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Hydrolase-catalyzed Michael addition of 1,3-dicarbonyl compounds to α,β-unsaturated compounds in organic solvent

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Abstract

A novel strategy to perform Michael additions between 1,3-dicarbonyl compounds and α,β-unsaturated compounds was developed by the catalysis of hydrolase. We found that 11 hydrolase could catalyze the enzymatic Michael addition reaction to form the carbon–carbon bond. In 2-methyl-2-butanol D-aminoacylase showed high Michael addition activity. The influence of substrate and Michael acceptor structure on Michael addition was evaluated systematically. Some control experiments demonstrated that the active site of D-aminoacylase was responsible for the enzymatic Michael addition reaction. This novel Michael addition activity of hydrolase is of practical significance in expanding the application of enzymes and in the evolution of new biocatalysts.

Keywords: Enzymes; Michael additions; 1,3-Dicarbonyl compounds; D-Aminoacylase; Catalysis

1. Introduction

Enzyme catalysts are efficient biotransformation tools in both organic and bioorganic synthesis. Since many of them have displayed activity with unnatural substrates in organic solvents, this study has expanded rapidly in the last decades [1–5]. Among all of them, hydrolase are the most used enzymes because they are stable in organic solvents and exhibit high activity with a broad spectrum of substrates. Besides, many of them are commercially available and they work under mild reaction conditions.

The Michael addition reaction is among the most fundamental types of reactions in organic synthesis. Michael additions are generally promoted by harsh bases or strong acid, which would lead to environmentally hazardous residues and undesirable by-products [6–10]. To avoid these problems, various types of catalysts have been developed. The most common catalysts reported for Michael additions are transition metals or lanthanide catalysts [11]. An alternative to these catalysts is enzymes. Some natural lipase [12–16] and protease [17–19] have been applied in the Michael-type addition reaction to form the carbon–nitrogen and carbon–sulfur bond. Engineered mutant of CAL B had been used to catalyze the Michael addition to form the carbon–carbon bond [20]. However, the relative report about the use of natural hydrolase for the carbon–carbon bond formation reaction was rare.

In our former work, we found that a zinc-dependent acylase, D-aminoacylase from *Escherichia coli*, displayed a promiscuous activity to catalyze the carbon–carbon bond formation reaction of 1,3-dicarbonyl compounds to methyl vinyl ketone in organic media [21]. In the present work, we found that 11 natural hydrolase possess the promiscuous activity to catalyze the carbon–carbon bond formation reaction (Scheme 1). The effects of enzyme resource, organic solvent, substrate structure and Michael acceptor structure on the enzymatic Michael addition were evaluated in details. The catalytic specificity of hydrolase was demonstrated by some control experiments. This novel Michael addition activity of hydrolase is of practical significance in expanding the application of enzymes and in the evolution of new biocatalysts [22–24].

2. Experimental

2.1. Materials

D-aminoacylase from *Escherichia coli* (10,000 u/mg, 1 u is defined as enzyme quantity which produces 1 μmol of D-amino

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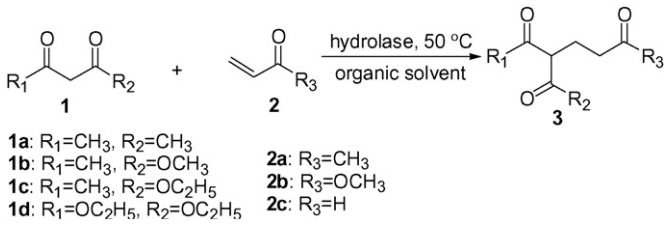


Scheme 1. Hydrolase-catalyzed Michael addition of 1,3-dicarbonyl compounds to α,β-unsaturated compounds.

acid per 30 min) and Acylase "Amano" (AA) from *Aspergillus oryzae* (≥30,000 u/g, 1 u is defined as enzyme quantity which produces 1 μmol of L-amino acid per 30 min) were purchased from Amano Enzyme Inc. (Japan). Lipase from *Mucor javanicus* (9.9 u/mg, 1 u corresponds to the amount of enzyme which liberates 1 μmol oleinic acid from trioleoyl glycerol per minute at pH 8.0 and 37 °C), lipase from *Candida cylindracea* (1.6 u/mg, 1 u corresponds to the amount of enzyme which liberates 1 μmol oleic acid per minute at pH 8.0 and 40 °C), lipase from hog pancreas (2.4 u/mg, 1 u is the amount of immobilized enzyme which forms 1% octyl laurate from 0.5 mmol lauric acid and 1.0 mmol 1-octanol in 10 ml water-saturated isooctane in 1 h at 20 °C), lipozyme immobilized from *Mucor miehei* (42 u/g, 1 u corresponds to the amount of enzyme which liberates 1 mol oleic acid at pH 8.0 and 40 °C per minute) and proteinase from *Aspergillus oryzae* (1.7 u/mg, 1 u is the amount of enzyme which hydrolyzes 1 μmol of L-ieucine-*p*-nitroanilide per minute) were purchased from Fluka (Switzerland). Amano Lipase M from *Mucor javanicus* (≥10,000 u/g enzyme activity, pH 7.0, 40 °C), Lipase Type VII from *Candida rugosa* (706 u/mg, 1 u will hydrolyze 1.0 mequiv. of olive oil from a triglyceride in 1 h at pH 7.7 at 37 °C), lipase immobilized on acrylic resin from *Candida antarctica* (≥10,000 u/g, recombinant, expressed in *Aspergillus oryzae*) and lipase from porcine pancreas (30–90 u/mg protein, 1 u will hydrolyze 1.0 mequiv. of triacetin in 1 h at pH 7.7 at 37 °C) were purchased from Sigma (Steinheim, Germany). Lipase AY 30 (700–1500 u/mg solid, 1 u will hydrolyze 1.0 mequiv. of olive oil from a triglyceride in 1 h at pH 7.7 at 37 °C) was purchased from Acros (New Jersey, USA). Alkaline protease from *Bacillus subtilis* (10 u/mg, 1 u corresponds to the amount of enzyme which liberates 1 μmol folin-positive amino acids and peptides per minute at pH 7.5 and 37 °C) was obtained from Wuxi Enzyme Co. Ltd. (Wuxi, PR China). All solvents were analytical grade and were dried by storing over activated 3 Å molecular sieves before use. All other reagents were used as received.

2.2. Analytical methods

The process of reactions was monitored by TLC on silica with Petroleum ether/EtOAc (3/1%, v/v). The ^{1}H and ^{13}C NMR spectra were recorded with TMS as internal standard using a Bruker AMX-500 MHz spectrometer. Chemical shifts were expressed in ppm and coupling constants (*J*) in Hz. Analytical GC was performed using a Agilent 6890 series with SE-54 capillary column and FID detection. HPLC was carried out using a Agilent 1100 series with chiral Chiralpak AD-H column (hexane/EtOH = 85/15, 1.0 mL/min and 210 nm). IR spectra were measured with a Nicolet Nexus FTIR 670 spectrophotometer.

2.3. Synthesis of 3-acetyl-heptane-2,6-dione (*3a*)

A suspension of 1 mmol acetylacetone and 10 mg D-aminoacylase in 1 ml 2-methyl-2-butanol was incubated at 50 °C and 200 rpm (orbitally shaken) for 20 min. Then, 2 equiv. of methyl vinyl ketone were added in order to initiate the reaction. The mixture was shaken for 16 h. The reaction was terminated by filtering of the enzyme. The crude product was purified by chromatography on silica gel by eluting with petroleum/ethyl acetate (3:1 vol.%). The yield was 94%. The product was colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.68 (t, 1H, $J = 6.93$, C(3)–H), 2.45 (t, 2H, $J = 7.00$, C(5)–H), 2.20 (s, 6H, $CH_3COCHCOCH_3$), 2.13 (s, 3H, C(7)–H), 2.08 (m, 2H, C(4)–H). ^{13}C NMR ($CDCl_3$, δ, ppm): 207.7, 204.3, 67.1, 44.2, 40.7, 29.5 and 21.6. IR (cm^{-1}): 1716 (–C=O), 1358 ($–CH_2$) and 1167 (C–O).

2.4. Synthesis of 2-acetyl-5-oxo-hexanoic acid methyl ester (*3b*)

2-Acetyl-5-oxo-hexanoic acid methyl ester was synthesized by the same synthetic procedure as for **3a**. The yield of product was 90% after 24 h. The product was colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.75 (s, 3H, $–OCH_3$), 3.53 (t, 1H, $J = 7.41$, O=CC*H*C=O), 2.50 (t, 2H, $CH_3COCH_2–$), 2.26 (s, 3H, $CH_3COCH–$), 2.12 (s, 3H, $CH_3COCH_2CH_2–$), 2.09 (m, 2H, $CH_3COCHCH_2CH_2–$). ^{13}C NMR ($CDCl_3$, δ, ppm): 207.7, 203.0, 170.1, 58.1, 52.6, 40.6, 30.1, 29.2 and 21.8. IR (cm^{-1}): 1743 (O=C–O–), 1716 (–C=O), 1360 ($–CH_2$) and 1154 (C–O).

2.5. Synthesis of 2-acetyl-5-oxo-hexanoic acid ethyl ester (*3c*)

2-Acetyl-5-oxo-hexanoic acid ethyl ester was synthesized by the same synthetic procedure as for **3a**. The yield of product was 81% after 24 h. The product was colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.20 (q, 2H, $–OCH_2–$), 3.50 (t, 1H, $J = 7.1$, O=CC*H*C=O), 2.50 (t, 2H, $J = 7.00$, $CH_3COCH_2–$), 2.20 (s, 3H, $CH_3COCH–$), 2.13 (s, 3H, $CH_3COCH_2CH_2–$), 2.08 (m, 2H, $CH_3COCHCH_2CH_2–$), 1.28 (t, 3H, $–OCH_2CH_3$). ^{13}C NMR ($CDCl_3$, δ, ppm): 207.6, 203.0, 169.6, 61.6, 58.4, 40.6, 30.0, 29.1, 21.8 and 14.2. IR (cm^{-1}): 1739 (O=C–O–), 1715 (–C=O), 1360 ($–CH_2$) and 1153 (C–O).

2.6. Synthesis of 2-(3-oxo-butyl)-malonic acid diethyl ester (*3d*)

2-(3-Oxo-butyl)-malonic acid diethyl ester was synthesized by the same synthetic procedure as for **3a**. The yield was 1% after 48 h. The product was colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.20 (m, 4H, $–OCH_2–$), 3.39 (t, 1H, $J = 7.3$, O=CC*H*C=O), 2.54 (t, 2H, $J = 7.30$, $CH_3COCH_2–$), 2.16 (m, 2H, $CH_3COCHCH_2–$), 2.13 (s, 3H, $CH_3COCH_2CH_2–$), 1.27 (m, 6H, $–OCH_2CH_3$). ^{13}C NMR ($CDCl_3$, δ, ppm): 207.4, 169.4, 61.7,

50.9, 40.7, 30.1, 22.7 and 14.3. IR (cm^{-1}): 1727 (O=C–O–), 1367 (–CH_2) and 1186 (C–O).

2.7. Synthesis of 4-acetyl-5-oxo-hexanal (*3e*)

4-Acetyl-5-oxo-hexanal was synthesized by the same synthetic procedure as for **3a**. The reaction was carried out at 25 °C for 6 h. The yield was 86%. The product was colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 9.76 (s, 1H, C*H*O), 3.55 (t, 1H, J = 7.1, O=CC*H*C=O), 2.54 (t, 2 H, J = 7.10, OHCCH_2–), 2.26 (s, 6H, CH_3COCH–), 2.16 (m, 2H, CH_3COCHC$H_2$$CH_2$–). ^{13}C NMR ($CDCl_3$, δ, ppm): 202.7, 201.1, 58.1, 52.8, 41.2, 29.3 and 20.3. IR (cm^{-1}): 2728, 1716, 1360 (–CH_2) and 1155 (C–O).

2.8. Synthesis of 2-acetyl-pentanedioic acid 1-ethyl ester 5-methyl ester (*3f*)

2-Acetyl-pentanedioic acid 1-ethyl ester 5-methyl ester was synthesized by the same synthetic procedure as for **3a**. The yield was 1% after 48 h. The product was colorless liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.20 (m, 2H, –OCH_2–), 3.68 (s, 3H, –OCH_3), 3.39 (t, 1H, J = 7.3, O=CC*H*C=O), 2.54 (t, 2H, J = 7.30, CH_3COCH_2–), 2.16 (m, 2H, CH_3COCHCH_2–), 2.13 (s, 3H, CH_3COC$H_2$$CH_2$–), 1.27 (m, 6H, –OC$H_2CH_3$). ^{13}C NMR ($CDCl_3$, δ, ppm): 207.4, 169.4, 61.7, 50.9, 40.7, 30.1, 22.7 and 14.3. IR (cm^{-1}): 1727 (O=C–O–), 1367 (–CH_2) and 1186 (C–O).

2.9. Synthesis of 3-(2-nitro-1-phenylethyl)pentane-2,4-dione (*3g*)

3-(2-Nitro-1-phenylethyl)pentane-2,4-dione was synthesized by the same synthetic procedure as for **3a**. The yield was 30% after 24 h. The product was light yellow solid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.33–7.29 (m, 3H), 7.19–7.18 (m, 2H), 4.64–4.62 (t, 2H), 4.38–4.36 (m, 1H), 4.25 (m, 1H), 2.30 (s, 1H), 1.95 (s, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 202.0, 201.2, 136.3, 129.6, 128.8, 128.2, 78.4, 71.0, 43.1, 30.7 and 29.8. IR (cm^{-1}): 1731, 1702, 1604, 1544 and 704. The ee value of product was detected by HPLC with chiral Chiralpak AD-H column (hexane/EtOH = 85/15, 1.0 mL/min, 210 nm, 17.0 min and 27.8 min).

3. Results and discussion

3.1. Effect of solvent

Generally, organic solvents strongly affected the enzymatic Michael addition. In order to improve the activity of D-aminoacylase, some conventional organic solvents with different log P-values were screened and the results were shown in Fig. 1. We selected the Michael addition of ethyl acetoacetate with methyl vinyl ketone as the model reaction. In those solvents such as toluene, chloroform or isopropyl ether, the reactions were very poor and the yields were less than 10%. In *n*-hexane, the yield was about 30%. The yields were far from satisfaction in those solvents such as THF and dioxane. In highly polar solvents such as DMSO and DMF, the yields were less than 40%. D-Aminoacylase showed higher Michael addition activity in some tertiary alcohol solvents. The reaction could obtain 82% yield in 2-methyl-2-butanol after 24 h. Thus, the optimal solvent for D-aminoacylase was 2-methyl-2-butanol.

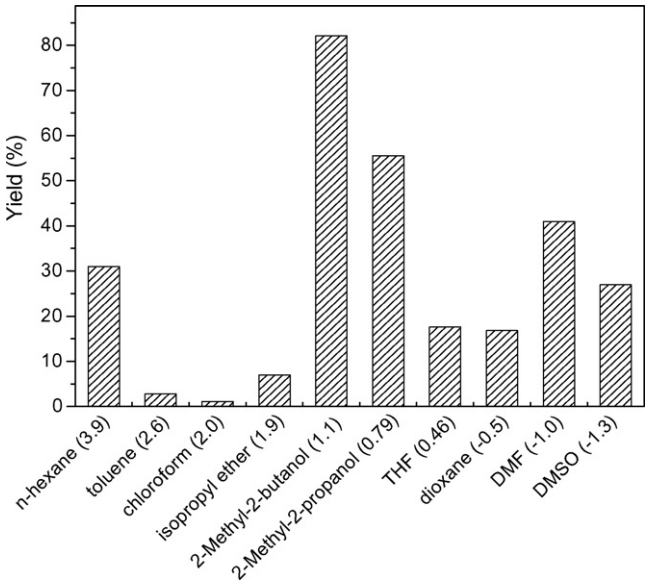


Fig. 1. The influence of organic solvents on the enzymatic Michael addition reaction of ethyl acetoacetate with methyl vinyl ketone.

3.2. Effect of enzymes

In order to test whether other types of hydrolase could also catalyze the enzymatic carbon–carbon bond formation, 14 commercially available hydrolase were screened. The results were shown in Table 1. Alkaline protease from *Bacillus subtilis*, lipase from *porcine pancreas*, lipase from *hog pancreas* and D-aminoacylase could obtain the corresponding product in moderate to high isolated yield. Poor yields were obtained for those hydrolase such as lipase from *Candida cylindracea*,

Table 1
Enzyme screen for the enzymatic Michael addition reaction[a]

Entry	Enzyme	Yield[b] (%)
1	Alkaline protease from *Bacillus subtilis*	50.8
2	Proteinase from *Aspergillus oryzae*	13.9
3	Lipase from porcine pancreas	63.9
4	Lipase from hog pancreas	39.9
5	Lipase Type VII from *Candida rugosa*	11.2
6	Lipase from *Candida cylindracea*	0.89
7	Lipase acrylic resin from *Candida antarctica*	2.67
8	Lipase AY 30	31.4
9	Lipase from *Mucor javanicus*	18.3
10	Amano lipase M from *Mucor javanicus*	20.6
11	Lipozyme, immobilized from *Mucor miehei*	24.0
12	Acylase Amano	3.26
13	D-Aminoacylase	82.0

[a] Reactions were carried out on 1 mmol scale of ethyl acetoacetate with 2 equiv. of methyl vinyl ketone catalyzed by 10 mg enzyme in 1 ml 2-methyl-2-butanol at 50 °C for 24 h.

[b] Yields were determined by GC.

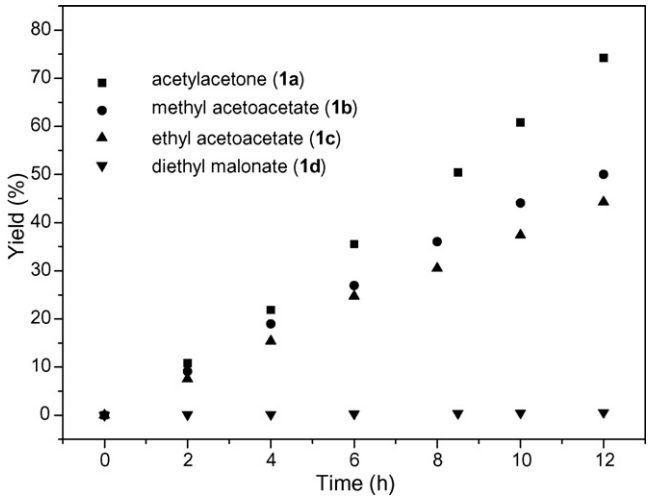


Fig. 2. Progress curve of Michael addition of 1,3-dicarbonyl compounds to methyl vinyl ketone catalyzed by D-aminoacylase. Reaction conditions: 1,3-dicarbonyl compounds (1 mmol), methyl vinyl ketone (2 mmol), 2-methyl-2-butanol (1 mL), D-aminoacylase (10 mg) at 50 °C.

CAL B and Acylase "Amano". Other examined hydrolase also could catalyze the carbon–carbon bond formation, although the yields were relatively low. Among the examined hydrolase, D-aminoacylase showed the highest activity. Thus D-aminoacylase was used to catalyze the Michael addition reaction.

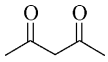
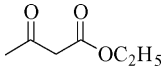
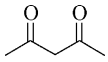
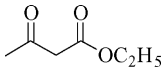
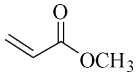
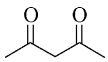
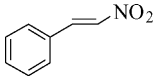
3.3. Influence of substrate structure

The substrate structure affected the enzymatic Michael addition reaction. We examined the Michael addition of four kinds of 1,3-dicarbonyl compounds, methyl acetoacetate, ethyl acetoacetate, acetylacetone and diethyl malonate with methyl vinyl ketone in 2-methyl-2-butanol. The progress curves were shown in Fig. 2. According to the time course, the initial reaction rates were also calculated. The Michael addition reaction of diethyl malonate with methyl vinyl ketone was very poor and the yield was only 1% after 24 h. The Michael addition reaction of methyl acetoacetate, ethyl acetoacetate with methyl vinyl ketone proceeded smoothly. Both the reactions could obtain good yield after 24 h. Comparing to ethyl acetoacetate, methyl acetoacetate exhibited higher Michael addition activity. The Michael addition of acetylacetone with methyl vinyl ketone proceeded fastest. The reaction activity decreased as the following order: acetylaceone, methyl acetoacetate, ethyl acetoacetate, diethyl malonate, which was in agreement with the acidity of α-protons.

3.4. Influence of Michael acceptor structure

The structure of Michael acceptor also strongly affected the enzymatic Michael addition reaction. We examined the enzymatic Michael addition reaction of acetylacetone, ethyl acetoacetate with different Michael acceptors and the results were summarized in Table 2. The Michael addition of acetylacetone with methyl vinyl ketone proceeded smoothly and 94% isolated yield was obtained after 16 h at 50 °C (entry 1, Table 2). Comparing to methyl vinyl ketone, the reaction activity of acrolein was higher. The enzymatic Michael addition of acetylacetone with acrolein was carried out at 25 °C and the reaction could obtain 86% yield after 6 h (entries 1 and 3, Table 2). The enzymatic Michael addition of methyl acrylate was rather poor and the yield was less than 1% in 48 h (entry 4, Table 2). Thus the reaction activity decreased in the following order: acrolein, methyl vinyl ketone, methyl acrylate. This result was in agreement with their electrophilicity of Michael acceptors.

Table 2
The influence of Michael acceptor on the enzymatic Michael addition[a]

Entry	Donor	Acceptor	Time (h)	Yield[b] (%)
1			16	94
2			24	81
3[c]			6	86
4			48	1
5			24	30

[a] Reaction conditions: 1 mmol 1,3-dicarbonyl compound, 2 mmol acceptor, 10 mg enzyme in 1 ml 2-methyl-2-butanol at 50 °C for 24 h.
[b] Isolated yields.
[c] Reaction was run at 25 °C.

In order to confer versatility to this enzymatic reaction, conjugated nitroalkene was introduced as the Michael acceptor. D-aminoacylase could catalyze the Michael addition of acetylacetone and *trans*-β-nitrostyrene under the similar conditions. The yield was about 30% after 24 h under the catalysis of 10 mg D-aminoacylase (entry 5, Table 2). We then examined the ee value of the product by chiral HPLC. To our disappointment, no enantioselectivity could be observed for the above-tested reaction with the catalysis of D-aminoacylase. Similar results were reported for the enzymatic Michael addition catalyzed by CAL B [16]. The reason for this will be further investigated.

3.5. The demonstration of catalytic specificity of D-aminoacylase

In order to demonstrate that the active site of D-aminoacylase catalyzed the enzymatic Michael addition reaction, we designed and performed some control experiments and the results were shown in Table 3. The Michael addition of acetylacetone with methyl vinyl ketone was used as the model reaction. The reaction in the absence of enzyme proceeded very slowly. However, the reaction rate in the presence of D-aminoacylase improved about 40-fold (entries 1 and 2, Table 3). We also observed that initial reaction rate is almost proportional to the enzyme amount. This result indicated the catalytic effect of the D-aminoacylase (entries 2 and 3, Table 3). Acylase "Amano" from *Aspergillus oryzae*, which is also one kind of zinc-dependent

Table 3
Initial rates (V_0) of the Michael addition between acetylacetone (1 M) and methyl vinyl ketone (2 M) in different reaction conditions

Entry	Catalyst	Amount (mg)	V_0 (mM h^{-1})	V_r[a]
1	–	–	1.5	1.0
2	D-Aminoacylase	10	60.4	40.3
3	D-Aminoacylase	5	30.8	20.5
4	Acylase "Amano"	10	2.2	1.5
5	BSA	10	2.7	1.8
6	Denatured[b]	10	2.3	1.5

[a] Relative initial rate to the reaction in absence of enzyme.
[b] Pre-treated with urea at 100 °C for 6 h.

acylases, did not show any Michael addition activity (entry 4, Table 3). When the reaction was catalyzed by denatured D-aminoacylase or bovine serum albumin (BSA), both of the initial rates were almost equal to the background reaction (entries 5 and 6, Table 3). These results excluded the possibility that the surface amino acid of the protein has accelerated the reaction. These results indicated that the tertiary structure and the specific spatial conformation of D-aminoacylase were essential for the enzymatic Michael addition reaction.

4. Conclusion

We have developed a facile biotransformation path to perform Michael additions between 1,3-dicarbonyl compounds and α,β-unsaturated compounds by the catalysis of hydrolase. Solvents and enzyme resource played an essential role in the enzymatic addition reaction. The result of addition was affected by the structure of substrate and Michael acceptor. The catalytic specificity was demonstrated by some control experiments. Future work using enzyme engineering and substrate design to obtain some grade of enantioselectivity will be concerned in our lab.

Acknowledgements

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