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Asymmetric synthesis of (*S*)-homocitric acid lactone

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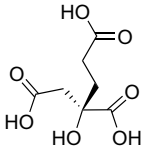
Dedicated to Professor Ben-Li Huang on the occasion of his 80th birthday

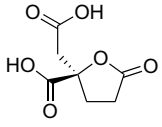
Abstract—Starting from (*S*)-phenylalanine, an asymmetric synthesis of (*S*)-homocitric acid lactone was achieved using Seebach's SRS methodology. An intermediate for the synthesis of the (*S*)-per-homocitric acid lactone has also been synthesized.

1. Introduction

Due to the important roles played both in the α-aminoadipate pathway of lysine biosynthesis in yeast and some fungi,[1] and in clarifying the mechanism of biological nitrogen fixation,[2] the synthesis[3–5] of (*R*)-homocitrate **1**[6] has attracted attention. Due to the enantiomeric homocitrate not being commercially available, the importance of their asymmetric synthesis is thus important. To date, only three asymmetric syntheses[7,8] of enantiomeric homocitric acids have been reported. Most of the reported asymmetric syntheses use Seebach's SRS (self-regeneration of stereocenters) methodology[9–11] with either L-lactic acid, or L-serine[7a] and D- or L-malic acid[7b,c] as the starting material. Considering that (*R*)-malic acid, the requisite starting material for the synthesis of (*R*)-homocitrate, is four times more expensive than (*R*)-phenylalanine, a chiral pool for the synthesis of antidiabetic agent nateglinide,[12] and aminopeptidases inhibitors such as phebestin, probestin, and bestatin,[13] we were interested in exploring the use of the less expensive (*R*)-phenylalanine as a starting material for (*R*)-homocitrate. Herein we report an alternative approach to (*S*)-homocitric acid starting from (*S*)-phenylalanine.



1. (*R*)-homocitric acid



2. (*R*)-homocitric acid lactone

2. Results and discussion

Due to the instability of homocitric acid, all the syntheses of homocitric acid **1** ended with the isolation of homocitric acid lactone **2**. In our approach to (*S*)-homocitric acid lactone **2** using Seebach's SRS methodology,[9] (*S*)-phenylalanine was considered as a suitable starting material, because a phenyl group can be oxidatively cleaved to give a carboxylic group.[14]

Thus, as outlined in Scheme 1, the known chiral inducer **5** was prepared from (*S*)-phenylalanine by the known procedures: diazotization[15] and *cis*-diastereoselective *t*-butyl-5-benzyl-1,3-dioxolanone formation.[11a] The key allylation of (*S*)-**5** with allyl bromide (LDA, THF, −78 °C; AllBr) led exclusively to **6** in 42% yield (Scheme 1). The chemical yield of the allylation is consistent with that reported by Seebach et al.[11a] When a more reactive allyl iodide was used, the yield was improved to 71% and **6** was obtained as the only diastereomer, as judged by ^{1}H NMR recorded at 500 MHz. Using LHMDS as a base led to complex products. The stereochemistry of the allylated product was ascertained by comparing both the specific rotation and the ^{1}H NMR data with those reported {**6**: $[\alpha]_D^{20} = +4.9$ (*c* 1.6, $CHCl_3$) {lit.[11a] $[\alpha]_D^{20} = +5.2$ (*c* 2.5, $CHCl_3$)}. The stereochemical outcome of the reaction can be understood in terms of the bulky *t*-butyl group controlled *trans*-diastereoselective allylation on the enolate intermediate **A**, namely,

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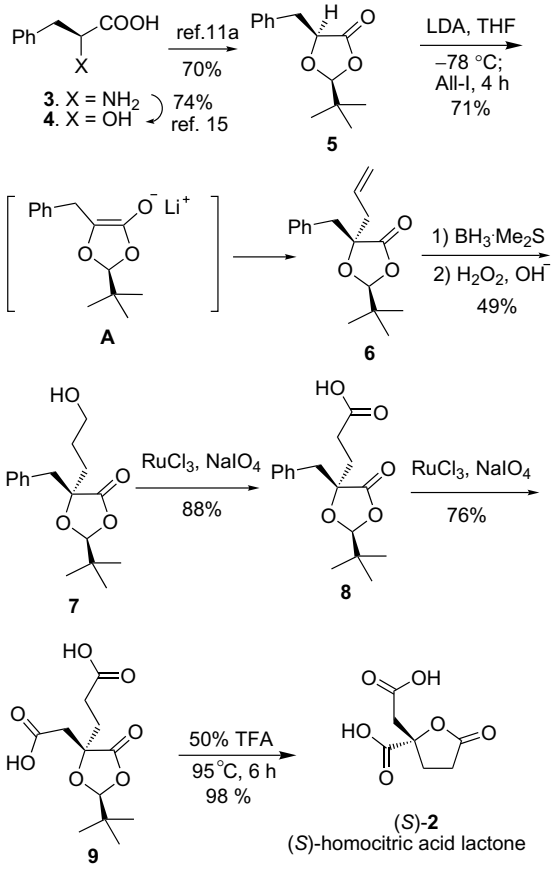
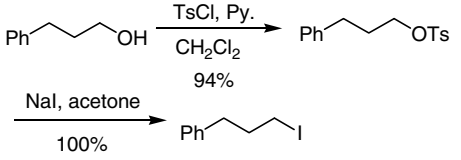


Scheme 1.

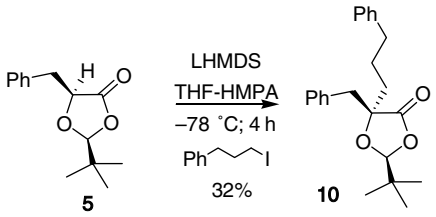
the well known principle of self-regeneration of stereocenters (SRS).

The subsequent oxidative hydroboration was performed at 35 °C with prolonged reaction time ($BH_3{\cdot}SMe_2$, 35 °C, 2 days; 30% H_2O_2, 1 M NaOH, 35 °C, 2 days), which gave the desired alcohol **7** as the sole isolated regioisomer. At room temperature, the reactions were very slow and uncompleted. These may reflect the steric hindrance of the system, which slows down both the formation and reaction of the dendritic trialkylborane intermediate. The steric hindrance may also account for the observed high regioselectivity of the hydroboration.

Next, we attempted a one-pot hydroxyl group oxidation and phenyl group oxidative degradation using an $RuCl_3/NaIO_4$ system (CCl_4–MeCN–H_2O, rt, 4 days). However, the products were very complex. The desired oxidations were finally achieved in a stepwise manner: the oxidation of the primary alcohol ($RuCl_3$ 0.04 equiv–$NaIO_4$ 3 equiv, CCl_4–MeCN–H_2O = 2:2:3, 0 °C–rt, 4 h) gave the corresponding carboxylic acid **8** in 88% yield. With a prolonged reaction time, the oxidative degradation of the more stable phenyl group was achieved ($RuCl_3$ 0.05 equiv–$NaIO_4$ 14 equiv, CCl_4–MeCN–H_2O = 2:2:3, 0 °C–rt, 3 days), which provided **9** in 76% yield. Compound **9** was then converted to (*S*)-homocitric acid lactone (*S*)-**2** by the known procedure.[7c]



Scheme 2.



Scheme 3.

In view of the successful use of the phenyl group as a latent carboxyl group, the alkylation of **5** with 3-phenylpropanyl iodide, easily available from 3-phenylpropanol (Scheme 2), was studied. The desired compound **10** was obtained in 32% yield (Scheme 3), which constitutes as an intermediate for the synthesis of (*S*)-per-homocitric acid.

3. Conclusion

In conclusion, we have developed an alternative approach to (*S*)-homocitric acid lactone starting from (*S*)-phenylalanine. The overall yield of homocitric acid lactone from (*S*)-phenylalanine was 11.8%. This method is, a priori, applicable for the asymmetric synthesis of (*R*)-homocitric acid lactone if (*R*)-phenylalanine is used as the starting material, which will constitute a more economical approach to (*R*)-homocitric acid lactone and its higher homologous.

4. Experimental

4.1. General

Melting points were determined on a Yanaco MP-500 micromelting point apparatus and are uncorrected. The freeze dryer was a LABCONCO Stoppering Tray Dryer-Freezone 18. Infrared spectra were measured with a Nicolet Avatar 360 FT-IR spectrometer using film KBr pellet techniques. ^1H NMR spectra were recorded in $CDCl_3$ on a Varian unity +500 spectrometer with tetramethylsilane as an internal standard. Chemical shifts are expressed in δ (ppm) units downfield from TMS. Mass spectra were recorded by a Bruker Dalton ESquire 3000 plus liquid chromatography–mass spectrum (direct injection). Optical rotations were measured with a Perkin–Elmer 341 automatic polarimeter. Flash column chromatography was carried out with silica gel (300–400 mesh). THF was distilled over sodium. Dichloromethane was distilled over P_2O_5.

4.2. (2*S*,5*S*)-5-Allyl-5-benzyl-2-(*tert*-butyl)-1,3-dioxolan-4-one 6

To a cooled solution (−78 °C) of LDA (3.7 mmol) in 14.1 mL of a mixed solvent system (THF–hexane = 9:1) was added a THF solution (7 mL) of (2*S*,5*S*)-5-benzyl-2-(*tert*-butyl)-1,3-dioxolan-4-one *cis*-**5** (823 mg, 3.5 mmol), mp 54–56 °C (EtOAC/Et_2O); lit.[11a] mp 56–58 °C; $[\alpha]_D^{20} = -45.6$ (*c* 1.2, $CHCl_3$); lit.[11a] $[\alpha]_D^{20} = -45.9$ (*c* 1.80, $CHCl_3$)}, prepared[11a] from (*S*)-2-hydroxy-3-phenylpropionic acid **4**.[15] After 30 min, allyl iodide (0.48 mL, 5.3 mmol) was added and stirring continued at the same temperature for 4 h. The reaction was quenched with 30 mL of an aqueous solution of ammonium chloride (15.7% w/w) and extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (eluent: diethyl ether–petroleum ether = 1:40) to give **6** (685 mg, yield: 71%) as a colorless oil, which was diastereomerically pure as judged by ^1H NMR recorded at 500 MHz. $[\alpha]_D^{20} = +4.9$ (*c* 1.6, $CHCl_3$) {lit.[11a] $[\alpha]_D^{20} = +5.2$ (*c* 2.5, $CHCl_3$)}. IR (film): 2962, 1793, 1641 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.76 (s, 9H, C(CH_3)$_3$), 2.47 (dd, $J = 7.64$, 14.15 Hz, 1H, CH_2CH=CH_2), 2.54 (dd, $J = 7.21$, 14.15 Hz, 1H, CH_2CH=CH_2), 3.02 (d, $J = 14.23$ Hz, 1H, CH_2Ph), 3.14 (d, $J = 14.23$ Hz, 1H, CH_2Ph), 5.18 (s, 1H, CH(C(CH$_3$)$_3$)), 5.21–5.25 (m, 2H, CH_2=CH), 5.82–5.91 (m, 1H, CH=CH_2), 7.22–7.30 (m, 5H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.2 (9C), 34.4, 39.4, 41.6, 82.9, 108.7, 120.6, 127.0, 128.2, 130.8, 130.9, 134.9, 174.4; MS (ESI) *m*/*z* 297 ([M+Na]$^+$, 100%), 292 ($M^+ + NH_4^+$, 50%), 275 (M+H$^+$, 7%), 274 (M^+, 26%). HRMS calcd for $[C_{17}H_{22}O_3+Na]^+$: 297.1467; found: 297.1461.

4.3. (2*S*,5*S*)-5-Benzyl-2-(*tert*-butyl)-5-(3-hydroxypropyl)-1,3-dioxolan-4-one 7

To a solution of **6** (361 mg, 1.32 mmol) in anhydrous CH_2Cl_2 (2.6 mL) was added dropwise $BH_3{\cdot}Me_2S$ (44 μL, 18.00 mmol) under nitrogen atmosphere at 0 °C and then warmed to 35 °C and stirred for 2 days. The resulting mixture was quenched with ethanol (0.64 mL) at 0 °C, and then to the mixture was added a 1 M NaOH (0.39 mL) followed by a 30% H_2O_2 aqueous solution (0.12 mL). The mixture was warmed to 35 °C and stirred for 2 days. To the resulting mixture was added cooled water (1.5 mL), and the aqueous layer extracted with Et_2O (3 × 2 mL). The combined organic phases were washed with brine (1 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (eluent: ethyl acetate–petroleum ether = 1:2) to afford **7** (188 mg, yield: 49%) as a colorless solid. $[\alpha]_D^{20} = -7.1$ (*c* 1.2, $CHCl_3$). Mp 60–61 °C (EtOAc/PE); IR (film): 3427, 2961, 1790 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.70 (s, 9H, C(CH$_3$)$_3$), 1.43 (s, 1H, OH), 1.58–1.82 (m, 4H, (CH_2)$_2$CH$_2$OH), 2.96 (d, $J =$ 14.20 Hz, 1H, CH_2Ph), 3.09 (d, $J = 14.20$ Hz, 1H, CH_2Ph), 3.58 (t, $J = 6.11$ Hz, 2H, CH_2OH), 5.06 (s, 1H, CH(C(CH$_3$)$_3$)), 7.14–7.22 (m, 5H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.2, 26.9, 31.0, 34.4, 41.3, 62.4, 82.7, 108.6, 127.0, 128.2, 130.7, 134.9, 174.8; MS (ESI) *m*/*z* 315 ([M+Na]$^+$, 100%), 310 ($M^+ + NH_4^+$, 45%). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 70.18; H, 8.37.

4.4. (2*S*,5*S*)-5-Benzyl-2-(*tert*-butyl)-5-(carboxyethyl)-1,3-dioxolan-4-one 8

To a cooled (0 °C) solution of alcohol **7** (196 mg, 0.67 mmol) in a mixed solvent system (CCl_4 1.9 mL/CH_3CN 1.9 mL/distilled H_2O 2.3 mL) was added $NaIO_4$ (414 mg, 1.88 mmol) in one portion. To the vigorously stirred mixture was added a 0.05 M $RuCl_3$ aqueous solution (0.58 mL, 0.029 mmol). Stirring was continued at room temperature for 4 hours. The reaction was quenched by diluting with brine (8 mL), filtered, and the filtrate extracted with ethyl acetate (4 × 5 mL). The combined organic layers were washed with 20% sodium bisulfite solution, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (eluent: ethyl acetate–petroleum ether = 1:2) to afford **8** (180 mg, yield: 88%) as a white solid. $[\alpha]_D^{20} = -10.7$ (*c* 1.1, $CHCl_3$); Mp 101–103 °C (EtOAc/PE); IR (film): 3035, 2962, 1792, 1712, 1184 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.65 (s, 9H, C(CH_3)$_3$), 2.00 (ddd, $J =$ 14.8, 6.5, 8.2 Hz, 1H, CH_2CH$_2$COOH), 2.11 (ddd, $J = 14.8$, 7.2, 8.2 Hz, 1H, CH_2CH$_2$COOH), 2.42 (ddd, $J = 15.4$, 8.2, 7.2 Hz, 1H, CH_2COOH), 2.54 (ddd, $J = 15.4$, 8.2, 6.5 Hz, 1H, CH_2COOH), 2.95 (d, $J = 14.22$ Hz, 1H, CH_2Ph), 3.07 (d, $J = 14.22$ Hz, 1H, CH_2Ph), 5.08 (s, 1H, CH(C(CH$_3$)$_3$)), 7.15–7.21 (m, 5H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.2, 28.3, 28.4, 34.2, 40.6, 81.8, 108.3, 127.2, 128.3, 130.7, 134.4, 174.1, 178.3; MS (ESI) *m*/*z* 329 ([M+Na]$^+$, 100%), 324 ($M^+ + NH_4^+$, 41%); HRMS calcd for $[C_{17}H_{22}O_5+H]^+$: 307.1540; found: 307.1537.

4.5. (2*S*,5*S*)-2-*tert*-Butyl-5-(carboxyethyl)-5-(carboxymethyl)-1,3-dioxolan-4-one 9

To an ice-bath cooled solution of compound **8** (123 mg, 0.40 mmol) in a mixed solvent system (CCl_4 1.6 mL/CH_3CN 1.6 mL/H_2O 2.0 mL) was added $NaIO_4$ (1.25 g, 5.83 mmol) in one portion. To the vigorously stirred mixture was added a 0.05 M $RuCl_3$ aqueous solution (0.40 mL, 0.020 mmol). The mixture was stirred at room temperature for 3 days. The resulting mixture was quenched with brine (4 mL), filtered, and the filtrate then extracted with ethyl acetate (4 × 7 mL). The combined organic layers were washed with 20% sodium bisulfite solution and dried over anhydrous Na_2SO_4. After being concentrated in vacuum, the residue was purified by flash chromatography (eluent: ethyl acetate) affording **9** (84 mg, yield: 76%) as a white solid. $[\alpha]_D^{20} = +16.5$ (*c* 0.77, $CHCl_3$). Mp 139–142 °C (EtOAc/PE); IR (film): 3408, 3058, 2967, 1797, 1712, 1184 cm^{-1}; ^1H NMR (500 MHz, CD_3OD): δ 0.98 (s, 9H, C(CH_3)$_3$), 2.04 (ddd, $J = 6.7$, 7.9, 14.0 Hz, 1H, CH_2CH$_2$COOH), 2.24 (ddd, $J = 7.1$, 8.1, 14.0 Hz, 1H, CH_2CH$_2$COOH), 2.44 (ddd, $J = 7.1$, 7.9, 15.6 Hz,

1H, CH_2CH_2COOH), 2.48 (ddd, $J = 6.7$, 8.1, 15.6 Hz, 1H, CH_2CH_2COOH), 2.81 (d, $J = 16.0$ Hz, 1H, CH_2COOH), 2.84 (d, $J = 16.0$ Hz, 1H, CH_2COOH), 5.24 (s, 1H, $CH(C(CH_3)_3)$); ^{13}C NMR (125 MHz, CD_3OD): δ 24.1, 28.9 (2C), 35.1, 39.8, 81.0, 109.1, 171.7, 175.7, 176.0; MS (ESI) m/z 273 ($[M-1]^-$, 24%), 187 ($[M-1-86]^-$, 100%). Anal. Calcd for $C_{12}H_{18}O_7$: C, 52.55; H, 6.62. Found: C, 52.81; H, 6.74.

4.6. Homocitric acid lactone 2

A solution of (2*S*,5*S*)-**9** (60 mg) in 3 mL of TFA (50% solution) was heated to reflux for 6 h. The solvents were removed under reduced pressure. The residue was dried in freeze dryer over 12 h to afford 40 mg of homocitric acid lactone **2** (yield: 98%). $[\alpha]_D^{20} = +20.2$ (*c* 1.18, CH_3OH) {lit.[7c] $[\alpha]_D^{20} = +21.3$ (*c* 1.12, CH_3OH)}; IR (film): 3428, 2930, 1777, 1730 cm^{-1}; ^1H NMR (500 MHz, D_2O): δ 2.36–2.43 (m, 1H, H_a-4), 2.50–2.56 (m, 1H, H_b-4), 2.65–2.72 (m, 2H, H-3), 3.01 (d, $J = 17.5$ Hz, 1H, CH_2COOH), 3.35 (d, $J = 17.5$ Hz, 1H, CH_2COOH); ^{13}C NMR (125 MHz, D_2O): δ 27.6, 31.1, 41.4, 84.6, 173.1, 174.6, 178.0; MS (ESI) m/z 211 ($[M+Na]^+$, 100%), 189 ($[M+H]^+$, 11%). HRMS calcd for $[C_7H_8O_6-1]^-$: 187.0240, found: 187.0237.

4.7. (2*S*,5*S*)-5-Benzyl-2-*tert*-butyl-5-(3-phenylpropyl)-1,3-dioxolan-4-one 10

To a solution of LHMDS (0.50 mmol) in 3.6 mL of a mixed solvent (THF–hexane = 9:1), was added a solution of *cis*-**5** (100 mg, 0.43 mmol) and HMPA (0.37 mL, 2.14 mmol) in 7 mL of THF at −78 °C. After 30 min, 3-phenylpropyl iodide (437 mg, 1.71 mmol) was added. After 4 h, the reaction mixture was quenched with 30 mL of an aqueous solution of ammonium chloride (15.7% w/w), and the aqueous layer extracted with Et_2O (3 × 2 mL). The combined organic phases were washed with brine (2 mL), and dried over anhydrous Na_2SO_4. After being concentrated in vacuum, the residue was purified by flash chromatography (eluent: diethyl ether–petroleum ether = 1:40) to afford **10** (48 mg, yield: 32%) as a colorless oil. $[\alpha]_D^{20} = +15.6$ (*c* 0.59, $CHCl_3$). IR (film): 2921, 1792, 1598 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.67 (s, 9H, $C(CH_3)_3$), 1.68–1.77 (m, 4H, $CH_2CH_2CH_2Ph$), 2.50–2.56 (m, 2H, $CH_2CH_2CH_2Ph$), 2.92 (d, $J = 14.25$ Hz, 1H, CH_2Ph), 3.05 (d, $J = 14.25$ Hz, 1H, CH_2Ph), 5.02 (s, 1H, $CH(C(CH_3)_3)$), 7.06–7.22 (m, 10H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.2 (3C), 25.5, 34.3, 34.4, 35.8, 41.4, 82.8, 108.6, 126.0, 127.0, 128.2, 128.4, 130.7, 135.0, 141.4, 174.8; MS (ESI) m/z 375 ($[M+Na]^+$, 100%), 370 ($[M+NH_4^+]^+$, 90%). HRMS calcd for $[C_{23}H_{28}O_3+Na]^+$: 375.1924, found: 375.1931.

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