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Enantioselective hydrogenation of β-dehydroamino acids on a cinchonidine-modified palladium catalyst

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ABSTRACT

Enantioselective hydrogenation of (*Z*)-β-dehydroamino acids on a cinchonidine-modified Pd/Al_2O_3 catalyst was explored. Comparative studies by using (*Z*)-β-dehydroamino acids and esters identified that the carboxylic group in dehydroamino acids was essentially important to get enantioselectivities (33% for aryl substituted and 46% for alkyl substituted β-dehydroamino acids). This result extended the range of enantioselective hydrogenation of α,β-unsaturated carboxylic acids on chirally modified Pd catalysts and offered a new approach to synthesize optically active β-amino acids.

1. Introduction

Chiral β-amino acids are important building blocks for the synthesis of biologically active products such as β-peptides [1,2] and β-lactam antibiotics [3,4]; they are commonly synthesized by enantioselective hydrogenation of β-dehydroamino esters catalyzed by homogeneous Rh, Ru and Ir complexes bearing chiral ligands [5–11], followed by hydrolysis of the chiral esters to chiral acids. In this field, enantioselective hydrogenation of α-dehydroamino esters with ee values of more than 99% has been industrialized [12,13], but enantioselective hydrogenation of β-dehydroamino esters still suffers from the low enantioselectivity or reaction efficiency due to the co-existence of (*Z*)- and (*E*)-isomers. The (*E*)-isomer was quite easily hydrogenated with a much higher enantioselectivity than the (*Z*)-isomer [14–23]. For example, enantioselective hydrogenation of (*E*)-methyl 3-acetamido-2-butenoate using a Ru-BINAP catalyst gave 96% ee, but hydrogenation of (*Z*)-methyl 3-acetamido-2-butenoate offered only 5% ee [14]. Synthesis of exclusively (*E*)-isomeric substrate is rather difficult because both (*Z*)- and (*E*)-isomers are formed simultaneously in most synthetic protocols, where the (*Z*)-isomer is dominant [24,25]. Separating the (*E*)-isomer from the more stable (*Z*)-isomer resulted in much low yields and sometimes even impossible [26].

Utilizing heterogeneous catalysts for practical applications is highly preferred considering their advantages in easy handling, separation and reuse as compared to the homogeneous system [27]. The major strategy is to immobilize the chiral homogeneous catalysts onto solid supports [28,29]; but it suffered from the rapid leaching of the metal ions in synthesizing amino acids. An alternative route is to combine the supported metal catalysts with the chiral modifiers [30,31]. For example, modification of heterogeneous palladium using cinchona alkaloids has been successfully applied to enantioselective hydrogenation of α,β-unsaturated carboxylic acids [32–35], and over 90% ee were obtained for aryl-substituted substrates [36–38]. However, for enantioselective hydrogenation of dehydroamino acids, this approach was limited only to the α-type substrate [39–44], and 58% ee was obtained in the enantioselective hydrogenation of 2-acetamidoacrylic acid [42]. Successful example for enantioselective hydrogenation of β-dehydroamino acids is still missing. Here, we report that enantioselective hydrogenation of (*Z*)-β-dehydroamino acids on a Pd/Al_2O_3 catalyst that was modified with cinchonidine offered a promising enantioselectivity of 46% under the optimized reaction conditions.

2. Experimental

2.1. General methods

Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^1H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on a Bruker-400 MHz spectrometer. High resolution mass spectra were obtained on a Micromass

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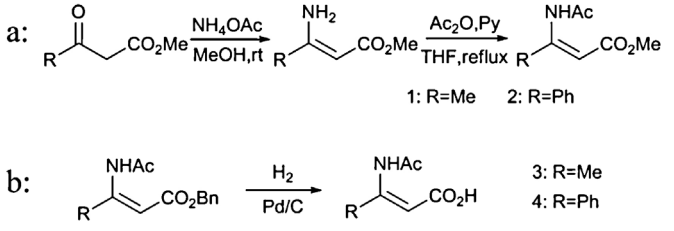


Scheme 1. Synthetic routes of (*Z*)-β-dehydroamino esters (a) and acids (b). Benzyl esters used in route (b) were obtained by the same method as the synthesis of methyl esters (a) except using benzyl β-keto esters as the starting materials.

HPLC-Q-TOF mass spectrometer. TEM images of the commercial Pd/Al_2O_3 catalyst (Alfa Aesar) were recorded on a Philips Tecnai G2 Spirit microscope operated at 120 kV. The specimen was prepared by ultrasonically dispersing the solid powder into ethanol and drops of the suspension were deposited onto a clean carbon-enhanced copper grid and then dried in air. Enantiomeric excess was analyzed by GC and HPLC. Flash column chromatography was performed on silica gel (200–300 mesh).

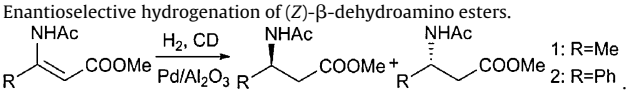
2.2. Synthesis of the substrates

(*Z*)-β-Dehydroamino esters were synthesized by the reaction of β-keto esters with ammonium acetate (Scheme 1a) [25]. A solution of β-keto esters (120 mmol) and NH_4OAc (46 g, 600 mmol) in methanol (150 mL) was stirred at room temperature for 3 days. The solvent was evaporated under reduced pressure, and the residue was diluted with dichloromethane (200 mL). The resulting solid was filtered off and washed with CH_2Cl_2 (2×100 mL). The combined filtrate was washed with water and brine, and dried over sodium sulfate. Evaporation of the solvent gave the enamine intermediate that was then mixed with 120 mL THF, 16 mL pyridine and 60 mL acetic anhydride. The mixture was refluxed until the starting material was totally dissolved. After being cooled down to room temperature, the volatiles were evaporated. The residue was dissolved in ethyl acetate (200 mL), and the solution was washed with water (100 mL), 1 N HCl (100 mL), $NaHCO_3$ (saturated, 100 mL), and brine (100 mL). The solution was dried over sodium sulfate. The solvent was evaporated while the solid residue was subject to column chromatography (SiO_2; 1:9 EtOAc/hexane) to afford (*Z*)-β-dehydroamino esters. Analyses and identifications of these substrates are detailed in the Supporting Information.

2.3. Enantioselective hydrogenation

Enantioselective hydrogenation reactions were carried out in a stainless steel autoclave with a quartz liner (50 mL) under magnetic stirring (650 rpm). The reaction mixture included: 25 mg Pd/Al_2O_3 (5 wt% Pd, Alfa Aesar), 1 mmol substrate, certain amounts of cinchonidine and benzylamine, 3 mL solvent. The reaction temperature was 5 or 25 °C and the pressure of H_2 was 0.5–4.0 Mpa. Before the reaction, the mixture was stirred for 15 min and flushed with hydrogen for five times. After the reaction, the catalyst was filtered off. A small amount of sample was subjected to chiral analysis. The products of **1** and **2** were analyzed using off-line gas chromatography (Agilent 6890N) equipped with a β-cyclodextrin capillary column (Chirasil-Dex CB, Varian) and a flame ionization detector. The following GC conditions were used: initial temperature 110 °C for 2 min, then heated to 180 °C at a rate 5 °C/min and maintained at 180 °C for 10 min. Retention time: t_1 = 8.859 min, t_2 = 9.393 min for **1**; t_1 = 19.237 min, t_2 = 20.314 min for **2**. The products of **3** and **4** were analyzed using a HPLC (Agilent 1200) equipped with a Chirex 3126 Chiral column (Phenomenex) and a UV detector. The following HPLC conditions were used: isopropanol/2 mM copper sulfate = 15/85, flow = 1 mL/min, detector: 210 nm, 30 °C. Retention time: t_1 = 30.096 min, t_2 = 33.688 min for **3**; t_1 = 90.828 min, t_2 = 112.406 min for **4**. The products of **3** and **4** were also confirmed by transformed them into methyl esters using diazomethane ethereal solution and compared with the products of **1** and **2**. The enantiomeric excess was calculated with the equation: $ee\% = |(E_1 - E_2)/(E_1 + E_2)| \times 100$, where E_1 and E_2 are the concentrations of the product enantiomers. The reactions were repeated twice and the results were reproducible within ±1%.

Table 1
Enantioselective hydrogenation of (*Z*)-β-dehydroamino esters.



Entry	Substrate	Modifier	Base	Solvent	ee%
1	**1**	No	No	*i*-PrOH	0
2	**1**	Yes	No	*i*-PrOH	3
3	**1**	Yes	Yes	*i*-PrOH	3
4	**1**	No	No	Toluene	0
5	**1**	Yes	No	Toluene	2
6	**1**	Yes	Yes	Toluene	2
7	**2**	Yes	No	*i*-PrOH	5
8	**2**	Yes	Yes	*i*-PrOH	6
9	**2**	Yes	No	Toluene	3
10	**2**	Yes	Yes	Toluene	3

Reaction conditions: 25 mg Pd/Al_2O_3, 1 mmol substrate, 0.05 mmol cinchonidine, 1 mmol benzylamine (as noted), 3 mL solvent; 25 °C, 2 MPa H_2, 4 h.
Substrates: (*Z*)-methyl 3-acetamidobut-2-enoate (**1**); (*Z*)-methyl 3-acetamido-3-phenylacrylate (**2**).

3. Results and discussion

3.1. Enantioselective hydrogenation of (Z)-β-dehydroamino esters

Fig. 1a shows a TEM image of the commercial Pd/Al_2O_3; Pd particles were uniformly dispersed on the Al_2O_3 support. The average size of Pd particles was about 3 nm estimated by counting approximate 500 particles (Fig. 1b). Table 1 summarizes the reaction results of enantioselective hydrogenation of (*Z*)-β-dehydroamino esters (**1** and **2**) on the Pd/Al_2O_3 catalyst. Full conversions were achieved within 4 h but nearly racemic products were obtained; the enantioselectivity was almost independent of the presence of the chiral modifier, the use of base additive and the polarity of the solvent. These results indicate that the Pd/Al_2O_3 catalyst is poorly enantioselective for hydrogenation of (*Z*)-β-dehydroamino esters. Hydrogenation of α-keto esters over cinchonidine-modified platinum catalysts provided much higher enantioselectivities toward optically active alcohols; the origin was attributed to the strong interaction between the carbonyl group in the substrate and the chiral modifier through hydrogen bond [30]. Therefore, it is reasonable to infer that the acetamido group in β-dehydroamino esters interacted insufficiently with the chiral modifier for generating appreciable enantioselectivity.

3.2. Enantioselective hydrogenation of (Z)-β-dehydroamino acids

It is known that the interaction between the carboxylic group in α,β-unsaturated carboxylic acids and the amine group in cinchona type chiral modifiers through an acid–base type governed the enantioselectivity [30]. Therefore, the (*Z*)-β-dehydroamino esters were transformed into (*Z*)-β-dehydroamino acids (Scheme 1b). It should be noted that (*Z*)-β-dehydroamino acids could not be simply obtained from the hydrolysis of the methyl esters because it would preferentially deacylate the amide group, which would strongly absorb to the palladium surface and subsequently hinder

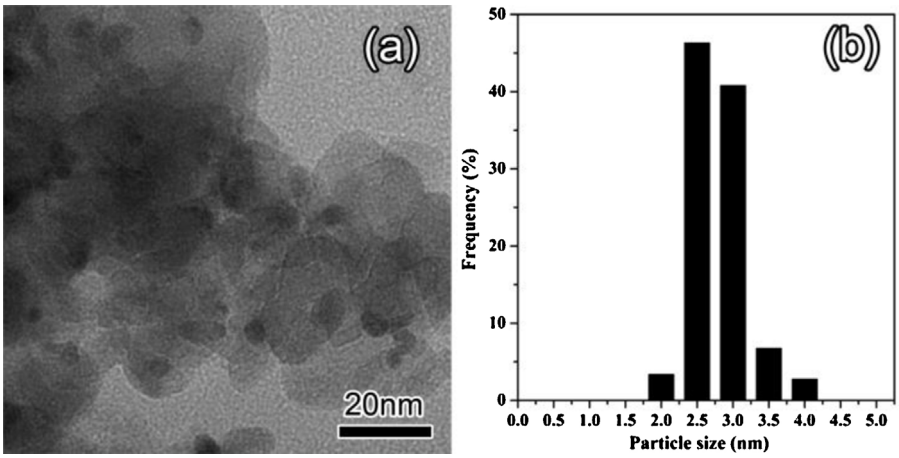
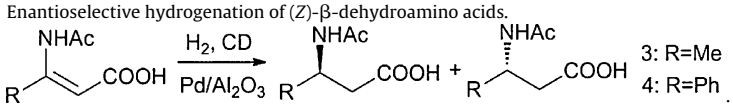


Fig. 1. A TEM image (a) and the size distribution of Pd particles (b) of the Pd/Al_2O_3 catalyst.

the hydrogenation process. A catalytic hydrogenolysis approach that was commonly used to remove the protecting groups in organic synthesis was adopted to fulfill this target [45,46]. Pure (*Z*)-β-dehydroamino acids (**3** and **4**) were obtained with the yields of 70–99% from the corresponding benzyl esters over a commercial Pd/C catalyst. Enantioselective hydrogenation of (*Z*)-3-acetamidobut-2-enoic acid (**3**) was initially examined (Table 2). Full conversion was achieved within 6 h and 46% ee value was obtained under the optimized reaction condition. The intrinsic activity of the catalyst, expressed in turnover frequency (TOF), was 74.9 h^{-1}. This sets the first example of heterogeneous enantioselective hydrogenation of β-dehydroamino acids over a chirally modified metal catalyst.The enantioselectivity was strongly dependent on the polarity of the solvent (entries 1–5). Unlike α,β-unsaturated carboxylic acids, β-dehydroamino acids have two functional groups that may interact with the chiral modifier: the acid-base interaction between the intramolecular carboxylic and amine groups and the acetamido group (C—NH) with the hydroxyl group in the chiral modifier through a hydrogen bond. In non-polar solvents, like toluene, the two functional groups in β-dehydroamino acids were apt to interact with each other to form an intramolecular hydrogen bond, which would prevent their further interactions with the chiral modifier. In strong polar solvents, for example water, both the intramolecular hydrogen bond and the intermolecular hydrogen bond between the acetamido group of the substrate and the hydroxyl group in the chiral modifier weakened considerably, reducing the generation of enantioselectivity. In alcohols with lower polarity, the intramolecular hydrogen bond was weakened but the intermolecular hydrogen bond between the substrate and the chiral modifier favored the formation of a stable substrate–chiral modifier intermediate and thus yielded a higher enantioselectivity. As a consequence, isopropanol that had a moderate polarity served as the most suitable solvent and provided a much higher ee value. Increase in the amount of the chiral modifier (CD) enhanced the enantioselectivity; the optimal enantioselectivity of 40% was obtained at a CD/substrate ratio of 0.05, whereas further increasing in the amount of CD did not promote the enantioselectivity anymore (entries 5–7).

The pressure of hydrogen and the reaction temperature affected the enantioselectivity remarkably (entries 8–10; Fig. 2). As

Table 2
Enantioselective hydrogenation of (*Z*)-β-dehydroamino acids.



Entry	Substrate	CD/substrate (mol%)	Solvent	Temp. (°C)	H_2 (MPa)	ee (%)
1	**3**	5	MeOH	25	1	25
2	**3**	5	EtOH	25	1	23
3	**3**	5	Toluene	25	1	18
4	**3**	5	Water	25	1	20
5	**3**	5	i-PrOH	25	1	40
6	**3**	2	i-PrOH	25	1	27
7	**3**	10	i-PrOH	25	1	40
8	**3**	5	i-PrOH	25	0.5	31
9	**3**	5	i-PrOH	25	2	37
10	**3**	5	i-PrOH	5	1	46
11	**3**	5	i-PrOH	5	1	11[a]
12	**3**	5	i-PrOH	5	1	45[b]
13	**4**	5	MeOH	25	1	12
14	**4**	5	Toluene	25	1	9
15	**4**	5	i-PrOH	25	1	23
16	**4**	10	i-PrOH	25	1	25
17	**4**	10	i-PrOH	25	0.5	27
18	**4**	10	i-PrOH	5	0.5	33

Reaction conditions: 25 mg Pd/Al_2O_3, 1 mmol substrate, 3 mL solvent, certain amounts of cinchonidine as noted in the CD/substrate ratio, 6 h.

[a] Addition of 1.0 equivalent benzylamine.

[b] Cinchonine (CN) was used as chiral modifier and the product was in opposite configuration. Substrates: (*Z*)-3-acetamidobut-2-enoic acid (**3**); (*Z*)-3-acetamido-3-phenylacrylic acid (**4**).

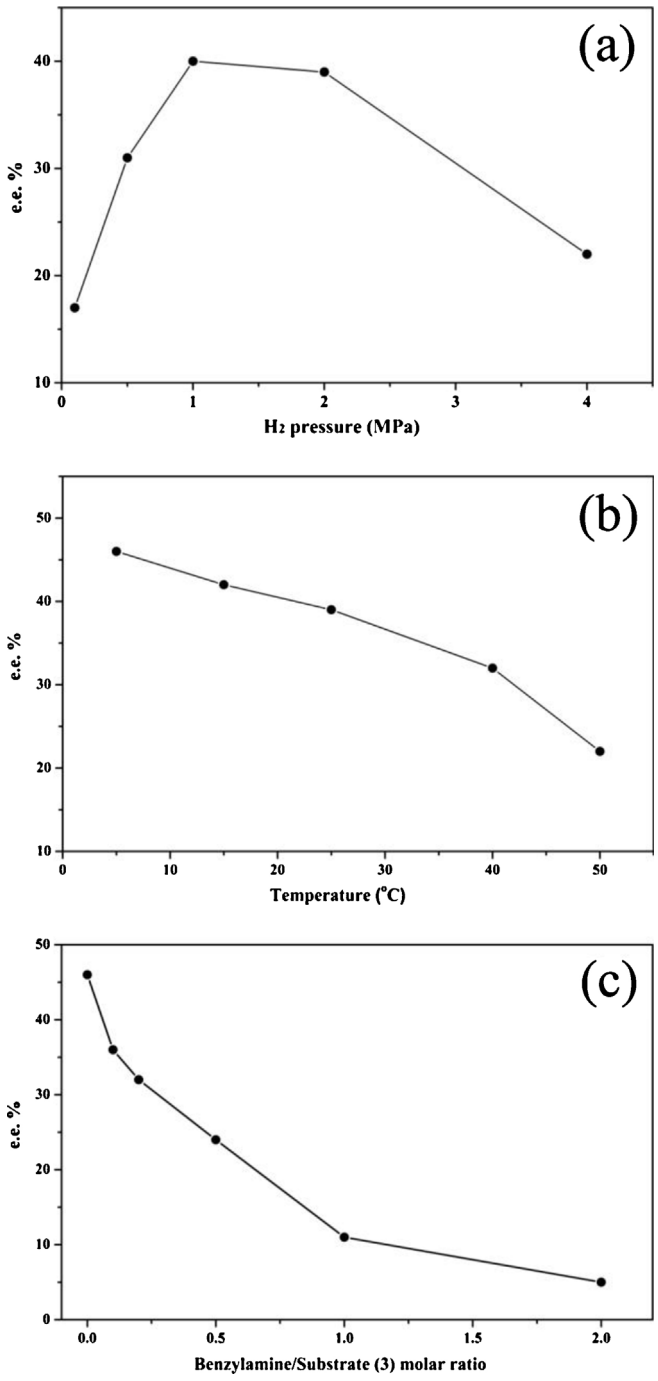


Fig. 2. Effects of hydrogen pressure (a), reaction temperature (b) and amine addition (c) on the enantioselectivity in hydrogenation of (*Z*)-3-acetamidobut-2-enoic acid (**3**). Reaction conditions: 25 mg Pd/Al_2O_3, 1 mmol substrate, 0.05 mmol cinchonidine, 3 mL *i*-PrOH, 25 °C, 6 h. The hydrogen pressure was fixed at 1 MPa in the temperature and amine addition effects tests; the reaction temperature was fixed at 25 °C and 5 °C in the H_2 pressure and amine addition tests.

cinchona alkaloid type chiral modifier favors to adsorb onto Pd surface through its quinoline ring [30], higher hydrogen pressure and reaction temperature caused partial hydrogenation of this anchoring moiety and thus weakened its adsorption strength. Moreover, higher reaction temperature also lowered the solubility of hydrogen [32] and in turn weakened the adsorption strength of the substrate–chiral modifier intermediate, resulting in loss in the enantioselectivity.

Another interesting observation was that the addition of benzylamine to the reaction media lowered the enantioselectivity (entry 11; Fig. 2). Only 0.1 equivalent of amine decreased the ee value from 46% to 36% while 2.0 equivalent of amine resulted in a ee value of only 5%. It was previously observed that the addition of amine enhanced the enantioselectivity in hydrogenations of α,β-unsaturated carboxylic acids on supported Pd catalysts [37], probably through expediting the desorption of the product [47,48]. Similarly, addition of benzylamine to the reaction media promoted the enantioselectivity in hydrogenation of α-dehydroamino acids on a Pd/Al_2O_3 catalyst, which had very similar structure to the β-dehydroamino acids except for the different position of the acetamido group [42]. This result confirms that the minor structural variation in dehydroamino acids may cause remarkable change in the enantioselectivity. It is most likely that β-dehydroamino acids interact preferably with the amines, instead of the chiral modifier, during the enantio-differentiating step and thus losing the enantioselectivity. For comparison, cinchonine (CN) which had opposite absolute configuration at the C8 and C9 atoms to CD was also used as the chiral modifier [49]; product with similar enantioselectivity but opposite configuration was obtained (entry 12). This result suggests that the absolute configurations at these two carbon atoms primarily determined the enantioselectivity of the product, similar to the case of enantioselective hydrogenation of α,β-unsaturated carboxylic acids [50].

Enantioselective hydrogenation of (*Z*)-3-acetamido-3-phenylacrylic acid (**4**) was also investigated (entries 13–18). Under the optimized conditions, the enantioselectivity approached 33% and the TOF was 88.5 h^{-1}. The ee value was lower than that of the β-methyl substituted substrate (**3**). This decrease in enantioselectivity might be linked to the steric constrain between the β-acetylamino group and the β-phenyl substituent in (*Z*)-3-acetamido-3-phenylacrylic acid. Since a phenyl group in the β-position of α,β-unsaturated carboxylic acids inverted the adsorption mode of the substrate on Pd surface [51], it is most probably that the bulky phenyl in substrate 4 tilted the configuration of the substrate–chiral modifier intermediate and consequently lowered the enantioselectivity.

4. Conclusions

β-Dehydroamino acids were synthesized using a facile approach from the corresponding esters, and enantioselective hydrogenation of β-dehydroamino acids was investigated over a cinchonidine-modified Pd/Al_2O_3 catalyst. It was identified that the carboxylic group in β-dehydroamino acids was essential to get promising enantioselectivities (33% for aryl substituted and 46% for alkyl substituted β-dehydroamino acids). This result broadened the range of enantioselective hydrogenation of α,β-unsaturated carboxylic acids using a cinchonidine-modified heterogeneous palladium catalyst and also provided a new route to obtain optically active β-amino acids.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2013.08.004.

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