at 100 °C. This temperature was maintained about 1.5 h and then raised to 120 °C while the pressure was lowered to 0.2 mm. A distillate of 72.2 mg was obtained, which was diluted to 1.00 mL with dry benzene, and a rotation of +0.056° (1 dcm) at 589 nm was observed. The ^{31}P NMR spectrum showed only a single peak at δ 33.4 (consistent for **3a**), but the ^{1}H NMR spectrum revealed the sample contained 55 mol % ethanol. Therefore, the distillate actually contained only 47.5 mg (20% yield) of partially resolved (+)-**3a**, $[\alpha]_D$ +1.18° (*c* 4.75, benzene), when corrected for its observed purity. From the following results, this product should be 6% ee, hence the specific rotation of 100% ee **3a** would be 19.6°.

(−)-*O*-Ethyl *S*-Methyl Methylphosphonothiolate (5). The benzene solution of (+)-**3a** (47.5 mg, 0.439 mmol) from above was treated with 14.1 mg (0.439 mmol) of sulfur and 79.6 mg (0.439 mmol) of dicyclohexylamine (DCHA). The sulfur dissolved completely after stirring overnight at ca. 25 °C. The product [DCHA salt of (−)-4] was not isolated, but the benzene solution was directly treated with an excess of methyl iodide (225 mg, 1.6 mmol) in 1 mL of dry benzene. The reaction mixture was warmed to 50 °C and then was cooled to room temperature. The DCHA·HI that was obtained after standing overnight was filtered, and the filtrate was concentrated under reduced pressure. The residue was taken up in petroleum ether, refiltered, and then reconcentrated to yield 58.6 mg of an oil, **5**, α_{obsd} −0.264° (1 dcm) in 1.00 mL of dry chloroform. The ^{31}P NMR spectrum of this solution showed a single peak at δ 55.9. The ^{1}H NMR revealed a mixture of 63.9 mol % **5**, 9.7 mol % ethanol, and 26.5 mol % water, which corresponds to 91.4 wt % of **5**. Therefore, the isolated product actually contained 53.5 mg (80% yield) of (−)-**5**, $[\alpha]^{25}_D$ −4.93° (*c* 5.4, chloroform), when corrected for its observed purity, 6% ee, based upon $[\alpha]_D$ +83° reported for 100% ee (*R*)-(+)-**5**.[9a]

Reaction of (Ethyl methyl methylphosphonite)pentacarbonylmolybdenum (1b) with Two Equivalents of Triphenylphosphine. Compound **1b**, bp 53–56 °C (3 μm), was prepared from the reaction of diazomethane with racemic **1a** (obtained from its dicyclohexylamine salt[2]), as described for that of (+)-**1a** obtained from its ephedrine salt.[2] The ester (1.91 g, 5.30 mmol) was mixed with an excess over 2 equiv of freshly sublimed triphenylphosphine (3.06 g, 11.7 mmol) in a distillation apparatus. The system was evacuated to 0.5 mm under dry nitrogen while the apparatus was flame-dried, and the mixture was heated to 120 °C. The temperature was then raised during 1 h to 165 °C at 0.5 mm, and these conditions were maintained for 1 h, while the receiver was cooled in a dry ice/acetone bath. The vacuum was removed, the receiver was warmed to room temperature, and the distillate (0.36 g) was taken up in 2 mL of dry benzene. The ^{31}P NMR spectrum revealed a mixture of MeP(OEt)(OMe) (**3b**; δ 180.6; 47%), $MeP(OMe)_2$ (δ 183.5; 24%), $MeP(OEt)_2$ (**3c**; δ 177.9; 22%), species at δ 34.3 (2%) and 31.6 (3%), assigned as MeP(O)(H)(OMe) and MeP(O)(H)(OEt) (**3a**), respectively, and seven trace components, 2% total. The P^{III} species were assigned from comparison of these data to those which had been earlier recorded for these species, from other studies.[12,13]

(Diethyl methylphosphonite)pentacarbonylmolybdenum (1c). A mixture of diethyl methylphosphonite[14] (**3c**) (42.2 g, 0.309 mol), molybdenum hexacarbonyl (81.8 g, 0.310 mol), and 300 mL of dry toluene was vigorously stirred at ca. 90 °C for 23 h in a 1-L flask under nitrogen. After the mixture was cooled to room temperature, 300 mL of petroleum ether (bp 30–60 °C) was added to precipitate unreacted molybdenum hexacarbonyl. The mixture was filtered under nitrogen, and the filtrate was concentrated on a rotary evaporator while the vacuum was slowly taken down to 0.5 mm. The residue was twice distilled on a McCarter molecular still at 50–60 °C (10 μm) to give 84 g (73%) of **1c**: ^{31}P NMR (neat) δ 183.0 (lit.[2] δ 182.9); ^{1}H NMR (neat) δ 1.67 (d, J_{PH} = 3 Hz, 3 H, CH_3P), 1.3 (t, J_{HH} = 7 Hz, 6 H, CH_3CH_2OP), 3.91 (m, J_{HH} = 7 Hz, $J_{PH} \sim$ 7 Hz, 4 H, CH_3CH_2OP).

Reaction of 1c with One Equivalent of Triphenylphosphine. A mixture of **1c** (3.41 g, 9.16 mmol) and triphenylphosphine (2.40 g, 9.16 mmol) was heated at 115 °C for 80 min to give a yellow oil. ^{31}P NMR: *cis*-**2**, δ 185 (d) and 39 (d, J = 31 Hz for both), 39% of integrated area; *trans*-**2**, δ 193 (d) and 49 (d, J = 78 Hz for both), 18%; **1c**, δ 183, 14%; triphenylphosphine, δ −5.0, 15%; eight other phosphorus compound signals, 14%. An additional 20 mol % of triphenylphosphine (0.48 g) was then added, and the heating was continued for another 90 min. At this point, a ^{31}P NMR spectrum revealed that the unreacted **1c** had been reduced from 28% to 6% of that originally taken, accompanied by a corresponding increase in the *cis*- and *trans*-**2** isomer content (2/1, respectively).

***cis*-(Diethyl methylphosphonite)(triphenylphosphine)-pentacarbonylmolybdenum (2).**[15] A solution of *cis*-$(C_5H_{10}NH)[(C_6H_5)_3P]Mo(CO)_4$[16] (3.00 g, 5.40 mmol) and **3c** (1.10 g, 8.08 mmol) in 20 mL of dichloromethane was refluxed for 30 min and then concentrated at 0.5 mm to a yellow residue. The latter crystallized from chloroform/methanol to give 1.76 g of *cis*-**2**, which was recrystallized to give a light beige product, mp 104–105 °C, >95% pure by ^{31}P NMR: δ 185 (d) and 39 (d, J = 30.8 Hz for both) for the two ligands, respectively. In an attempt to isomerize *cis*-**2** to the pure *trans*-**2** isomer, it was heated in toluene at 110 °C for 1 h. However, the ^{31}P NMR spectrum revealed a mixture of 39% *cis*-**2** and 40% *trans*-**2** isomers, 10% of (apparently) triphenylphosphine oxide (δ 25.7), 4% **1c** (δ 184), and three unidentified products. Heating this sample for an additional 2 h gave no significant change.

Acknowledgment. We thank Leonard J. Szafraniec for the synthesis of *cis*-**2**, Linda L. Szafraniec and William T. Beaudry for the ^{31}P NMR and much of the ^{1}H NMR spectral data, and Professor Charles Kraihanzel for helpful discussions.

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(14) This compound was obtained from the Chemical Process Laboratory, CRDEC. It is now available from Alpha Products, Danvers, MA, or Strem Chemicals, Newburyport, MA.
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An Efficient Enantioselective Synthesis of the (−)-*N*-(Ethoxycarbonyl)methyl Geissman-Waiss Lactone: A Practical Synthetic Route to (+)-Retronecine

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Pyrrolizidine alkaloids having retronecine (1) as the necine base are known to exhibit potent hepatotoxicity and, in certain cases, antitumor activity and carcinogenicity.[1] The challenging structures and the varied range of biological activities of pyrrolizidine alkaloids have made them attractive synthetic targets. The first synthesis of (+)-retronecine (1) was reported in 1962 by Geissman and Waiss.[2] While many synthetic routes to racemic retro-

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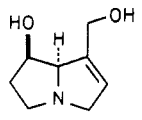
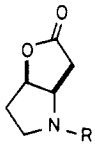
necine (1) have, since then, been reported,[3] it is only recently that rather a few routes to optically active retronecine (1) have been developed.[4] As the key intermediate in the synthesis of retronecine (1), Geissman and Waiss synthesized 6-aza-2-oxabicyclo[3.3.0]octan-2-one, the Geissman–Waiss lactone (2) in racemic form.[2] Recently, the enantioselective synthesis of this lactone 2 has been achieved by two groups, starting from 4-hydroxy-L-proline and a carbohydrate precursor, respectively.[4b,c] Herein we report an efficient enantioselective synthesis of the (−)-*N*-(ethoxycarbonyl)methyl Geissman–Waiss lactone (3), starting from (*R*)-(+)-malic acid. Since compound 3 can be converted into (+)-retronecine (1) in high yield (ca. 50%),[4b] the present work provides a practical route for the enantioselective synthesis of (+)-retronecine (1).

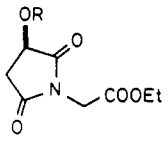


1



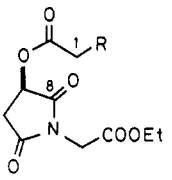
2 R = H

3 R = CH_2COOEt



4 R = Ac

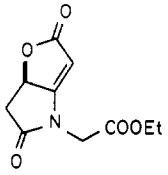
5 R = H



6 R = Br

7 R =  $\cdot Br^-$

8 R = $^+PPh_3 \cdot Br^-$



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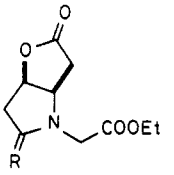

10 R = O

11 R = S

Successive treatment of (*R*)-(+)-malic acid in one flask with acetyl chloride, glycine ethyl ester in dichloromethane, and acetyl chloride again afforded the imide 4 in almost quantitative yield. Acidic ethanolysis of 4 gave the hydroxy imide 5 (92% yield), which on bromoacetylation [$BrCH_2COBr$ (1.1 equiv), pyridine (1.2 equiv)] in ether gave the bromoacetoxy imide 6 (97% yield). It should be noted that the use of an excess of pyridine in the bromoacetylation of 5 resulted in the formation of the pyridinium salt 7 as the major product and the yield of 6 was dramatically decreased. Construction of the carbon–carbon bond between C-1 and C-8 (pyrrolizidine numbering) in 6 was achieved by the intramolecular Wittig reaction in one-pot procedure: the reaction of 6 with triphenylphosphine in acetonitrile gave the phosphonium salt 8, which was subsequently treated with triethylamine to furnish the conjugated lactone 9 (92% yield from 6). Hydrogenation of 9 at atmospheric pressure in ethyl acetate using 5% rhodium on alumina afforded the lactone 10 in quantitative yield. The remaining problem for the synthesis of 3 was the selective reduction of the lactam carbonyl group among the three carbonyl groups in 10. According to the Borch's method,[5] the lactone 10 was treated first with triethyloxonium tetrafluoroborate in dichloromethane and subsequently with sodium borohydride in ethanol to afford 3 (31% yield) with recovery of 10 (54% yield). The alternative and much better method for the reduction of the lactam group in 10 was established: the reaction of 10 with 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide (Lawesson's reagent)[6-8] in toluene gave the thiolactam 11, which on treatment with triethyloxonium tetrafluoroborate in dichloromethane followed by reduction with sodium cyanoborohydride in methanol–acetic acid (92:8) provided 3 [mp 52.0–53.0 °C, $[\alpha]^{16}_D$ −35.2° (*c* 0.563, $CHCl_3$), >98% ee by ^1H NMR shift analysis using $Eu(hfc)_3$] (76% yield from 10). The spectral (IR, ^1H NMR, MS) and chromatographic properties of synthetic 3 were identical with those of authentic 3 prepared by N-(ethoxycarbonyl)-methylation[2] of the racemic Geissman–Waiss lactone (2).

Thus the *N*-(ethoxycarbonyl)methyl Geissman–Waiss lactone (3) in optically active form has been synthesized from (*R*)-(+)-malic acid in 62% overall yield.

Experimental Section

Melting points are uncorrected. Infrared (IR) spectra were recorded on a JASCO Model IR-810 spectrophotometer. Proton nuclear magnetic resonance (^1H NMR) spectra were determined on a JEOL FX-90QE (90 MHz) or a JEOL JNM-C675 (270 MHz) spectrometer in $CDCl_3$. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane using the δ scale. Significant ^1H NMR data are tabulated in the following order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constants in hertz, and number of protons. Optical rotations were measured on a JASCO DIP-181 polarimeter. Mass spectra were measured on a JEOL JMS-LG2000 instrument. Fuji-Davison silica gel BW-820-MH was used for column chromatography. Merck precoated silica gel 60 F_{254} plates, 0.25 mm thickness, were used for analytical thin layer chromatography (TLC). Unless otherwise stated, materials were obtained from commercial suppliers and used without further purification. All the solvents and reagents described below were distilled under nitrogen. Ether was freshly distilled from sodium–benzophenone ketyl. Dichloromethane, acetonitrile, pyridine, and triethylamine were distilled from calcium hydride. Toluene was distilled from sodium. Methanol and ethanol were distilled from magnesium methoxide and magnesium ethoxide, respectively. Acetyl chloride was distilled from phosphorus pentachloride. Bromoacetyl bromide was distilled just before use. The organic solutions obtained by extractive workup were washed with saturated brine, dried over anhydrous sodium sulfate, and concentrated with a rotary evaporator under reduced pressure.

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Preparation of Imide 4. A solution of (*R*)-(+)-malic acid (4.0 g, 30 mmol) in acetyl chloride (32 mL) was kept under reflux for 4 h, cooled to room temperature, and concentrated to give an oil, which was dissolved in dichloromethane (8 mL). To the solution was added a solution of glycine ethyl ester (8.0 g, 78 mmol) in dichloromethane (8 mL), and the mixture was heated at reflux for 3 h. After cooling, the mixture was concentrated and the resulting oil was dissolved in acetyl chloride (40 mL). After being refluxed for 2.5 h, the solution was concentrated. The oily residue was purified by column chromatography (5:1 benzene–ethyl acetate) to yield 7.2 g (99%) of **4** as crystalline material: mp 51.5–53.0 °C (ether); $[\alpha]^{13}_D$ +12.4° (*c* 0.82, $CHCl_3$); IR ($CHCl_3$) 1795 (weak), 1750, 1725, 1230, 1160, 1020 cm^{-1}; ^1H NMR (90 MHz) δ 1.29 (t, *J* = 7.0, 3 H), 2.17 (s, 3 H), 2.73 (dd, *J* = 5.1, 18.5, 1 H), 3.27 (dd, *J* = 8.6, 18.5, 1 H), 4.22 (q, *J* = 7.0, 2 H), 4.28 (s, 2 H), 5.56 (dd, *J* = 5.1, 8.6, 1 H); mass spectrum, *m/z* (relative intensity) 243 (M^+, 22), 198 (24), 171 (100), 170 (96), 112 (67), 111 (68), 110 (87), 100 (80). Anal. Calcd for $C_{10}H_{13}NO_6$: C, 49.38; H, 5.39; N, 5.76. Found: C, 49.28; H, 5.38; N, 5.75.

Preparation of Hydroxy Imide 5. Acetyl chloride (0.45 mL, 6.28 mmol) was added to a solution of **4** (509 mg, 2.09 mmol) in ethanol (10 mL). The mixture was stirred at 50 °C for 3.5 h, cooled to room temperature, and concentrated to give an oil. Benzene (ca. 5 mL) was added to the oil and the solution was concentrated: this procedure was repeated three times. The resulting oil was purified by column chromatography (3:1 → 1:1 benzene–ethyl acetate) to afford 387 mg (92%) of **5** as a colorless oil: $[\alpha]^{12}_D$ +45.0° (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) 3580, 3480, 1795 (weak), 1750, 1720, 1230, 1175, 1020 cm^{-1}; ^1H NMR (270 MHz) δ 1.29 (t, *J* = 7.2, 3 H), 2.77 (dd, *J* = 5.0, 18.4, 1 H), 3.17 (dd, *J* = 8.4, 18.4, 1 H), 3.19 (br s, 1 H, OH), 4.22 (q, *J* = 7.2, 2 H), 4.27 (s, 2 H), 4.75 (m, 1 H); mass spectrum, *m/z* (relative intensity) 201 (M^+, 69), 173 (15), 156 (43), 145 (26), 130 (92), 129 (72), 128 (62), 111 (40), 102 (97), 55 (100); HRMS, calcd for $C_8H_{11}NO_5$ (M^+) *m/z* 201.0637, found *m/z* 201.0627.

Preparation of Bromoacetoxy Imide 6. Bromoacetyl bromide (0.18 mL, 2.09 mmol) was added to the stirred solution of **5** (382 mg, 1.90 mmol) and pyridine (0.18 mL, 2.28 mmol) in ether (10 mL) cooled at 0 °C under nitrogen. The mixture was stirred at room temperature for 1 h, diluted with cold water (5 mL), and extracted with dichloromethane (30 mL, then 2 × 5 mL). The combined organic extracts were washed successively with saturated copper(II) sulfate solution, water, and saturated sodium bicarbonate solution, dried, and concentrated to give an oil. Purification by column chromatography (3:1 → 1:1 benzene–ethyl acetate) afforded 595 mg (97%) of **6** as an oil: $[\alpha]^{12}_D$ +7.7° (*c* 0.81, $CHCl_3$); IR ($CHCl_3$) 1800 (weak), 1750, 1730, 1230, 1170, 1020 cm^{-1}; ^1H NMR (270 MHz) δ 1,23 (t, *J* = 7.3, 3 H), 2.74 (dd, *J* = 4.8, 18.5, 1 H), 3.24 (dd, *J* = 8.6, 18.5, 1 H), 3.86 (s, 2 H), 4.16 (q, *J* = 7.3, 2 H), 4.24 (s, 2 H), 5.57 (dd, *J* = 4.8, 8.6, 1 H); mass spectrum, *m/z* (relative intensity) 323 (M^+ + 2, 3), 321 (M^+, 2), 279 (3), 278 (3), 277 (3), 276 (4), 251 (16), 250 (20), 249 (16), 248 (17), 111 (100); HRMS, calcd for $C_7H_7{}^{79}BrNO_4$ ($M^+ - COOC_2H_5$) *m/z* 247.9558, found *m/z* 247.9541.

Preparation of Conjugated Lactone 9. Triphenylphosphine (569 mg, 2.17 mmol) was added in one portion to the stirred solution of **6** (630 mg, 1.97 mmol) in acetonitrile (40 mL) under nitrogen. The mixture was stirred at 50 °C for 3 h, and then triethylamine (0.29 mL, 2.08 mmol) was added. The mixture was further stirred at 50 °C for 13 h, cooled to room temperature, and concentrated. The resulting oil was separated by column chromatography (7:1 benzene–ethyl acetate) to give 404 mg (92%) of **9** as crystals: mp 92.5–94.5 °C (benzene); $[\alpha]^9_D$ +97.4° (*c* 0.70, $CHCl_3$); IR ($CHCl_3$) 3150, 1770, 1750, 1660, 1300, 1220, 1170, 1130, 960, 855, 805 cm^{-1}; ^1H NMR (270 MHz) δ 1.31 (t, *J* = 7.1, 3 H), 2.77 (dd, *J* = 9.1, 16.1, 1 H), 3.15 (dd, *J* = 7.9, 16.1, 1 H), 4.25 (q, *J* = 7.1, 2 H), 4.32 (d, *J* = 17.5, 1 H), 4.39 (d, *J* = 17.5, 1 H), 5.2–5.3 (m, 2 H); mass spectrum, *m/z* (relative intensity) 225 (M^+, 82), 197 (10), 179 (21), 152 (80), 135 (36), 126 (33), 110 (77), 82 (100). Anal. Calcd for $C_{10}H_{11}NO_5$: C, 53.28; H, 4.92; N, 6.24. Found: C, 53.28; H, 4.92; N, 6.24.

Preparation of Lactone 10. A mixture of **9** (328 mg, 1.46 mmol) and 5% rhodium–alumina (66 mg) in ethyl acetate (8 mL) was vigorously stirred at room temperature under hydrogen for 2.5 h. The mixture was filtered by suction through a pad of Celite. The filtrate was concentrated to give 330 mg (quantitative) of **10** as a colorless oil, which was shown to be pure by TLC and ^1H NMR analysis: $[\alpha]^{11}_D$ +12.4° (*c* 1.28, $CHCl_3$); IR ($CHCl_3$) 1790, 1740, 1710, 1230, 1170, 1050, cm^{-1}; ^1H NMR (270 MHz) δ 1.29 (t, *J* = 7.3, 3 H), 2.6–2.9 (m, 4 H), 3.64 (d, *J* = 17.8, 1 H), 4.21 (m, 2 H), 4.44 (d, *J* = 17.8, 1 H), 4.61 (ddd, *J* = 1.7, 5.3, 5.3, 1 H), 5.16 (ddd, *J* = 2.2, 5.3, 5.3, 1 H); mass spectrum, *m/z* (relative intensity) 227 (M^+, 46), 183 (19), 154 (92), 112 (100); HRMS, calcd for $C_{10}H_{13}NO_5$ (M^+) *m/z* 227.0794, found *m/z* 227.0822.

Preparation of Thiolactam 11 and (–)-*N*-(Ethoxycarbonyl)methyl Geissman–Waiss Lactone (3). To a solution of **10** (60.9 mg, 0.268 mmol) in toluene (1 mL) was added 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide (Lawesson's reagent) (57 mg, 0.141 mmol) under argon. The mixture was heated at 105 °C for 1 h, cooled to room temperature, and concentrated. The resulting solid was separated by column chromatography (1:1 chloroform–ethyl acetate) to give 73.5 mg of crystalline **11**: mp 157.0–158.0 °C (ethyl acetate); $[\alpha]^{12}_D$ +57.0° (*c* 0.44, $CHCl_3$); IR (KBr) 1790, 1780 (shoulder), 1740, 1480, 1220, 1210, 1160 cm^{-1}; ^1H NMR (270 MHz) δ 1.30 (t, *J* = 7.2, 3 H), 2.83 (m, 2 H), 3.43 (m, 2 H), 4.08 (d, *J* = 17.2, 1 H), 4.23 (m, 2 H), 4.87 (d, *J* = 17.2, 1 H), 4.89 (ddd, *J* = 2.8, 5.4, 5.4, 1 H), 5.20 (ddd, *J* = 1.5, 5.4, 5.4, 1 H); mass spectrum, *m/z* (relative intensity) 243 (M^+, 100), 210 (27), 197 (35), 171 (90).

A solution of triethyloxonium tetrafluoroborate (76 mg, 0.402 mmol) in dichloromethane (0.6 mL) was added to the stirred solution of **11** (73.5 mg, 0.302 mmol) in dichloromethane (1.5 mL) cooled at 0 °C under nitrogen. The mixture was stirred at 0 °C for 5 min and then at room temperature for 3 h. To the stirred mixture cooled at 0 °C was added a solution of sodium cyanoborohydride (84 mg, 1.34 mmol) in methanol (0.92 mL)–acetic acid (0.08 mL). The mixture was stirred at 0 °C for 1 h and subsequently at room temperature for 3 h and concentrated. A saturated sodium bicarbonate solution was added to the residue and the pH of the mixture was adjusted to 9.0. The mixture was extracted with chloroform (5 × 5 mL). The combined organic extracts were washed with brine, dried, and concentrated to give an oily residue. Purification by column chromatography (40:1 chloroform–ethyl acetate) provided 43.4 mg (76% from **10**) of **3** as crystals: mp 52.0–53.0 °C (hexane–ether); $[\alpha]^{16}_D$ –35.2° (*c* 0.563, $CHCl_3$); IR ($CHCl_3$) 1775, 1735, 1190, 1175, 910 cm^{-1}; ^1H NMR (270 MHz) δ 1.28 (t, *J* = 7.2, 3 H), 2.13 (m, 1 H), 2.30 (m, 1 H), 2.53 (dd, *J* = 2.3, 17.8, 1 H), 2.62 (dd, *J* = 5.9, 17.8, 1 H), 2.78 (ddd, *J* = 8.1, 8.1, 9.1, 1 H), 3.22 (ddd, *J* = 3.8, 8.1, 9.1, 1 H), 3.33 (d, *J* = 17.0, 1 H), 3.50 (d, *J* = 17.0, 1 H), 3.68 (ddd, *J* = 2.3, 5.9, 5.9, 1 H), 4.18 (q, *J* = 7.2, 2 H), 5.00 (ddd, *J* = 2.6, 5.9, 6.9, 1 H); mass spectrum, *m/z* (relative intensity), 213 (M^+, 33), 141 (45), 140 (100), 112 (33). Anal. Calcd for $C_{10}H_{11}NO_4$: C, 56.33; H, 7.09; N, 6.59. Found: C, 55.97; H, 7.13; N, 6.51. The IR, ^1H NMR, and mass spectra and the TLC behaviors (several solvent systems) of synthetic **3** proved identical in all respects with those of authentic **3** prepared by N-(ethoxycarbonyl)methylation[2] of the Geissman–Waiss lactone (**2**).

Preparation of (–)-*N*-(Ethoxycarbonyl)methyl Geissman–Waiss Lactone (3) by Borch's Process. To the stirred solution of **10** (70.1 mg, 0.309 mmol) in dichloromethane (5 mL) was added a solution of triethyloxonium tetrafluoroborate (170 mg, 0.895 mmol) in dichloromethane (5 mL) under nitrogen. The mixture was stirred at room temperature for 23 h and concentrated to give an oil, which was dissolved in ethanol (6 mL). To the ethanolic solution was added with stirring a solution of sodium borohydride (35 mg, 0.93 mmol) in ethanol (5 mL) under nitrogen. After being stirred at room temperature for 24 h, the reaction mixture was concentrated to afford an oily residue, which was dissolved in water (10 mL). The pH of the aqueous mixture was adjusted to 9.0 with 20% sodium carbonate solution and the mixture was extracted with chloroform (4 × 20 mL). The combined organic extracts were washed with brine, dried, and concentrated. Separation of the oily residue by column chromatography (ethyl acetate) provided 20.2 mg (31%) of **3** as crystals and 37.7 mg (54%) of **10** as a colorless oil, respectively. The product **3** was proved to be identical with authentic **3** by spectral (IR, ^1H NMR, MS) comparison.

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