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Efficient synthesis of vitamin E intermediate by lipase-catalyzed regioselective transesterification

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ABSTRACT

Trimethylhydroquinone-1-monoacetate (TMHQ-1-MA) is a valuable synthetic intermediate for vitamin E acetate. Immobilized Lipozyme RM IM from *Mucor miehei* was shown to be the best biocatalyst for the production of TMHQ-1-MA through regioselective transesterification between trimethylhydroquinone diacetate (TMHQ-DA) and alcohol. The effects of lipase-catalyzed reaction conditions including solvent, acyl receptor, substrate mole ratio, reaction temperature and agitation speed were investigated. The optimum conditions for Lipozyme RM IM catalyzed regioselective transesterification were achieved at a substrate mole ratio of 1:1, an agitation of 200 rpm at 50 °C in MTBE/*n*-hexane (3:7). Under the above conditions, Lipozyme RM IM exhibited high substrate tolerance (substrate concentrations of 1.06 M). Recycling experiments demonstrated that Lipozyme RM IM was quite steady under the reaction conditions. The analysis of kinetic experiment showed that the enzymatic reaction obeys the Ping–Pong bi–bi mechanism with *n*-butanol inhibition.

1. Introduction

Vitamin E (α-tocopherol), is a kind of effective chain-breaking lipid-soluble antioxidant that prevents the propagation of free radical reaction [1,2]. In addition, vitamin E has also been known as an essential nutrient for growth and reproduction with functions of maintaining normal permeability, enhancing skin blood capillary resistance, improving blood circulation and resisting aging [3]. Due to its powerful functions, vitamin E has been widely applied in forage, pharmaceutical, food and cosmetic with increasing demands [4].

The major commercial form of vitamin E is its acetate derivative. Trimethylhydroquinone-1-monoacetate (TMHQ-1-MA) is a valuable synthetic intermediate for vitamin E acetate [5]. Nowadays, industrial syntheses of (all-rac)-α-tocopherol are based on the condensation of trimethylhydroquinone (TMHQ) with isophytol, phytol or a derivative thereof, followed by acylation to the commercial form [6,7]. TMHQ is normally obtained from 2,3,6-trimethylphenol which is expensive. Alternatively, (all-rac)-α-tocopherol acetate can be synthesized by using TMHQ-1-MA as an aromatic starting material instead of TMHQ. The TMHQ-1-MA used in this alternative synthesis can be obtained from the much less expensive α-isophorone via ketoisophorone and trimethylhydroquinone diacetate (TMHQ-DA), the latter having to undergo an absolutely regioselectively converted into TMHQ-1-MA which is difficult to achieve by chemical methods. Compared with TMHQ, the condensation reaction performed by starting from TMHQ-1-MA would be advantageous, since the synthesis of tocopheryl acetate is then achieved in a direct manner, which improves atom economy and reduces reaction steps [4].

Recently, the enzymatic synthesis of vitamin E intermediate has attracted considerable interest due to its high regioselectivity, mild operating conditions, and environmentally friendly nature [8–10]. It has now been reported that TMHQ-1-MA can be prepared from TMHQ-DA by a selective enzymatic hydrolysis using a lipase such as *Thermomyces lanuginosus* lipase (TLL) and *Pseudomonas fluorescens* lipase (PFL) in water saturated solvent with high regioselectivity and conversion [4,5]. However, from an economic point of view, the bottlenecks for lipase catalytic TMHQ-1-MA production in the reported patent are the relatively low substrate concentration and its low reaction rate.

Herein our aim in this paper was to develop an efficient biocatalytic process for synthesis of TMHQ-1-MA. Lipase-catalyzed regioselective transesterification between TMHQ-DA and short chain alcohol in organic solvent was used as a model reaction (Scheme 1). Subsequently, the effect of reaction conditions including nature of biocatalyst, solvent, acyl receptor, substrate mole ratio, reaction temperature, agitation speed and substrate

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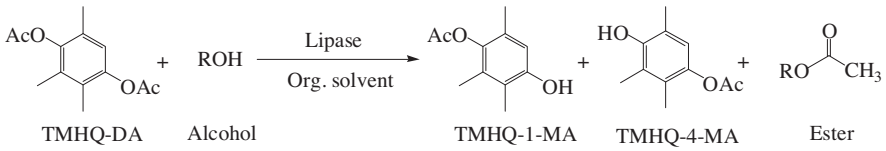


Scheme 1. General reaction of transesterification between TMHQ-DA and an alcohol.

concentration were systematically examined to deduce mechanism and kinetics. Besides, enzyme reusability was investigated.

2. Materials and methods

2.1. Enzymes

Lipozyme 435 (CAL-B, lipase B from *Candida Antarctica* immobilized on macroporous polyacrylate resin, 10,000 U/g), Lipozyme RM IM (RML, *Mucor miehei* immobilized on ionic resin, 20,000 U/g), Lipozyme TL IM (TLL, *T. lanuginosus* immobilized on silica, 50,000 U/g) were supplied by Novozymes A/S (Bagsvaerd, Denmark); Lipase PS IM (PCL, *Pseudomonas cepacia* lipase immobilized on diatomaceous earth, 30,000 U/g) was purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan); Lipase AK (PFL, *P. fluorescens* lipase, 20,000 U/g), Lipase A (ANL, *Aspergillus niger* lipase, 120,000 U/g), and Lipase AY (CRL, *Candida rugosa* lipase, 700,000 U/g) were obtained from Sigma-Aldrich (shanghai) Trading Co. Ltd. (Shanghai, China).

2.2. Chemicals

TMHQ-DA was kindly provided by Zhejiang Medicine Co. Ltd (Zhejiang, China). The other chemicals used herein were of analytical grade and purchased from local suppliers. All solvents and reactants were pretreated by 4 Å molecular sieves.

2.3. Experimental setup

2.3.1. General procedure for lipase catalyzed transesterification of TMHQ-DA

Transesterification reaction was carried out in a 50 ml capped vial by adding a certain quantities of TMHQ-DA (0.42–10.59 mmol) and alcohol (0.42–10.59 mmol) with 0.05 g lipase in 10 ml organic solvent. The reaction mixtures were shaken in the C76 water bath shaker at an agitation speed range of 100–300 rpm and a temperature range of 20–60 °C. All experiments were conducted in triplicate.

2.3.2. Purification of product

After the reaction, the immobilized enzyme was separated by filtration. The filtrate was concentrated in a rotary evaporator under reduced pressure at 95 °C for 20 min. Then, the product was precipitated by adding ethanol (approximately 10 times the volume of the residue), followed by dropwise adding deionized water at 4 °C.

2.4. Analytical methods

Analysis was done by gas chromatography (Agilent 6890N, Agilent Technology, Avondal, PA, USA) equipped with a flame ionization detector (FID) and column HP-5 (30 m × 0.32 mm × 0.25 μm, Agilent Technologies, USA). The carrier gas was nitrogen with an inlet flow of 1 ml/min and a split ratio of 1:20. The column temperature was held at 100 °C for 2 min, increased to 180 °C at 10 °C/min, and maintained for 5 min. The retention times of TMHQ-1-MA and TMHQ-DA were 12.3 and 13.6 min, respectively.

Table 1
Performance of seven commercial available lipases for the transesterification of TMHQ-DA[a].

Entry	Enzyme	Yield (%)b	1′-Regioselectivity (%)
1	Lipozyme RM IM	99.14	100
2	Lipase PS IM	35.1	100
3	Lipozyme 435	32.54	77.68
4	Lipozyme TL IM	16.36	100
5	Lipase AK	17.20	100
6	Lipase AY	0.69	100
7	Lipase A	–	–

[a]The reactions were carried out in 10 ml MTBE contained 0.424 mmol TMHQ-DA and 0.848 mmol *n*-butanol at 200 rpm and 30 °C by adding the lipases with the amount of lipase activity (100 U/ml), and the reaction was stopped at 6 h.
[b]The yields of TMHQ-1-MA were determined by GC.

3. Results and discussion

3.1. Enzyme screening

Seven commercially available lipases, including four immobilized enzymes and three enzyme powders, were evaluated for their capacity for TMHQ-1-MA production by regioselective transesterification between TMHQ-DA and short chain alcohol. Fortunately, all tested lipases displayed absolute 1′-regioselectivities towards TMHQ-DA except for Lipozyme 435. The 1′-regioselectivity of Lipozyme 435 was only 77.68%. Yang et al. reported that excellent selectivity was observed in the butanoylation of arbutin catalyzed by Novozym 435, Lipozyme TL IM or Lipase PS IM [11]. Therefore, activity was the only factor to be considered. As shown in Table 1, a general regularity that immobilized lipases showed higher activity towards TMHQ-DA than lipase powders was observed. One of the possible reasons is that native enzymes are likely to aggregate in apoloar solvent. Among these enzymes, Lipozyme RM IM exhibited highest activity (99.14%) and no activity was detected of Lipase A (ANL) during the transesterification process. Thus, Lipozyme RM IM was selected as the best biocatalyst for TMHQ-1-MA synthesis from TMHQ-DA.

3.2. Effect of solvent

As reaction medium, organic solvent has a direct effect on enzymatic activity. It has been reported that a minimum quantity of water is essential surrounding the immobilized lipase for maintaining the enzyme activity. Therefore, hydrophobic solvents are more preferred as compared to hydrophilic solvents since the latter causes striping of the essential water layer around the enzyme, which is necessary for enzyme activity [12–14]. Herein, the influence of various solvents on the enzymatic reaction was investigated. It was observed that both yield and initial rate were low in polar solvents (Log P < 2), while MTBE was an exception, solvents with Log P values in the range of 2–4 were found to be favourable for the synthesis of TMHQ-1-MA. Similar results were obtained as reported in earlier literatures that the transesterification yield was relatively high in non-polar solvents (Log P > 2) instead of in polar solvents (Log P < 2) [15,16]. *n*-Hexane having Log P value of 3.764 was found to be the best single solvent in the present study, offering the maximum yield compared with others (Table 2).

Table 2
Influence of solvents on the transesterification of TMHQ-DA[a].

Solvent	Log *P*[b]	Solubility (10^{-1} g/ml)[c]	Initial rate (10^{-1} mM/min)[d]	Yield (%)
Acetonitrile	−0.33	5.88	0.07	0.19
THF	0.47	4.27	0.14	1.00
tert-Butanol	0.58	0.56	0.64	4.19
MTBE	1.29	0.97	10.38	77.96
Dichloromethane	1.41	6.05	0.53	6.33
Toluene	2.72	2.73	12.18	79.67
Cyclohexane	3.16	0.12	11.85	78.51
Hexane	3.76	0.07	16.64	90.55
Isooctane	4.37	0.07	10.60	76.26
MTBE/hexane (3:7)	–	0.21	22.80	97.61

[a] The reactions were carried out in 10 ml of different solvents contained 0.424 mmol TMHQ-DA and 0.848 mmol *n*-butanol, 0.05 g Lipozyme RM IM at 200 rpm and 30 °C, 1 h (reaction was stopped at 1 h).
[b] Data of Log *P* at 25 °C was cited from SciFinder Scholar.
[c] Solubility of TMHQ-DA in different solvents was determined at 30 °C.
[d] Initial reaction rate was determined according to the yield of product within 10%.

In consideration of TMHQ-DA solubility, yield and solvent toxicity, subsequently, the effect of mixed solvents of MTBE and *n*-hexane on transesterification of TMHQ-DA was examined. Different volume ratios of MTBE and *n*-hexane were carried out under otherwise similar conditions, demonstrating that 3:7 of MTBE and *n*-hexane was the best choice with highest yield (97.61%) and initial rate (2.28 mM/min) for the present study. Therefore, 3:7 of MTBE and *n*-hexane was used as a solvent for further studies.

3.3. Effect of acyl receptor

Lipozyme RM IM catalyzed regioselective transesterification of TMHQ-DA was studied with different alcohols such as methanol, ethanol, *n*-propanol, 2-propanol and *n*-butanol, keeping all other parameters constant. As shown in Fig. 1, the transesterification between TMHQ-DA and *n*-butanol has the highest yield in the first 60 min. Compared with primary alcohol, the reaction yield achieved with 2-propanol had a remarkable decrease. A further study showed that the variation in yield have been associated with the change of chain length and type of alcohol during esterification and transesterification reactions catalyzed by lipase, but not caused by the denaturation effect of Lipozyme RM IM. Based on the

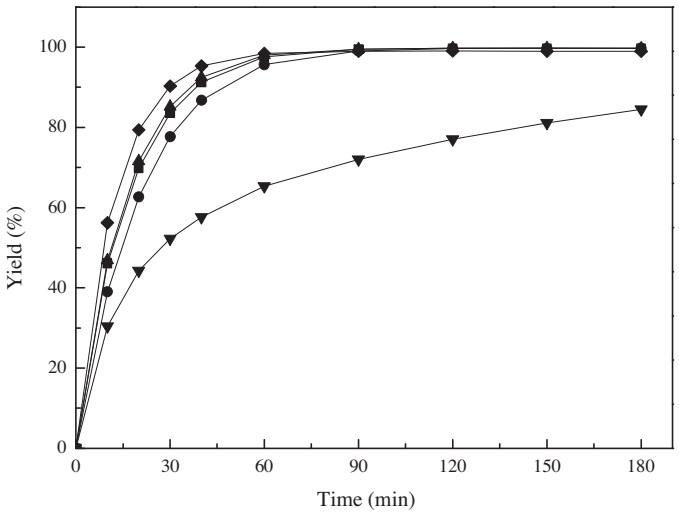


Fig. 1. Effect of different acyl receptors on transesterification of TMHQ-DA. Reaction conditions: TMHQ-DA 0.424 mmol, acyl receptor 0.848 mmol, MTBE:*n*-hexane (3:7) 10 ml, Lipozyme RM IM 0.005 g/ml, temperature 30 °C, speed of agitation 200 rpm. Symbols: methanol (■); ethanol (●); *n*-propanol (▲); 2-propanol (▼); *n*-butanol (♦).

Table 3
Effect of substrate mole ratio on transesterification of TMHQ-DA[a].

Entry	Substrate mole ratio[b]	Yield (%)
1	1:1	93.06
2	1:2	89.18
3	1:3	84.46
4	1:4	79.13

[a] The reactions were carried out in 10 ml MTBE/*n*-hexane (3:7) contained 0.424 mmol TMHQ-DA and 0.424–1.696 mmol *n*-butanol, 0.05 g Lipozyme RM IM at 200 rpm and 30 °C for 30 min.
[b] Mole ratio of TMHQ-DA to *n*-butanol.

above results, *n*-butanol was chosen as the optimum alcohol in the following work.

3.4. Effect of mole ratio of TMHQ-DA to n-butanol

TMHQ-1-MA synthesis was notably influenced by the addition of *n*-butanol. The effect of the substrate mole ratio on transesterification reaction was studied using different mole ratios of TMHQ-DA to *n*-butanol in the range of 1:1–1:4, while keeping the moles of TMHQ-DA constant. It was observed that the maximum yield and reaction rate were obtained at a mole ratio 1:1 of TMHQ-DA:*n*-butanol (Table 3). By further increasing substrate mole ratio from 1:2 to 1:4, a decrease in yield and reaction rate was followed. This could be attributed to the inhibitory effect of *n*-butanol on the Lipozyme RM IM. The enzyme is hydrophobic in nature and *n*-butanol contains the hydrophobic tail and polar head. There may be a hydrophobic–hydrophobic interaction between the enzyme and *n*-butanol. This interaction increases the residence time of *n*-butanol with enzyme which would lead to partial dehydration which may destabilize the native conformation of enzyme leading to inhibitory effect caused by *n*-butanol [17]. Therefore, it can be concluded that *n*-butanol at high concentration interacts with enzyme to form dead-end inhibitory complex. A molar ratio of 1:1 was considered as the optimum substrate ratio.

3.5. Effect of temperature

The reaction temperature is an important parameter that affects enzyme-catalyzed reactions. Herein, the influence of reaction temperature on transesterification reaction was investigated in the range of 20–60 °C. In general, an elevated temperature within a certain range could accelerate initial reaction rate and improve yield. Conversely, the treatment at high temperature may disrupt enzyme tertiary structure, making it inactivation. Similar results were achieved in the present study (Fig. 2). The initial rate increased proportionally from 2.381 to 4.254 mM/min in the range of 20–50 °C. However, with further increase of temperature to 60 °C, only a slight enhance of initial rate and yield were observed. In consideration of the volatility of solvent (Boiling point of MTBE: 55.2 °C) and enzyme stability, thus 50 °C was selected in the following work.

3.6. Effect of agitation speed

Agitation speed influenced diffusion and partition of substrate and product in reaction system. The effect of agitation speed on Lipozyme RM IM catalyzed transesterification of TMHQ-DA was studied in the range of 100–300 rpm (figure not shown). An increase in agitation speed from 100 to 200 rpm resulted in a remarkable increase in reaction rate due to the decrease of mass transfer resistance. However, there was no significant change in reaction rate up to 200 rpm. This can be attributed to the cause that a certain amount of catalyst particles were thrown out of the liquid phase on the reactor wall above 200 rpm. Therefore, an agitation speed of 200 rpm was chosen.

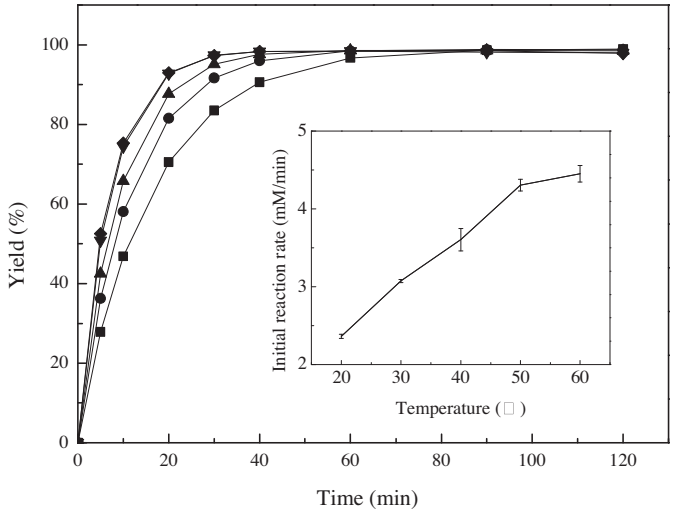


Fig. 2. Effect of temperature on transesterification of TMHQ-DA and initial reaction rate. Reaction conditions: TMHQ-DA 0.424 mmol, *n*-butanol 0.424 mmol, MTBE:*n*-hexane (3:7) 10 ml, Lipozyme RM IM 0.005 g/ml, speed of agitation 200 rpm. Symbols: 20 °C (■); 30 °C (●); 40 °C (▲); 50 °C (▼); 60 °C (♦).

3.7. Effect of substrate concentration

A high substrate concentration would be beneficial for the practical application of a biocatalytic process because it could improve the space-time yield and reduce the cost of product isolation to a large extent [18]. Therefore, it was of significance to optimize the substrate concentration to maximize the value of the certain enzyme. Herein, the effect of substrate concentration on yield as well as initial reaction rate was investigated at a fixed amount of enzyme (0.005 g/ml). As shown in Fig. 3, the product formation was significantly increased from 41.2 mM to 1.02 M when substrate concentration was raised from 42.4 mM to 1.06 M after 12 h. Moreover, the initial reaction rate increased proportionally to substrate concentration in the range of 42.4–211.9 mM. By further increasing

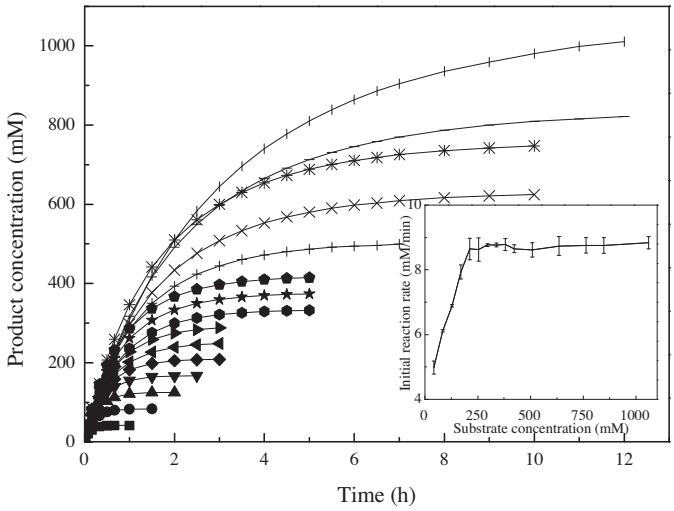


Fig. 3. Effect of substrate concentration on transesterification of TMHQ-DA. Reaction conditions: TMHQ-DA:*n*-butanol (1:1), MTBE:*n*-hexane (3:7) 10 ml, Lipozyme RM IM 0.005 g/ml, temperature 50 °C, speed of agitation 200 rpm. Symbols: 42.4 mM (■); 84.7 mM (●); 127.1 mM (▲); 169.5 mM (▼); 211.9 mM (♦); 254.2 mM (◄); 296.6 mM (►); 339.0 mM (⬟); 381.4 mM (★); 423.7 mM (⬟); 508.5 mM (+); 635.6 mM (×); 762.7 mM (*); 847.5 mM (—); 1059.3 mM (|).

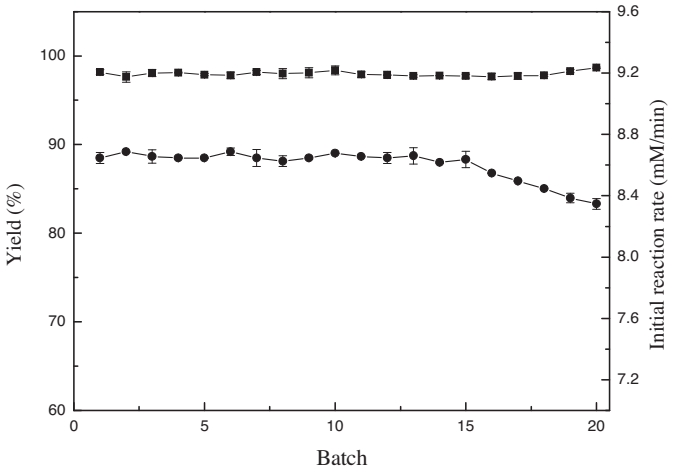


Fig. 4. Effect of reusability of biocatalyst on transesterification of TMHQ-DA. Reaction conditions: TMHQ-DA 2.12 mmol, *n*-butanol 2.12 mmol, MTBE:*n*-hexane (3:7) 10 ml, Lipozyme RM IM 0.005 g/ml, temperature 50 °C, speed of agitation 200 rpm, reaction time 3 h. Symbols: yield (■); initial reaction rate (●).

substrate loading, no drop of initial rate was observed, thus indicating that Lipozyme RM IM was tolerant against high concentrations of both substrate and product.

3.8. Reusability of the enzyme

The reusability of enzyme is another essential factor to reduce cost for industrial production. Catalyst reusability studies were carried out to evaluate the stability of Lipozyme RM IM under the optimum reaction conditions. To evaluate the reusability of biocatalyst, Lipozyme RM IM was isolated from organic solvent after each reaction by filtration and washed with *n*-hexane for twice, then reused. As shown in Fig. 4, the yield of product was remaining after 20 cycles of reuse. And the initial reaction rate was not decrease until the 15th repeating circle. The result suggested that Lipozyme RM IM was quite stable in present system and had great potential for practical application for TMHQ-1-MA production.

3.9. Kinetic study

To analysis the reaction mechanism of Lipozyme RM IM catalyzed transesterification between TMHQ-DA and *n*-butanol, the effect of concentration of both substrates (TMHQ-DA and *n*-butanol) on initial reaction rate was investigated under earlier optimized parameters. The Lineweaver–Burk plots of reciprocal rate versus reciprocal concentration of TMHQ-DA (A) were illustrated in Fig. 5. When *n*-butanol (B) was at low concentrations (25–55 mM), the initial reaction rate increased with the increase of the concentration of *n*-butanol and reached the maximum at 55 mM. Therefore, it can be concluded that no inhibition by *n*-butanol in the range of 25–55 mM. As expected, there was no evidence of inhibition by TMHQ-DA at any concentration tested which agreed with the former conclusion. A series of parallel lines without common intersection given in Fig. 5 demonstrated that the transesterification of TMHQ-DA and *n*-butanol was corresponding with Ping–Pong bi–bi mechanism [10,19–23]. However, further increase in *n*-butanol concentration (above 55 mM) resulted in the initial reaction rate to fall and the slops of Lineweaver–Burk double inversion plot to rise (data not shown), which implied that *n*-butanol at higher concentration reacted with the enzyme to form dead end inhibitory complex. Hence, a sequential mechanism called Ping–Pong bi–bi mechanism with *n*-butanol inhibition was ruled out.

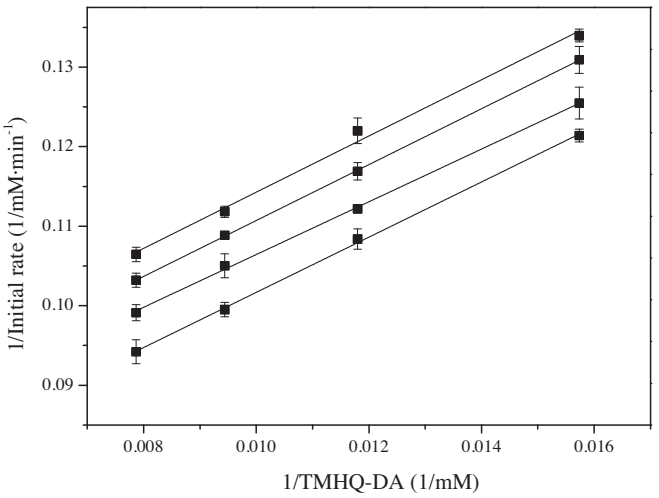
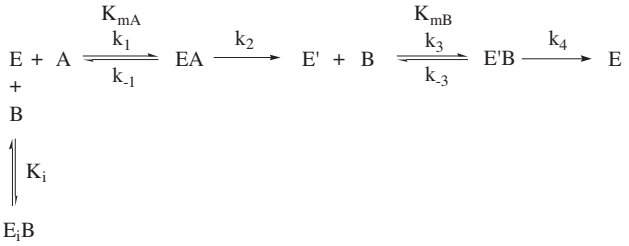


Fig. 5. Lineweaver–Burk double inversion plot for different concentrations of *n*-butanol. Reaction conditions: MTBE: *n*-hexane (3:7) 10 ml, Lipozyme RM IM 0.005 g/ml, temperature 50 °C, speed of agitation 200 rpm. Symbols: 55 mM (■); 45 mM (●); 35 mM (▲); 25 mM (▼).



Scheme 2. Ping–Pong bi–bi mechanism with single substrate inhibition.

By analogy to the classical Ping–Pong bi–bi mechanism with alcohol inhibition by lipase catalyzed transesterification (Scheme 2), it is assumed that TMHQ-DA [A] first binds to the free enzyme [E] and forms a noncovalent enzyme-substrate complex [EA], which releases the first product and modified enzyme [E′]. The second substrate, *n*-butanol [B], reacts with E′ to give the complex E′B and gives the product and free enzyme [E]. Along with this, B also forms the dead-end complex [E_iB] by binding to the free enzyme [E]. The rate equation for the Ping–Pong bi–bi mechanism with alcohol inhibitory is as follows:

$$v = \frac{v_m[A][B]}{K_{mB}[A] + K_{mA}[B](1 + [B]/K_i) + [A][B]}$$

where K_{mA} is the Michaelis constant for TMHQ-DA, K_{mB} is the Michaelis constant for *n*-butanol, and K_i is the inhibition constant due to *n*-butanol. v and v_m are the initial reaction rate and maximum reaction rate, respectively.

To verify the application of Ping–Pong bi–bi mechanism, the same data were analyzed by non-linear regression using the Software Package Polymath 6.0. The kinetic parameters determined by Polymath 6.0 were given in Table 4, which showed excellent correlation coefficient (data not shown). This suggests that the proposed model for Lipozyme RM IM catalyzed transesterification of TMHQ-DA and *n*-butanol is valid.

Table 4
Values of the kinetic parameter for Ping–Pong bi–bi mechanism with *n*-butanol inhibition.

Kinetic parameter	Value
Apparent v_m (mM/min)	17.23
Apparent K_{mA} (mM)	59.79
Apparent K_{mB} (mM)	9.82
Apparent K_i (mM)	90.60

4. Conclusion

A new biocatalytic process for the production of TMHQ-1-MA has been developed. The optimum conditions for Lipozyme RM IM catalyzed regioselective transesterification between TMHQ-DA and *n*-butanol were achieved at a substrate mole ratio of 1:1, an agitation of 200 rpm at 50 °C in MTBE/*n*-hexane (3:7). Under the above conditions, the substrate loading was increased as high as 1.06 M with 99% yield. Furthermore, it was demonstrated that Lipozyme RM IM was active after 20 cylces. Meanwhile, based on the initial rate data and concentration profiles, a kinetic model called Ping–Pong bi–bi mechanism with *n*-butanol inhibition was proposed. The kinetic parameters were evaluated by using non-linear regression analysis with excellent correlation coefficient.

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