 2 h, and then treated with water. The mixture was extracted with AcOEt and the extract was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel using hexane–AcOEt (9 : 1) as the eluant to afford **12** (81 mg, 86.7%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 3300. ^{1}H-NMR ($CDCl_3$) δ: 0.02, 0.05 (each 3H, each s, $SiMe_2$), 0.86—1.97 (11H, m, *n*-Bu, 2-H_2), 2.36 (1H, br s, OH), 3.33—3.39 (1H, m, 3-H), 3.71 (2H, br s, 1-H_2), 3.97 (1H, dt, J=4.3, 7.9 Hz, 4-H), 4.55, 4.61 (each 1H, each d, J=11.6 Hz, CH_2Ph), 7.28—7.35 (5H, m, aromatic protons). MS *m/z*: 309 ($M^+ - tert$-Bu).

(3*S,4*S**)-4-Benzyloxy-3-*tert*-butyldimethylsilyloxyoctanal (13)** A solution of **12** (105 mg, 0.29 mmol) in CH_2Cl_2 (10 ml) was added to a stirred suspension of PCC (180 mg, 0.84 mmol) and sodium acetate (20 mg, 0.24 mmol) in CH_2Cl_2 (70 ml) at room temperature and the mixture was further stirred for 1 h. After dilution with Et_2O, the mixture was filtered through a Celite pad to remove insoluble material and the filtrate was concentrated to give a residue, which was subjected to column chromatography on silica gel. Elution with hexane–AcOEt (20 : 1) gave **13** (95 mg, 91.0%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 1720. ^{1}H-NMR ($CDCl_3$) δ: 0.02, 0.04 (each 3H, each s, $SiMe_2$), 0.85 (9H, s, *tert*-Bu), 0.86—1.67 (9H, m, *n*-Bu), 2.49 (1H, ddd, J=2.2, 7.9, 15.8 Hz, 2-H), 2.68 (1H, ddd, J=1.8, 4.3, 15.8 Hz, 2-H), 3.32—3.38 (1H, m, 3-H), 4.39 (1H, ddd, J=3.7, 4.3, 7.9 Hz, 4-H), 4.52, 4.57 (each 1H, each d, J=11.6 Hz, CH_2Ph), 7.28—7.38 (5H, m, aromatic protons), 9.76 (1H, dd, J=1.8, 2.2 Hz, CHO). MS *m/z*: 307 ($M^+ - tert$-Bu).

Ethyl (5*S,6*S**)-6-Benzyloxy-5-*tert*-butyldimethylsilyloxy-3-oxodecanoate (14)** A solution of **13** (30 mg, 0.08 mmol) in CH_2Cl_2 (5 ml) was added dropwise to a stirred solution of ethyl diazoacetate (20 mg, 0.16 mmol) and a catalytic amount of $SnCl_2$ in CH_2Cl_2 (5 ml) at ambient temperature over a period of 10 min. The mixture was further stirred for 4 h, and then poured into aqueous NH_4Cl, and extracted with CH_2Cl_2. The extract was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was subjected to column chromatography on silica gel. Elution with hexane–AcOEt (20 : 1) gave **14** (35 mg, 94%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 1720. ^{1}H-NMR ($CDCl_3$) δ: 0.04, 0.06 (each 3H, each s, $SiMe_2$), 0.89 (9H, s, *tert*-Bu), 0.91—1.71 (12H, m, *n*-Bu, Me), 2.66 (1H, dd, J=7.9, 15.9 Hz, 4-H), 2.81 (1H, dd, J=3.7, 15.9 Hz, 4-H), 3.33—3.38 (1H, m, 5-H), 3.47 (2H, s, 2-H_2), 4.22 (2H, q, J=7.3 Hz, OCH_2Me), 4.46—4.53 (1H, m, 6-H), 4.50, 4.62 (each 1H, each d, J=11.6 Hz, CH_2Ph), 7.30—7.41 (5H, m, aromatic protons). MS *m/z*: 393 ($M^+ - tert$-Bu).

Ethyl (5*S,6*S**)-6-Benzyloxy-5-hydroxy-3-oxodecanoate (15)** A solution of **14** (156 mg, 0.35 mmol) and 10% HCl (10 drops) in EtOH (10 ml) was stirred at room temperature for 2 h, and the mixture was extracted with an excess of CH_2Cl_2. The organic layer was washed with aqueous $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel using hexane–AcOEt (5 : 1) to afford **15** (103.5 mg, 88.9%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 1720. ^{1}H-NMR ($CDCl_3$) δ: 0.91 (3H, t, J=7.3 Hz, Me), 1.24—1.71 (9H, m, Me, 3 × CH_2), 2.61—2.74 (3H, m, 4-H_2, OH), 3.32—3.45 (1H, m, 6-H), 3.51 (2H, s, 2-H_2), 4.12—4.17 (1H, m, 5-H), 4.18 (2H, q, J=7.3 Hz, OCH_2Me), 4.49, 4.63 (each 1H, each d, J=11.6 Hz, CH_2Ph), 7.26—7.39 (5H, m, aromatic protons). MS *m/z*: 318 ($M^+ - H_2O$).

(1*S,6*S**)-6-(1-Benzyloxypentyl)-3,4,5,6-tetrahydropyran-2,4-dione (16)** A 10% NaOH solution (2 ml) was added to a solution of **15** (10 mg, 0.03 mmol) in THF (5 ml) and the resulting mixture was stirred at room temperature for 2 h. After neutralization with 10% HCl, the mixture was extracted with AcOEt and the extract was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel using hexane–AcOEt (5 : 1) to afford **16** (7 mg, 81%) as a colorless oil. IR ($CHCl_3$) cm^{-1}: 1720. ^{1}H-NMR ($CDCl_3$) δ: 0.88—0.94 (3H, t, J=7.1 Hz, Me), 1.26—1.77 (6H, m, 3 × CH_2), 2.57 (1H, dd, J=4.3, 17.1 Hz, 5-H), 2.76 (1H, dd, J=5.5, 17.1 Hz, 5-H), 3.29, 3.34 (each 1H, each d, J=20.1 Hz, 3-H_2), 3.34—3.36 (1H, m, 7-H), 4.43, 4.58 (each 1H, each d, J=11.0 Hz, CH_2Ph), 4.62 (1H, ddd, J=4.3, 5.5, 7.9 Hz, 6-H), 7.24—7.39 (5H, m, aromatic protons). MS *m/z*: 290 (M^+). High-resolution MS Calcd for $C_{17}H_{22}O_4$ (M^+): 290.1516. Found: 290.1514.

(±)-Pestalotin Benzyl Ether (17) A solution of **16** (7 mg, 0.02 mmol), K_2CO_3, and Me_2SO_4 (3 drops) in acetone (5 ml) was stirred at room temperature for 2 h. After dilution with water, the mixture was extracted with AcOEt and the extract was washed with water and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was subjected to column chromatography on silica gel. Elution with hexane–AcOEt (2 : 1) gave **17** (6 mg, 81.9%) as a colorless oil, whose spectroscopic data were identical with those reported.[2i] IR ($CHCl_3$) cm^{-1}: 1690, 1620: ^{1}H-NMR ($CDCl_3$) δ: 0.89 (3H, t, J=7.3 Hz, Me), 1.26—1.74 (6H, m, 3 × CH_2), 2.26 (1H, dd, J=3.7, 17.1 Hz, 5-H), 2.69 (1H, ddd, J=1.8, 12.8, 17.1 Hz, 5-H), 3.59 (1H, dt, J=4.3, 8.5 Hz, 7-H), 3.74 (3H, s, OMe), 4.51 (1H, ddd, J=3.7, 4.3, 12.8 Hz, 6-H), 4.61, 4.66 (each 1H, each d, J=11.6 Hz, CH_2Ph), 5.13 (1H, d, J=1.8 Hz, 3-H), 7.26—7.35 (5H, m, aromatic protons). MS *m/z*: 304 (M^+). High-resolution MS Calcd for $C_{18}H_{24}O_4$ (M^+): 304.1673. Found: 304.1672.

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