# A FACILE ASYMMETRIC SYNTHESIS OF COREY LACTONE UTILIZING $C_2$-SYMMETRIC DIMETHYL 3,7-DIHYDROXY-*CIS*-BICYCLO[3.3.0]OCTAN-2,6-DIENE-2,6-DICARBOXYLATE

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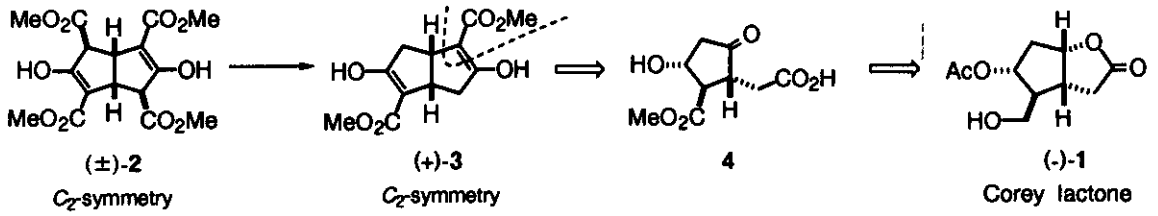
**Abstract** - Optically pure Corey lactone [(-)-1] was conveniently synthesized from an optically pure $C_2$-symmetric diester [(+)-3] which was prepared by lipase-catalyzed demethoxycarbonylation of bicyclic tetraester (2).

A synthetic method with Corey lactone [(-)-1][1] as a key intermediate is a significant procedure for the syntheses of prostaglandins and their analogs.[2] Much attention has been focused on the syntheses of Corey lactone derivatives.[3] As a part of our program aimed at utilizing an enzymatic process for organic synthesis, we found recently that the lipase-catalyzed demethoxycarbonylation of tetraester (2), which was easily prepared by Weiss reaction[4] from dimethyl 3-oxoglutarate and glyoxal in a flask, gave $C_2$-symmetric dimethyl 3,7-dihydroxy-*cis*-bicyclo[3.3.0]octan-2,6-diene-2,6-dicarboxylate [(+)-3] in high enantiomeric excess.[5] Here we report a facile asymmetric synthesis of Corey lactone [(-)-1] using an enantiomerically pure diester [(+)-3][5] as a synthetic intermediate.

**Scheme 1**

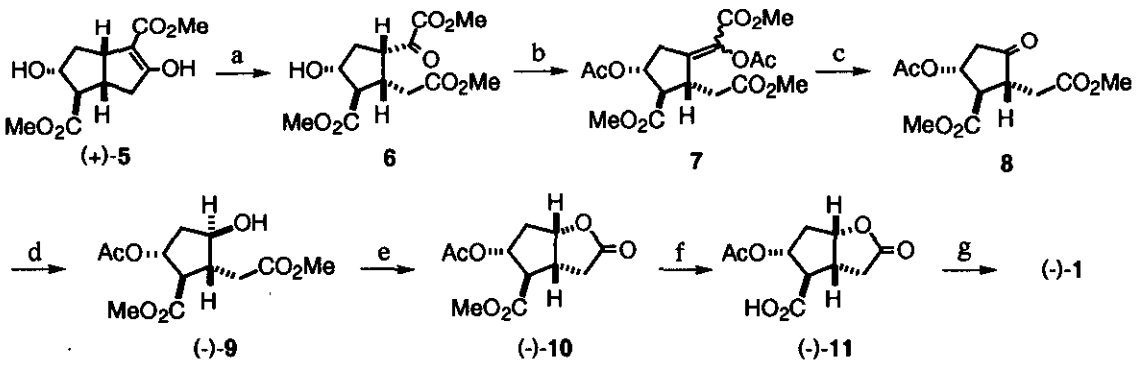



We planned a synthesis of Corey lactone [(-)-1] from tetraester (2), as outlined in Scheme 1. Our objective in this scheme was removal of the acetate unit based on double ozonolysis of one of the two enol groups in *the $C_2$-symmetric* diester [(+)-3]. Cyclopentanone derivative (4) produced by the above ozonolysis after partial reduction of the enol groups has appropriate functional groups at suitable positions for the synthesis of the lactone (1), which will be useful as its synthetic intermediate.

Our practical synthetic route of (-)-1 is shown in Scheme 2. The optically pure alcohol [(+)-5] was

prepared by partial reduction utilizing the $C_2$-symmetry of diester [(+)-3] which was obtained by enzymatic and chemical demethoxycarbonylation.[5] After *O*-methylation of the remaining enol with diazomethane, ozonolysis of the double bond in the enol ether gave α-keto ester (**6**) as an unstable compound, which was gradually decomposed during purification on silica gel. α-Keto ester group in **6** exists in only keto form, not in an enol form, unlike (+)-**5** which consists of the enol form (60%) and the keto form (40%), which were determined by $^1$H-NMR spectroscopy. A transformation from the keto form to the fixed enol form was required for the second ozonolysis to remove the α-keto ester moiety in **6**. Then, acetylation of the crude product (**6**) with acetic anhydride in pyridine afforded inseparable enol acetates (**7**) as a 5 : 1 regioisomeric mixture in 96.5% overall yield from (+)-**5**. Ozonolysis of **7** using dimethyl sulfide as a reductant of the ozonide gave the desired cyclopentanone (**8**) which was an equivalent of the expected intermediate (**4**).

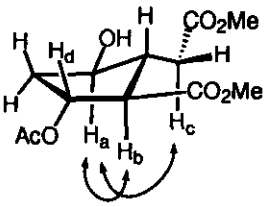
**Scheme 2.** A Facile Asymmetric Synthesis of Corey Lactone




a) i) $CH_2N_2$, ii) $O_3$, MeOH then $Me_2S$; b) $Ac_2O$-pyridine; c) $O_3$, MeOH then $Me_2S$; d) $LiAl(t\text{-}BuO)_3H$, THF, 0 °C; e) *p*-TsOH, benzene reflux; f) $AlBr_3$-$Me_2S$, rt; g) $BH_3$·$Me_2S$, THF, 0 °C

We initially expected that the reduction of cyclopentanone (**8**) would afford an α-alcohol with *S* configuration due to the steric strain of the hydride to the adjacent methoxycarbonylmethyl substituent. If the reduction gives an α-alcohol, the lactone (**10**) must be easily formed under weak acidic conditions. In an attempt to obtain directly lactone (**10**) in the ozonolysis, we reduced the ozonide with sodium borohydride; however, the result was a complex mixture and neither the corresponding alcohol or lactone (**10**) was produced. We tried next the reduction of ketone (**8**) to α-alcohol in a stepwise method. However, the reducing agents (K-Selectride, N-Selectride, and sodium triethoxyborohydride) tested gave complex mixtures, and lithium tri-*tert*-butoxyaluminum hydride afforded a β-alcohol [(-)-**9**] exclusively in 81% yield, whose *R*-configuration on the alcoholic carbon was confirmed by NMR experiments. Thus, after the assignment of all the protons of (-)-**9** by $^1$H-$^1$H COSY spectrum, the NOE was observed between Ha and Hb, and between Ha and Hc, but not between Ha and Hd, as shown in Figure 1. Lactonization of the hydroxy ester [(-)-**9**] to γ-lactone [(-)-**10**] was performed by the use of drastic conditions with *p*-toluenesulfonic acid in benzene (54% yield, 3 steps from **7**). This reaction proceeds probably through an $S_N1$ process. The methyl ester in (-)-**10** was demethylated to give carboxylic acid [(-)-**11**] in 70% yield with the aluminum bromide - dimethyl sulfide system.[6]

**Figure 1**




NOE Difference Spectroscopy

Finally, reduction of the carboxylic acid [(-)-**11**] with a borane - dimethyl sulfide complex gave Corey lactone [(-)-**1**] in 82% yield, whose spectroscopic analyses and specific rotation {$[\alpha]_D^{23}$ -44.1° (c 0.88, $CHCl_3$)} were identical with those reported {lit.,[3h] $[\alpha]_D^{25}$ -44.2° (c 1.88, $CHCl_3$)}.

## EXPERIMENTAL

**General:** Melting points are taken with a micro hot-stage apparatus (Yanagimoto) and are uncorrected. IR spectra are recorded with a JASCO IR-810 diffraction grating infrared spectrophotometer or a Shimadzu FTIR-8000 Fourier transfer infrared spectrophotometer. $^1$H-NMR spectra are obtained with a Varian XL-300 NMR spectrometer. Signals are given in ppm using tetramethylsilane as an internal standard. MS spectra are determined on a JEOL JMS SX-102A QQ. Specific rotations were recorded on a Horiba SEPA-200 polarimeter in the indicated solvent. Combustion analyses were performed by a Yanaco CHN-corder MT-3. Wakogel C-200 (100-200 mesh, Wako Pure Chemical), Wakogel C-300 (200-300 mesh, Wako Pure Chemical) and Kieselgel 60 Art. 9385 (Merck) were used for open-column chromatography. Kieselgel 60 $F_{254}$ plates (Merck) was used for thin layer chromatography (TLC). Preparative TLC (PTLC) was done with Kieselgel 60 $F_{254}$ plates (0.25 mm, Merck). If necessary, compounds were purified by a recycle HPLC (LC-908, Japan Analytical Industry Co., Ltd.) on GPC columns (JAIGEL 1H and 2H) after purification on silica gel.

**Materials:** THF, ether, and benzene were distilled from sodium benzophenone ketyl under a nitrogen atmosphere before use. K-Selectride, N-Selectride, and lithium tri-*tert*-butoxyaluminum hydride were purchased from Aldrich Chemical Company, Inc.

**Methyl (1*S*,2*R*,3*R*,5*S*)-2-(2-Methoxycarbonyl-3-hydroxy-5-methoxalylcyclopentyl)acetate (6)**

To a solution of (+)-5[5] (2.45 g, 9.56 mmol) in ether (250 mL) and methanol (30 mL) was added a ether solution of diazomethane (30 mL) at 0 °C. After being stirred for 20 h, nitrogen gas was bubbled through the reaction mixture for 30 min, then the solvent was evaporated *in vacuo*. An analytical sample of dimethyl (1*S*,2*R*,3*R*,5*S*)-3-hydroxy-7-methoxybicyclo[3.3.0]oct-6-ene-2,6-dicarboxylate was purified by silica gel chromatography (hexane: ethyl acetate = 1 : 2). colorless oil; $[\alpha]_D^{24}$ +80.6° (c 0.89, $CHCl_3$); $^1$H-NMR (300 MHz, $CDCl_3$) δ: 4.33-4.22 (m, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 3.38-3.26 (m, 1H), 3.03-2.93 (m, 1H), 2.77-2.64 (m, 2H), 2.60-2.44 (m, 2H), 2.34 (br s, 1H), 1.51 (ddd, *J* = 13.0, 10.1 and 8.0 Hz, 1H); IR ($CHCl_3$): 3640-3320, 3000, 2950, 2905, 2855, 1723, 1692, 1625, 1456, 1432, 1378 $cm^{-1}$; MS (70 eV) m/z: 270 ($M^+$, 62), 239 (53), 238 (43), 193 (100), 161 (94), 135 (83), 133 (40), 91 (40), 77 (32), 59 (38); Anal. Calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.58; H, 6.67.

Ozone gas was bubbled through the solution of dimethyl (1*S*,2*R*,3*R*,5*S*)-3-hydroxy-7-methoxybicyclo[3.3.0]oct-6-ene-2,6-dicarboxylate in methanol (100 mL) for 1 h at -78 °C. The mixture was allowed to warm up to rt, then dimethyl sulfide (2.97 g, 47.8 mmol) was added. After being stirred for 20 h, the solvent was evaporated *in vacuo*. An analytical sample of **6** was purified by silica gel chromatography (hexane: ethyl acetate = 1 : 3). **6**: pale yellow oil; $^1$H-NMR (300 MHz, $CDCl_3$) δ: 4.44 (dt, *J* = 7.7 and 6.6 Hz, 1H), 4.10 (dt, *J* = 7.7 and 6.6 Hz, 1H), 3.89 (s, 3H), 3.74 (s, 3H), 3.62 (s, 3H), 2.94-2.81 (m,

1H), 2.71 (dd, $J$ = 10.3 and 6.6 Hz, 1H), 2.65-2.57 (m, 2H), 2.36 (dt, A part of AB, $J$ = 13.8 and 7.7 Hz, 1H), 1.90 (dt, B part of AB, $J$ = 13.8 and 6.6 Hz, 1H); MS (70 eV) m/z: 302 ($M^+$, 13 ), 271 (28), 252 (100), 224 (70), 210 (47), 152 (48), 124 (60), 99 (52), 81 (43), 53 (42).

**Methyl (1*R*,2*R*,3*R*)-2-[2-Methoxycarbonyl-3-acetoxy-5-(acetoxymethoxycarbonylmethylidene)cyclopentyl]acetate (7)**

To a solution of **6** in pyridine (6 mL) was added acetic anhydride (4 mL) at 0 °C. After being stirred for 36 h at rt, methanol (5 mL) was added at 0°C. After additional 20 min, the reaction mixture was concentrated *in vacuo*. The residue was diluted with ether (500 mL), then washed with saturated solution of ammonium chloride (30 mL x 3). The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. Silica gel chromatography (ethyl acetate : hexane = 1 : 1) of the residue gave **7** (3.57 g, 96.5 %, 3 steps from (+)-**5**). **7**: yellow oil; $^1$H-NMR (300 MHz, $CDCl_3$) δ: 5.40 (dt, $J$ = 6.3 and 5.0 Hz, 0.8H), 5.37-5.32 (m, 0.2H), 3.78 (s, 0.6H), 3.77 (s, 2.4H), 3.71 (s, 3H), 3.69 (s, 3H), 3.55-3.43 (m, 2H), 3.09-3.01 (m, 1.6H), 2.99-2.92 (m, 0.4H), 2.71-2.57 (m, 2H), 2.24 (s, 2.4H), 2.21 (s, 0.6H), 2.07 (s, 3H); IR ($CHCl_3$): 3050-3005, 2955, 1738, 1670, 1600, 1437, 1368 $cm^{-1}$; FAB(+)-MS m/z: 387 ($M^+$+1, 100); HRMS Calcd for $C_{17}H_{23}O_{10}$ ($M^+$+1): 387.1291, found 387.1278.

**Methyl (1*R*,2*R*,3*R*)-2-(2-Methoxycarbonyl-3-acetoxy-5-oxocyclopentyl)acetate (8)**

Ozone gas was bubbled through the solution of **7** (3.57 g, 9.23 mmol) in methanol (100 mL) for 1 h at -78 °C. The mixture was allowed to warm up to rt, then dimethyl sulfide (2.87 g, 46.1 mmol) was added to the reaction mixture. After being stirred for 24 h, the solvent was evaporated *in vacuo*. An analytical sample of **8** was purified by silica gel chromatography (hexane: ethyl acetate = 1 : 1). **8**: pale yellow oil; $^1$H-NMR (300 MHz, $CDCl_3$) δ: 5.47 (dt, $J$ = 8.5 and 8.1 Hz, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 3.23 (ddd, $J$ = 11.0, 8.5 and 0.8 Hz, 1H), 3.02 (ddd, A part of AB, $J$ = 18.8, 8.1 and 0.8 Hz, 1H), 2.96-2.69 (m, 3H), 2.48 (dd, B part of AB, $J$ = 18.8 and 8.5 Hz, 1H), 2.09 (s, 3H); MS (70 eV) m/z: 272 ($M^+$, 1.7 ), 230 (13), 212 (90), 181 (100), 127 (78), 99 (36), 93 (21), 59 (38).

**Methyl (1*R*,2*R*,3*R*,5*R*)-2-(2-Methoxycarbonyl-3-acetoxy-5-hydroxycyclopentyl)acetate [(-)-9]**

To a dry THF solution (30 mL) of **8** was added lithium tri-*tert*-butoxyaluminum hydride (3.52 g, 13.8 mmol) and then a mixture was stirred for 5 min at 0 °C. The reaction mixture was quenched with 1*N* HCl, then concentrated under reduced pressure. Water (20 mL) was added to the residue, then aqueous layer was extracted with dichloromethane (50 mL x 4). The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. An analytical sample of **9** was purified by silica gel chromatography (hexane : ethyl acetate = 1 : 1). **9**: colorless oil; $[\alpha]_D^{23}$ -2.1° (c 0.80, $CHCl_3$); $^1$H-NMR (300 MHz, $CDCl_3$) δ: 5.36 (q, $J$ = 5.2 Hz, 1H), 4.10 (q, $J$ = 7.5 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.36 (br s, 1H), 2.70 (dd, A part of AB, $J$ = 16.5 and 5.4 Hz, 1H), 2.57 (t, $J$ = 5.2 Hz, 1H), 2.57 (dd, B part of AB, $J$ = 16.5 and 8.5 Hz, 1H), 2.45-2.34 (m, 1H), 2.16-2.10 (m, 2H), 2.04 (s, 3H); IR ($CHCl_3$): 3620-3350, 3060, 3010, 2960, 1740, 1440, 1365 $cm^{-1}$; FAB(+)-MS m/z: 275 ($M^+$+1, 42); HRMS Calcd for $C_{12}H_{19}O_7$ ($M^+$+1): 275.1130, found 275.1144.

**(1*S*,5*R*,6*R*,7*R*)-2-Oxa-6-methoxycarbonyl-7-acetoxybicyclo[3.3.0]octan-3-one [(-)-10]**

A benzene solution (200 mL) of **9** and *p*-toluenesulfonic acid monohydrate (351 mg, 1.85 mmol) was refluxed for 24 h. The reaction mixture was poured into brine, then aqueous layer was extracted with ether (30 mL x 2) and dichloromethane (30 mL x 2). The combined organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. Silica gel chromatography (ethyl acetate : hexane = 1 : 2) gave (-)-**10** (1.21 g, 54 %, 3 steps from **7**). colorless crystalline; mp 88-90 °C (ethyl acetate - hexane); $[\alpha]_D^{25}$ -59.2° (c 1.39, $CHCl_3$); $^1$H-NMR (300 MHz, $CDCl_3$) δ: 5.40 (q, $J$ = 3.6 Hz, 1H), 5.11 (dt, $J$ = 6.8 and 3.6 Hz, 1H), 3.74 (s, 3H), 3.36 (dddd, $J$ = 10.9, 6.8, 3.6 and 2.6 Hz, 1H), 2.96 (t, $J$ = 3.6 Hz, 1H), 2.94 (dd, A

part of AB, $J$ = 18.4 and 10.9 Hz, 1H), 2.54 (dd, B part of AB, $J$ = 18.4 and 2.6 Hz, 1H), 2.31 (t, $J$ = 3.6 Hz, 2H), 2.05 (s, 3H); IR ($CHCl_3$): 3005, 2955, 2460, 1772, 1738, 1605, 1438, 1419, 1363 $cm^{-1}$; FAB(+)-MS m/z: 243 ($M^+$+1, 33); Anal. Calcd for $C_{11}H_{14}O_6$: C, 54.54; H, 5.83. Found: C, 54.42; H, 5.84.

**(1*S*,5*R*,6*R*,7*R*)-2-Oxa-6-carboxy-7-acetoxybicyclo[3.3.0]octan-3-one [(-)-11]**

To a solution of aluminum bromide (7.02 g, 26.3 mmol) in dimethyl sulfide (30 mL) was added a solution of **10** (1.06 g, 4.39 mmol) in dimethyl sulfide (10 mL) at 0 °C. After being stirred for 1 h at rt, the reaction mixture was poured into 2*N* HCl, then aqueous layer was extracted with ethyl acetate (50 mL x 5) by salting-out techniques. The combined organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The residue was washed with cold ethyl acetate (5 mL x 2) to give (-)-11 (702 mg, 70 %). colorless crystalline; mp 205-208 °C (ethyl acetate); $[\alpha]_D^{25}$ -88.4° (c 0.49, pyridine); $^1$H-NMR (300 MHz, DMSO-$d_6$) δ: 12.78 (s, 1H), 5.27 (dt, $J$ = 5.7 and 2.8 Hz, 1H), 5.05 (t, $J$ = 5.7 Hz, 1H), 3.27-3.18 (m, 1H), 2.98-2.87 (m, 2H), 2.55-2.50 (m, 1H), 2.22 (dt, A part of AB, $J$ = 15.5 and 5.7 Hz, 1H), 2.02 (br. d, B part of AB, $J$ = 15.5 Hz, 1H), 1.94 (s, 3H); IR (KBr): 3600-3250, 3200-2800, 1748, 1740, 1722, 1422, 1372, 1341, 1321, 1308, 1279 $cm^{-1}$; FAB(+)-MS m/z: 229 ($M^+$+1, 15); HRMS Calcd for $C_{10}H_{13}O_6$ ($M^+$+1): 229.0712, found 229.0721. Anal. Calcd for $C_{10}H_{12}O_6$ + 0.1 $H_2O$: C, 52.22; H, 5.35. Found: C, 52.00; H, 5.33.

**(1*S*,5*R*,6*S*,7*R*)-2-Oxa-6-(hydroxymethyl)-7-acetoxybicyclo[3.3.0]octan-3-one [(-)-1]**

To a THF solution (30 mL) of (-)-11 (500 mg, 2.19 mmol) was added dropwise borane - dimethyl sulfide complex (2.0 M, in tetrahydrofuran, 1.31 mL) at 0 °C. After being stirred for 12 h, an additional borane - dimethyl sulfide complex (2.0 M, in tetrahydrofuran, 0.22 mL) was added to the reaction mixture. After being stirred for the additional 3 h, the reaction mixture was quenched with water (5 mL) and poured into brine, then aqueous layer was extracted with ethyl acetate (50 mL x 3) by salting-out techniques. The combined organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. Silica gel chromatography (ethyl acetate : hexane = 3 : 1) of the residue gave (-)-1 (384 mg, 82 %); colorless oil; $[\alpha]_D^{25}$ -44.1° (c 0.88, $CHCl_3$); $^1$H-NMR (300 MHz, $CDCl_3$) δ: 5.10 (dt, $J$ = 6.4 and 4.6 Hz, 1H), 4.99 (dt, $J$ = 6.4 and 2.0 Hz, 1H), 3.65 (dd, A part of AB, $J$ = 11.2 and 5.3 Hz, 1H), 3.59 (dd, B part of AB, $J$ = 11.2 and 5.5 Hz, 1H), 2.93-2.79 (m, 2H), 2.56-2.47 (m, 1H), 2.40 (dt, $J$ = 15.6 and 6.3 Hz, 1H), 2.27-2.18 (m, 1H), 2.21 (br s, 1H), 2.14-2.03 (m, 1H), 2.06 (s, 3H); IR ($CHCl_3$): 3640, 3590-3300, 2960, 2890, 1770, 1730, 1420, 1380, 1365 $cm^{-1}$; FAB(+)-MS m/z: 215 ($M^+$+1, 60); HRMS Calcd for $C_{10}H_{15}O_5$ ($M^+$+1): 215.0919, found 215.0927.

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