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Efficient Synthesis of DOPA Analogues in Pepticinnamins E *via* Asymmetric Catalytic Hydrogenation of Dehydroamino Esters

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One practical synthetic procedure with five steps was developed to prepare a series of *N*-protected-2-(diethoxyphosphoryl)glycinates with good yields, which was treated with aldehydes under mild condition to give different dehydroamino esters with high yields and excellent *Z/E* selectivity. The subsequently homogeneous enantioselective hydrogenation of the dehydroamino esters affords a series of new DOPA analogues.

Key Words: *N*-protected-2-(diethoxyphosphoryl)glycinates, Dehydroamino esters, Asymmetric hydrogenation catalysis, DOPA analogues.

INTRODUCTION

Pepticinnamin E[1] (Fig. 1) is a major product of the pepticinnamins, which are isolated from the culture of *Streptomyces sp*. OH-4652. It shows rather potent inhibitory activity against farnesyl protein transferase (FPTase) with an IC_{50} of 0.3 μM and is the first competitive inhibitor derived from a natural product. Its structure contains a novel DOPA analogue **2**, whose configuration has been determined as S by the Waldmann group using the Schöllkopf method.[2] Our interest is to explore a new methodology to synthesize pepticinnamin E.[3a,3b] One emphasis was placed on preparing new DOPA analogues **7**, which could be applied in total synthesis of pepticinnamin E.[3b] This study reports the preparation of a series of new DOPA analogues through asymmetric hydrogenation of Z-dehydroamino acids, which were afforded by treating aldehyde with *N*-protected-2-(diethoxyphosphoryl) glycinates under stereoselective Horner-Wadsworth-Emmons condition. The obtained DOPA analogues would be valuable for the total synthesis of pepticinnamin E and its derivatives in different configuration.

EXPERIMENTAL

Melting points were determined with an electrothermal digital melting point apparatus and were uncorrected. Optical rotation was recorded on a Perkin-Elmer Model 341 polarimeter, at the sodium D line. Elemental analysis was undertaken on a Carlo-1106 model automatic instrument. Infrared spectra (IR) were run on a Nicolet MX-1 and Nicolet-560 MAGNA. ^{1}H NMR spectra were recorded on a Bruker-200 and Bruker-300 or on a Varian-400 at 25 ºC. ^{13}C NMR was given by a Bruker-200. ^{1}H and ^{13}C were referenced to TMS. MS-EI mass spectra were obtained on a VG 7070E. All reactions using air- or moisture-sensitive reagents were conducted in an inert nitrogen atmosphere. Anhydrous solvents were distilled prior to use. THF and toluene were distilled from sodium/benzophenone. CH_2Cl_2 was distilled from CaH_2. CH_3OH and pyridine were distilled from magnesium and KOH, respectively.

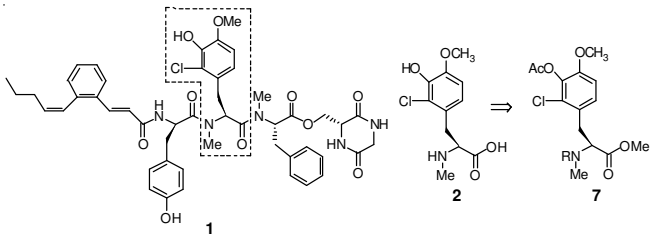


Fig. 1. Structures of petpticinnamin E and DOPA analogues

N-protected-2-(diethoxyphosphoryl)glycinate (3a-3e)

Preparation of *N*-Cbz-amino-methoxyglycinate 2: The compound **2** was obtained as white solid with yield of 92 % following the procedure reported in literature.[4] m.p. 76-78 ºC (lit.: 76-78 ºC). IR (KBr, ν_{max} cm^{-1}): 3310, 1753, 1689, 1536, 1455, 1361, 1267, 1226, 1196, 1104, 1031, 981, 762, 737, 699. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (s, 5H, Ar-H), 5.85 (bs, 1H, NH), 5.35 (d, *J* = 9.2 Hz, 1H, CH), 5.14 (s, 2H, CH_2Ph), 3.80 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3).

Preparation of *N*-Cbz-2-(diethoxyphosphoryl) glycinate (3a): To the solution of **2** (13.17 g, 52 mmol) in dry toluene (10 mL) was added dropwise the freshly distilled PCl_3 (7.14 g, 52 mmol). After the reaction was reacted at 72 ºC for 18 h, the fresh $(EtO)_3P$ (8.97 g, 54 mmol) was added dropwise. The reaction was kept stirring for 2 h at the same temperature. Then solvent was evaporated under vacuum and the residue was dissolved in EtOAc, washed by saturated $NaHCO_3$ solution until pH>7. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo* to give crude product, which was recrystallized from EtOAc/hexane to give **3a** (15.78 g, yield 85 %) as white solid. m.p. 74-75 ºC. IR (KBr, ν_{max} cm^{-1}): 3228, 3040, 2983, 2911, 1752, 1711, 1540, 1328, 1268, 1236, 1209, 1046, 986, 759, 702, 540. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.34 (s, 5H, Ar-H), 5.60 (d, *J* = 8.9 Hz, 1H, NH), 5.11 (s, 2H, CH_2Ph), 4.90 (d, *J* = 8.9 Hz, 2H, CH_2), 4.13 (m, 4H, 2-OCH_2), 3.81 (s, 3H, OCH_3), 1.29 (m, 6H, 2-CH_3).

Preparation of *N*-Boc-2-(diethoxyphosphoryl)-glycinate (3b): To the mixture of **3a** (3.59 g, 10 mmol) and 10 % Pd/C (0.36 g) was added methanol (20 mL) carefully. The suspension was hydrogenated until TLC showed that the starting material **3a** was consumed completely (need about 14.5 h). Then, the solid was filtered off and the filtrate was concentrated in *vacuo* to give amine **4** as colourless syrup, which was used for preparation of **3b**, **3d** and **3e** directly without further purification.

The above obtained amine **4** was dissolved in dry dichloromethane (10 mL), then $(Boc)_2O$ (2.4 g, 11 mmol) was added. The solution was stirred at room temperature for 12 h, then washed by cold 1N $KHSO_4$ and saturated solution of $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give crude product. To this crude product was added 10 mL (v/v) of ether/hexane with vigorous agitation, then the suspension was standed at -4 ºC overnight. The **3b** (3.11 g, yield 96 % for two steps) was collected by filtration as white solid. m.p. 62-63 ºC. IR (KBr, ν_{max} cm^{-1}): 3271, 2980, 1754, 1706, 1539, 1300, 1247, 1166, 1052, 1024, 974. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 5.35 (bd, *J* = 9.2 Hz, 1H, NH), 4.90 (d, *J* = 9.2 Hz, 1H, CH), 4.19 (q, *J* = 7.3Hz, 4H, 2-OCH_2), 3.85 (s, 3H, OCH_3), 1.45 (s, 9H, Boc-CH_3), 1.34 (t, *J* = 7.3 Hz, 6H, 2-CH_3).

Preparation of *N*-Acyl-2-(diethoxyphosphoryl) glycinate (3c): To the solution of **3a** (3.59 g, 10 mmol) in anhydrous methanol (30 mL) was added 5 % Pd/C (0.5 g) and fresh Ac_2O (2.5 mL, 25 mmol). The mixture was hydrogenated at 40 ºC for 10 h. Then, the solid was filtered off and the filtrate was concentrated in *vacuo* to give slight yellow slurry, which was recrystallized from EtOAc/hexane to obtain **3c** (2.5 g, yield 94 %) as white solid. m.p. 75-76 ºC. IR (KBr, ν_{max}, cm^{-1}): 3272, 2987, 2933, 1746, 1684, 1549, 1427, 1371, 1303, 1246, 1216, 1140, 1061, 1025, 975, 613, 524. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.52 (bs, 1H, NH), 5.2 (d, *J* = 8.9 Hz, 1H, CH), 4.18 (q, *J* = 7.2 Hz, 4H, 2-OCH_2), 3.82 (s, 3H, OCH_3), 2.09 (s, 3H, $COCH_3$), 1.34 (t, *J* = 7.2 Hz, 6H, 2-CH_3).

Preparation of *N*-chloroacyl-2-(diethoxyphosphoryl) glycinate (3d): To the solution of above obtained amine **4** in 8 mL of dichloromethane was added dropwise the solution of $ClCH_2COOH$ (0.95 g, 10 mmol) in 10 mL of dichloromethane, then followed by adding the DCC (2.27 g, 11 mmol) at -5~0 ºC. The reaction mixture was stirred at room temperature for 5 h. The white solid was filtered off and the filtrate was washed with cold 1N $KHSO_4$, saturated solution of $NaHCO_3$ and saturated solution of NaCl. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo* to give colourless syrup, which was dissolved in 8 mL of dichloromethane and stored at -4 ºC overnight. The DCU was filtered off and the filtrate was concentrated in *vacuo* to give **3d** (2.57 g, yield 83 % for two steps from 10 mmol of **3a**) as slight yellow solid. m.p. 47-48 ºC. IR (KBr, ν_{max}, cm^{-1}): 3259, 2987, 2952, 1750, 1692, 1534, 1438, 1327, 1255, 1163, 1027, 978, 550. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.31 (bd, *J* = 8.8 Hz, 1H, NH), 5.16 (d, *J* = 8.8 Hz, 1H), 4.21 (q, *J* = 6.9 Hz, 4H, 2-OCH_2), 4.12 (s, 2H, CH_2Cl), 3.83 (s, 3H, OCH_3), 1.36 (t, *J* = 6.9 Hz, 6H, 2-CH_3).

Preparation of *N*-Benzyl-2-(diethoxyphosphoryl)-glycinate (3e): To the solution of above obtained amine **4** in anhydrous pyridine (10 mL) was added dropwise fresh PhCOCl (1.69 g, 12 mmol) at -5-0 ºC. After reaction was stirred at 9 ºC overnight, EtOAc was added into reaction, then washed with 1N $KHSO_4$ and water until pH = 6-7. The organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give slight yellow syrup, which was recrystallized from EtOAc/hexane to afford **3e** (2.2 g, yield 67 %) as white solid. m.p. 105-106 ºC. IR (KBr, ν_{max}, cm^{-1}): 3263, 2981, 2921, 1756, 1660, 1547, 1311, 1248, 1214, 1055, 1020, 976, 696. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.87-7.43 (m, 5H, ArH), 6.90 (bd, *J* = 8.8 Hz, 1H, NH), 5.42 (d, *J* = 8.8 Hz, 1H, CH), 4.21 (m, 4H, 2-OCH_2), 3.88 (s, 3H, OCH_3), 1.35 (m, 6H, 2-CH_3).

Common procedure for preparation of dehydroamino esters (6a-6e): To the solution of *N*-protected-2-(diethoxy-phosphoryl)glycinates **3a-3e** (2.2 mmol, 1.1 eq) in 10 mL of fresh CH_2Cl_2 was added DBU (0.3 mL, 2.2 mmol, 1.1 eq) at 0-4 ºC, after stirring 1 min at the same temperature, the solution of aldehydes **5** (2.0 mmol, 1.0 eq) in 6 mL of fresh CH_2Cl_2 was added dropwise. Then reaction was kept stirring at room temperature for 2-3 h until TLC showed the completion of reaction. EtOAc was added and washed with cold 1N H_2SO_4. The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give crude product, which was purified by silica chromatography with petroleum / EtOAc as eluent to give dehydroamino esters **6a-6e** as white solid. Yields and Z/E ratios were presented in Table-1.

Data for dehydroamino acids 6a-6e, including m.p., EA, IR, ^{1}H NMR and MS-EI (6a): Yield 95 %, m.p. 117-118 ºC. Anal. calc. for $C_{21}H_{20}ClNO_7$: C 58.33, H 4.62, N 3.22, Found: C 58.20, H 4.71, N 3.23. FT-IR (KBr, ν_{max}, cm^{-1}): 3480, 3286, 3011, 2950, 1765, 1730, 1699, 1639, 1600, 1508, 1486, 1439, 1372, 1298, 1238, 1148, 1071, 1040, 901, 774, 697. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.45 (s, 1H, CH=), 7.42 (d, *J* = 8.9 Hz, 1H, ArH), 7.33 (s, 5H, ArH), 6.75 (d, *J* = 8.9 Hz, 1H, ArH), 6.38 (bs, 1H, NH), 5.09 (s, 2H, OCH_2), 3.92 (s, 3H, $ArOCH_3$), 3.82 (s, 3H, $COOCH_3$), 2.38 (s, 3H, $COCH_3$). EI-MS (m/z): 433 (M^+).

Compound 6b: Preparation and data of compound **6b** was reported in former work[3b].

Compound 6c: Yield 94 %, m.p. 147-148 ºC. Anal. calcd. for $C_{15}H_{16}NO_6Cl$: C 52.85, H 4.86, N 4.05, Found: C 52.79, H 4.69, N 4.11. FT-IR (KBr, ν_{max}, cm^{-1}): 3342, 3224, 3009, 2952,

1778, 1728, 1664, 1599, 1489, 1372, 1300, 1237, 1198, 1041, 751. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.47 (s, 1H, =CH), 7.37 (d, *J* = 8.5 Hz, 1H, ArH), 7.06 (bs, 1H, NH), 6.87 (d, *J* = 8.5 Hz, 1H, ArH), 3.86 (s, 6H, OCH_3, $COOCH_3$), 2.38 (s, 3H, $COCH_3$), 2.1 (s, 3H, $COCH_3$). EI-MS (m/z): 341 (M^+).

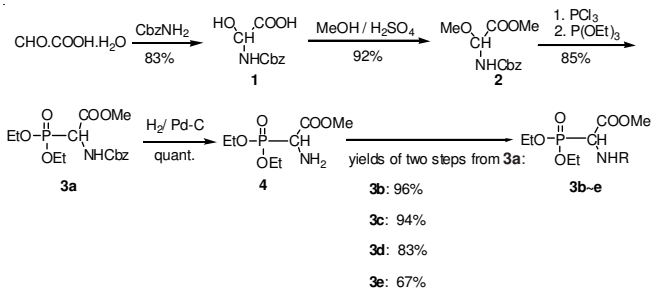
Compound 6d: Yield 98 %, m.p. 131-132 ºC. Anal. calcd. for $C_{15}H_{15}NO_6Cl_2$: C 47.88, H 4.10, N 3.64. Found: C 48.00, H 4.00, N 3.73. FT-IR (KBr, ν_{max}, cm^{-1}): 3331, 3256, 3007, 2952, 1757, 1732, 1667, 1600, 1522, 1492, 1434, 1371, 1303, 1248, 1221, 1116, 1046, 981, 901, 757. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.02 (bs, 1H, NH), 7.6 (s, 1H, =CH), 7.37 (d, *J* = 8.6 Hz, 1H, ArH), 6.87 (d, *J* = 8.6 Hz, 1H, ArH), 4.13 (s, 2H, CH_2Cl), 3.88 (s, 3H, $ArOCH_3$), 2.38 (s, 3H, $COCH_3$). EI-MS (m/z): 375 (M^+).

Compound 6e: Yield 94 %, m.p. 154-155 ºC. Anal. calcd. for $C_{20}H_{18}NO_6Cl$: C 51.66, H 3.79, N 3.63. Found: C 51.61, H 3.76, N 3.47. FT-IR (KBr, ν_{max}, cm^{-1}): 3308, 1775, 1722, 1698, 1666, 1597, 1512, 1484, 1303, 1248, 1196, 1035, 712. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.26-7.87 (m, 7H, ArH, =CH), 6.79 (d, *J* = 8.9 Hz, 1H, ArH), 3.89 (s, 3H, $ArOCH_3$), 3.81 (s, 3H, $COOCH_3$), 2.38 (s, 3H, $COCH_3$). EI-MS (m/z): 403 (M^+).

General process for asymmetric hydrogenation of 6 to prepare 7: To a solution of DIPAMP (2.7 mg, 0.0059 mmol) in 1.5 mL of absolute acetone (deoxygenization before use) was added [Rh(COD)BF_4 (2.4 mg, 0.0059 mmol) under Ar_2, after stirring at room temperature for 1 h, this catalyst with concentration of 0.0004 mmol/0.1 mL was prepared and which was used in next procedure right away. To a solution of compound **6a~e** (1.75 mmol) in absolute acetone (26 mL) (deoxygenization before use) was added catalyst prepared in above procedure, the reaction solution was hydrogenated under 1 atm for 42 h at room temperature. Then active carbon was added with stirring, after 0.5 min, the solid was filtered off through celite pad and the filtrate was concentrated to give crude product, *ee* value was determined by chiral OD, Hexane:*i*PrOH = 90:10, rate:1 mL/min). The crude product was recrystallized from ethyl acetate and hexane. Compounds **7a-7e** were confirmed by EI-MS (m/z): **7a**: 435 (M^+), **7b**: 403 (M^+), **7c**: 343 (M^+), **7d**: 377 (M^+), **7e**: 405 (M^+).

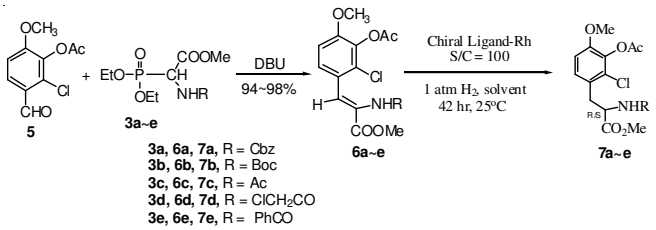
RESULTS AND DISCUSSION

N-Protected-2-(dialkoxyphosphoryl)glycinates were widely used in preparation of dehydroamino esters derivatives *via* a Horner-Wadsworth-Emmons reaction by reacting with an aldehyde.[5] Subsequent asymmetric hydrogenation of dehydroamino esters derivatives provides one of the most desirable ways to access natural and unnatural amino acids, especially the chiral amino acid[6]. Many literatures reported different synthetic methodologies for preparation of *N*-protected-2-(dialkoxyphosphoryl)glycinates and their analogues and also reported their application in preparation of versatile DDAA analogues and dehydropeptides[7]. Up to now, preparation their analogues have been attracting much attention.[7c,7d,7e] In our work, starting from commercially available 2-oxoacetic acid hydrate, the compound **2** was obtained in good yield referencing the similar method in literature[8]. Regarding the conversion of **2** into **3a**, suitable equivalent ratio of PCl_3 and reaction temperature were two important factors to affect the conversion. The isolated yields of **3a** were decreased by approximately 15 % and 10 % respectively, when more than one equivalent of PCl_3 and higher reaction temperature than 72 ºC (80 ºC in present case). Starting from **3a**, one-pot reaction afforded **3c** without isolating amine **4** since it could react with acetic anhydride *in situ*. However, in case of preparing compounds **3b, 3d, 3e**, isolation of amine was necessary, otherwise, much lower yields of **3b, 3d, 3e** would be obtained (**Scheme-I**).



Scheme-I Preparation of *N*-protected-2-(dialkoxyphosphoryl) glycinates

Based on the methodology in literatures,[9] traditional Horner-Wadsworth-Emmons reaction was employed to fulfill olefination between aldehyde **5** and glycinates **3a~3e** using DBU as base in dichloromethane to afford only Z-dehydroamino esters in excellent isolated yields (from 94 % to 98 %, **Scheme-II**). Subsequent enantionselective catalytic hydrogenation was explored to give new chiral DOPA analogues. The prior research reported that chiral ligands DPAMPP[10] and DIPAMP[11] have been applied in rhodium-catalyzed asymmetric hydrogenation of dehydroamino esters derivatives with high catalytic activity and excellent enantioselectivity (up to 99b% *ee*). This research result led us to employ DPAMPP and DIPAMP in hydrogenation of **6a~6e** to afford new DOPA analogues **7a~7e** (**Scheme-II** and Table-1).



Scheme-II: Enantioselective synthesis of DOPA analogues from Z-dehydroamino esters

No reaction was occurred to compound **6a** both with DPAMPP and DIPAMP as catalysts. While DPAMPP was employed as catalyst, the best conversions and the high enantioselectivity (from 77 % *ee* to 99 % *ee* in R configuration) were obtained for substrates **6c** and **6e** both with methanol and acetone as solvents; the comparatively good enantioselectivity (from 59 % to 99 %) for **6b**, **6c** and **6e** were reached. However, very low conversions for substrate **6b** (3 % in methanol and 3 % in acetone) were observed. Furthermore, it was strange that the configuration of products were all in S for Boc-protected compound **7b** both in acetone and methanol as solvent. When DIPAMP was used in catalytic hydrogenation reaction, only S configuration was produced for substrates

TABLE-1
ENANTIOSELECTIVE HYDROGENATION OF *Z*-DEHYDROAMINO ESTERS **6a~e**[a]

Substrate/product	R	(1S, 2R)-DPAMPP			(1R, 2R)-DIPAMP		
		Conv. (%)[b]	*ee* (%)[c]	Config.[d]	Conv. (%)[b]	*ee* (%)[c]	Config.[d]
6a/7a	Cbz	Nr[e]	-	-	Nr[e]	-	-
6b/7b	Boc	3[f]	59	S	13[f]	29	S
		3[g]	85	S	100[g]	87 (91 %[h])	S
6c/7c	Ac	100[f]	77	R	100[f]	25	S
		100[g]	88	R	100[g]	87	S
6d/7d	$ClCH_2CO$	5[f]	83	R	-	-	-
		89[g]	No separation	-	-	-	-
6e/7e	PhCO	100[f]	98	R	100[f]	31	S
		100[g]	99	R	100[g]	86	S

[a]The reaction run at 0.1 mmol scale for the substrates. [b]The conversion was determined by GC or HPLC analyses. [c]*ee* was detected by chiral GC with a Chirasil-L-Val column and Chiral HPLC with a Chiralcel OD column. [d]The configuration was determined by the retention times. [e]Nr: no reaction; [f]Methanol as solvent. [g]Acetone as solvent. [h]in 1.8 mmol scale

6b~d and also with best conversions (100 %) except for substrate **7b** in methanol (13 %). Furthermore, over 85 % *ee* was obtained using acetone as solvent, especially higher enantioselectivity (91 %) was reached even in large scale (with 1.8 mmol of substrate) in acetone. However lower *ee* were produced in methanol for substrates **6b~d** (29, 25 and 31 % respectively). It showed that acetone seems the better solvent than methanol for most of substrates in order to reach better conversion and *ee* value.

Conclusion

A practical and efficient procedure for preparation of dehydroamino esters was developed with high yield and excellent Z/E selectivity. The subsequent enantioselective hydrogenation of the dehydroamino esters affords a series of new DOPA analogues both in R and S configuration, which could be used in total synthesis of pepticinnamin E and its derivatives.

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