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Optimised Dynamic Kinetic Resolution of benzoin by a chemoenzymatic approach in 2-MeTHF

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ABSTRACT

Different influential parameters in the Dynamic Kinetic Resolution of racemic benzoin via lipase–ruthenium catalyst enantioselective transesterification have been improved in order to develop a more productive process. In this sense, 2-Methyltetrahydrofuran (2-MeTHF) is proposed as an excellent and greener substitute of THF for this biotransformation; on the other hand, by scaling up the reaction, much better results were obtained by using a much simpler one-pot methodology (compared to the previously described three-steps protocol), resulting not only in higher amounts of enantiopure product (85% conversion, >99% ee of the product), but also in an enhanced sustainability of the process, because lower acyl donor concentrations and lower ruthenium catalyst amounts (protected from oxygen deactivation) are required.

1. Introduction

Optically pure α-hydroxyketones are considered valuable building blocks for the fine chemical industry as well as pharmaceuticals. This acyloin intermediate is included in the synthesis of different natural products and biologically active compounds [1]. In virtue of the increasing interest towards these molecules, different strategies have been developed for obtaining α-hydroxyketones in an enantioselective manner. Although several attempts have been carried out by using asymmetric synthesis [1], biocatalysis is a real alternative, because more sustainable processes can be implemented [2,3]: in fact, the employment of enzymes and microorganisms as catalysts generally means a decrease in the number of reaction steps and in the waste production, as well as milder reaction conditions, resulting in more environmentally and economically attractive processes [4,5]. In this sense, chiral α-hydroxyketones can be efficiently prepared by different biocatalytic approaches, such as aldehydes carboligation catalysed by thiamine-diphosphate dependent lyases [6–8], stereoselective reduction of α-dicarbonyl compounds [9–11] or the Dynamic Kinetic Resolution (DKR) of racemic mixtures [12,13].

Kinetic Resolution (KR) of racemic mixtures has been shown to be the methodology of choice for the synthesis of many chiral secondary alcohols (including α-hydroxyketones [14–16]), particularly by using lipases as catalysts [17,18]. However, an important drawback of KR can limit its applicability, as just a maximum theoretical yield of 50% could be reached. This limitation can be overcome by the racemisation *in situ* of the remaining substrate in a Dynamic Kinetic Resolution (DKR) process, which allows the achievement of a theoretical 100% yield. A large number of protocols depict the synthesis of optically active alcohols by the combination of a lipase-catalysed enantioselective transesterification and an *in situ* racemisation of the unreacted enantiomer mediated by a transition metal catalyst [19–21]. Although the use of this last strategy is nowadays widespread, just few examples can be found describing a large-scale process for an ulterior industrial implementation [22,23].

As a part of our ongoing research about the enantioselective preparation of benzoins (1,2-diaryl-2-hydroxyethanone structures), we have previously reported an efficient DKR process of this type of α-hydroxyketones [13] by the combined action of lipase from *Pseudomonas stutzeri* and a ruthenium catalyst (Shvoĭs catalyst) in THF; later on, the productivity of the process was enhanced by lipase immobilization [24]. Although high conversions and excellent enantiomeric purity had been reached, reaction parameters should be modified and optimised in order to prepare a further scaling up of the process. Several factors may be considered in order to develop, not only a greener procedure by a biocatalytic strategy, but also a more economic process by the enlargement of the productivity, which also contributes to the sustainability of the system [19,25].

In this work we present the optimisation of the different parameters involved in the DKR process of benzoin obtaining promising results for further scale-up. Furthermore, it is proposed the

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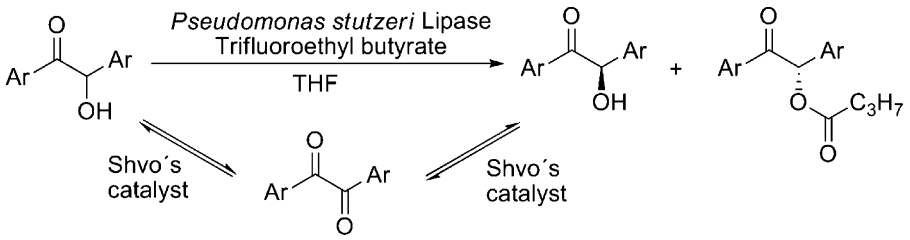


Scheme 1. DKR process of benzoins (1,2-diaryl-2-hydroxyethanones) catalysed by lipase from *Pseudomonas stutzeri* and Shvoĭs catalyst.

substitution of THF by 2-Methyltetrahydrofuran (2-MeTHF), considered a more environmentally friendly solvent [26,27].

2. Experimental

2.1. Materials and methods

Lipase (Triacylglycerol lipase EC 3.1.1.3) from *P. stutzeri* (Lipase TL®, Lot TH3401, 52% of protein content, Bradford methodology as previously reported [24]) was purchased from Meito & Sangyo Co. Ltd., Nagoya, Japan (see http://www5.mediagalaxy.co.jp/meito/kaseihin/index_e.html for details); Shvoĭs catalyst (1-hydroxytetraphenylcyclopentadienyl (tetraphenyl-2,4-cyclopentadien-1-one)-μ-hydrotetracarbonyldiruthenium (II) was obtained from Strem Chemicals Inc.; 2-MeTHF and other common reagents were obtained from Sigma–Aldrich.

HPLC analyses were performed with a chiral column Chiralcel® OD-H at room temperature; mobile phase *n*-hexane/2-propanol 90/10, at a flow rate of 1 mL/min.

NMR spectra were recorded on a Bruker AC-250. Chemical shifts (δ) are reported in parts per million (ppm) relative to $CHCl_3$ (^{1}H: δ 7.27 ppm) and $CDCl_3$ (^{13}C: δ 77.0 ppm).

2.2. General procedure for the Kinetic Resolution of benzoin

Different amounts of (*R,S*)-1 (20 mg, 94 μmol in the standard protocol) were dissolved in 1 mL of freshly distilled 2-MeTHF (or THF): subsequently, Lipase TL® (20 mg of the commercial preparation) and a certain amount of VB (vinyl butyrate, 71.6 μL, 564 μmol, in the standard conditions, molar excess 6:1) were added. The mixture was stirred at room temperature (20–25 °C). At fixed reaction times, samples (20 μL) were taken from the reaction medium, redissolved in 1 mL of *n*-hexane, and filtered through Millex®-GV (PVDF, 0.22 μm pore size) to stop the enzymatic reaction. As THF or MeTHF (polar solvents) may damage the chiral column (Chiralcel OD-H®), each sample was evaporated under vacuum and the solid collected was re-solved in 1 mL of *n*-hexane/2-propanol (50:50, v/v) before analyzing by HPLC to measure conversion and enantiomeric excess values.

2.3. General procedure for the 10 mL-Dynamic Kinetic Resolution of benzoin

Shvoĭs catalyst (13.5 mg, 0.0125 mmol; 0.5 mol %), Lipase TL® (150 mg) and (*R,S*)-1 (530 mg, 2.5 mmol) were added to a 25 mL flask. Anhydrous 2-MeTHF was incorporated and the reaction was started by the addition of trifluoroethyl butyrate (1.132 μL, 7.5 mmol). The mixture was stirred at 55 °C under Argon atmosphere. After 24 h, 50 mg of fresh lipase were added. Conversion and enantiomeric excess were determined by HPLC analysis, following a similar protocol to that described in the previous section. Product ((*S*)-2) was purified by silica column chromatography (*n*-hexane/ethyl acetate, 5/1) yielding a colorless oil (80% isolated yield). $[\alpha]^{20}_D$: +154.2 (*c* 4 $CHCl_3$). Spectroscopic data of (*S*)-2 are in accordance with those previously reported [13].

3. Results and discussion

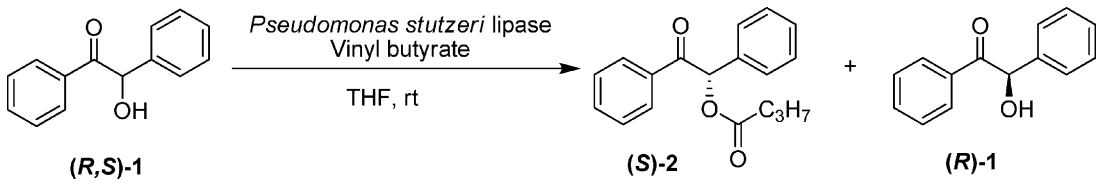
As it has been commented above, in our research group we have previously described the lipase from *P. stutzeri* (Lipase TL®) and the Shvoĭs catalyst as the most convenient catalysts for the DKR of benzoins (Scheme 1) [13].

The main requirement for a successful scalable DKR is the previous optimisation of the KR process and its successful combination with the *in situ* racemisation of the substrate.

Based on the work of Aoyagi and co-workers [16], Lipase TL® was identified as the best biocatalyst for benzoin resolution, and reaction conditions were improved, reaching maximum conversions and enantiomeric excess after 1 h in THF at 50 °C. This temperature was necessary for a posterior DKR reaction, in which Shvoĭs catalyst, which is completely compatible with the lipase, was able to racemise the unreacted substrate. With all these data, a further improvement is required as a previous step for a potential scaling up of the process: substrate concentration should be increased and the loading of acyl donor, enzyme and Shvoĭs catalyst should be reduced, for obvious productivity reasons. In this sense, the previously described protocol was employed as starting point for optimising the process, and KR of benzoin was chosen as standard reaction in order to find optimum conditions before the coupling with the ruthenium catalyst (Scheme 2). At this level, all test assays were performed in 1 mL volume at room temperature (typically, 20–25 °C), varying the different reaction parameters.

3.1. Effect of the solvent

2-MeTHF is a commercial solvent obtained from renewable sources and it has emerged as a greener substitute of traditional THF, suitable in different synthetic procedures [26,28,29] and gradually being introduced in the biocatalysis field [27,30]. Although lipases commonly present high activity in low polarity organic solvents, lipase from *P. stutzeri* has showed an excellent behav-



Scheme 2. Benzoin Kinetic Resolution catalysed by lipase from *Pseudomonas stutzeri*.

Table 1
Kinetic Resolution (KR) of benzoin catalysed by Lipase TL® in 2-MeTHF and THF.

Run	Solvent (1 mL)	Lipase (mg)	(*R*,*S*)-1 (mg)	VB (equiv.)	Conv[a]. (3 h) (%)	ee_p (%)	*E*[b]	V_o (μmol min^{-1})
1	THF	20	20	6	39	>99	>200	0.52
2	2-MeTHF	20	20	6	49	>99	>200	0.76

[a] Calculated based on the percentage of product appearance.
[b] Enantiomeric ratio.

ior in THF [13,24]. Physical properties of 2-MeTHF prompted us to carry out the benzoin resolution reaction in this solvent. Results are compared with those obtained by the use of THF in Table 1. As recently stated by Gardossi et al. [31], when describing a biocatalysed synthesis, reporting a value of conversion, yield or product concentration at a single timepoint is useful (reaction time must always be stated), although the progress curve has to be taken into account for monitoring the overall the process. Thus, in Fig. 1 the progression of both reactions at room temperature (20–25 °C) is represented.

It is worth mentioning that not only the sustainability of the biocatalytic reaction was increased but also the lipase activity was enhanced by the use of 2-MeTHF. Under the same reaction conditions, the initial rate (of the process in 2-MeTHF was almost 1.5-fold increased, and maximum conversion of a kinetic resolution (50%) was achieved just in 3 h, while it was needed al least 4 h to reach same conversion in THF. On the other hand, excellent enantioselectivity was maintained, without detecting any trace of the acylation of the *R* enantiomer of the substrate. Taking these results into account, 2-MeTHF was the solvent of choice to develop lipase-catalysed benzoin resolution.

3.2. Effect of acyl donor concentration

In previous studies vinyl butyrate was selected as the best acyl donor for benzoin ((*R*,*S*)-1) KR [13]. Thus, starting from the standard conditions (entry 3, Table 2, molar ratio acyl donor/substrate = 6/1) the effect of the acyl donor concentration was studied; while substrate concentration and lipase amount were held constant in 1 mL of 2-MeTHF, different amounts of vinyl butyrate were added, always in molar excess, due to the fact that an excess of acyl donor is needed for shifting the equilibrium towards the desired product [32,33]. Following the units recommended by Gardossi et al. [31], the values of initial rate V_0 (expressed as μmol of product obtained per minute), the maximum conversion (monitoring product appearance) and the productivity (μmoles of (*S*)-2 obtained by mg of commercial lipase per minute) were determined on each case and summarised in Table 2.

As can be seen in Table 2, it was necessary to add at least 3 equivalents of VB to obtain good conversions, although a great excess of this reagent was not required, as can be seen from the fact that better results were not obtained by adding more than 6 equivalents of VB. Although it is assumed that an excess of the acyl donor is needed for shifting the equilibrium towards the desired products [32,33], in fact this excess has to be controlled in order just to reduce waste and simplify product purification. In any case, the enantioselectivity of the lipase biocatalyst remained exquisite regardless the excess of acyl donor used, as shown in Table 2, always leading to *E* values higher than 200.

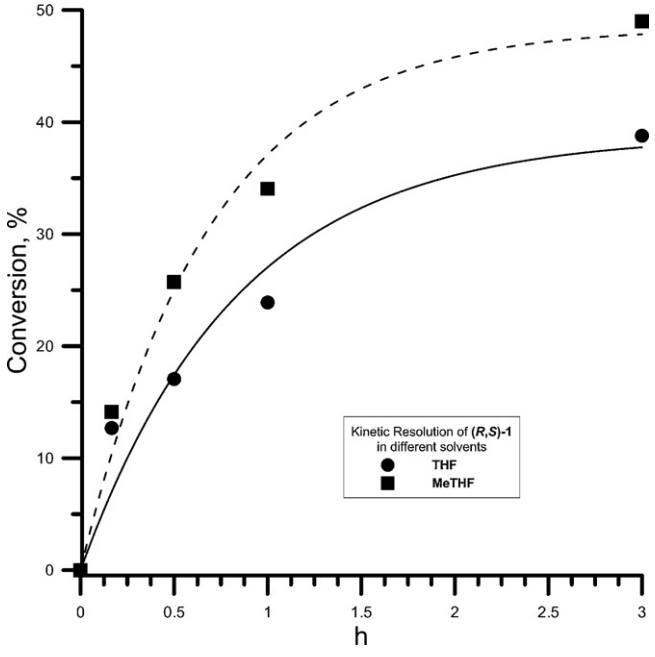


Fig. 1. Comparison of the benzoin KR progress catalysed by Lipase TL® in 2-MeTHF and THF at room temperature.

3.3. Effect of substrate concentration

With the aim of developing a more economically attractive procedure, the effect of substrate concentration over lipase activity was investigated. Acyl donor concentration was maintained constant and increasing substrate concentrations were employed. Thus, different relations substrate-acyl donor were studied, which would allow us to determine best reaction parameters. Results obtained working in 2-MeTHF are shown in Fig. 2, while the data derived from those curves are shown in Table 3 (entry 3 corresponds again to the initial conditions). Parallel experiments were performed in THF to confirm the suitability of its substitution in this biocatalytic process.

The comparison of the initial rates and productivity values measured in both solvents confirms the choice of 2-MeTHF as a better medium for developing the resolution of this α-hydroxyketone catalysed by Lipase TL®. In fact, when using 2-MeTHF not only the initial rate was higher than the rate measured in THF, but also the reaction time needed to obtain the optimal KR was reduced, which is directly related to a productivity increase.

As shown in Fig. 2, substrate concentration can be raised without a great increase of the reaction time needed to reach conversion values close to 50%. Taking into account the results shown in Table 3, in the case of benzoin concentrations higher than 280 mM, longer times were needed to render maximum conversion, but excellent enantioselectivity was maintained in all cases.

As can be observed, the productivity of this biotransformation is definitively enhanced, as the biocatalyst is able to carry out the acylation of amounts of substrate considerably higher than those previously described [13]. Not only 2-MeTHF was contributing to perform a greener process, but also the decrease on acyl donor loading and the substrate concentration raise collaborate in a reduction of the waste of the biotransformation, then decreasing the E(nvironmental) factor (kg waste per kg product) of the process [4,34,35].

Table 2
KR of benzoin employing different amounts of acyl donor and 2-MeTHF as solvent.

Entry	(*R,S*)-1 (mg)	Lipase (mg)	VB (equiv.)	V_0[a] (μmol min^{-1})	Conv. (%)	ee$_p$ (%)	*E*[b]	Productivity × 10^3 (μmol min^{-1} mg^{-1} lipase)[c]
1	20	20	1.5	0.73	23	>99	>200	4.8
2	20	20	3	0.75	49	>99	>200	5.7
3	20	20	6	0.76	>49	>99	>200	6.4
4	20	20	9	0.86	>49	>99	>200	6.8
5	20	20	12	0.86	>49	>99	>200	6.7

[a] Experimental error 5%.
[b] Enantiomeric ratio.
[c] Calculated at reaction times for maximum conversion in each case.

Table 3
Kinetic Resolution of different concentrations of benzoin in 1 mL of 2-MeTHF, catalysed by lipase from *Pseudomonas stutzeri*.

Entry	(*R,S*)-1 mg (mM)	Lipase (mg)	VB (equiv.)	V_0[a] (μmol min^{-1})	Conv. (%)	ee$_p$ (%)	*E*[b]	Productivity × 10^3 (μmol min^{-1} mg^{-1} lipase)[c]
1	5(24)	20	24	0.27 (0.17)[d]	>49	>99	>200	2.4 (1.6)[d]
2	10(47)	20	12	0.43 (0.32)[d]	>49	>99	>200	3.5 (2.6)[d]
3	20(94)	20	6	0.76 (0.52)[d]	>49	>99	>200	5.1 (3.8)[d]
4	30(141)	20	4	0.80 (0.61)[d]	>49	>99	>200	5.5 (4.2)
5	40(188.5)	20	3	1.00 (0.80)[d]	>49	>99	>200	6.6 (5.4)[d]
6	60(283)	20	2	1.34	>49	>99	>200	8.4
7	90(424)	20	1.3	2.26	47	>99	>200	13.6
8	110(518)	20	1.1	3.32	44	>99	>200	19.7
9	130(612)	20	0.9	4.08	42	>99	>200	23.8

[a] Experimental error 5%.
[b] Enantiomeric ratio.
[c] Calculated at the reaction time required for the maximum conversion quantified (ranging from 3 to 14 h).
[d] Calculated values in THF.

3.4. Dynamic Kinetic Resolution

As it was described above, lipase-catalysed KR can be coupled with a racemisation system, which allows the achievement of a theoretical conversion of 100%, in order to obtain a commercially viable process.

In this context, with the idea of optimising the synthesis of enantiomerically pure benzoin through a biocatalytic process, we investigated the combination of the optimised KR procedure with the racemisation of the unreacted enantiomer mediated by the Shvoĭs catalyst. 2-MeTHF had been chosen as a better solvent for the transesterification reaction, but it must be also compatible with the ruthenium catalyst. To check the viability of this method, the racemisation of (*R*)-1 in the presence of the Shvoĭs catalyst in 2-MeTHF at 55 °C under argon atmosphere was tested. The higher boiling point of 2-MeTHF than THF allowed the increase of the temperature from 50 to 55 °C, which would be more convenient for the catalyst activation. In fact, starting from pure (*R*)-1, racemic (*R,S*)-1 was obtained in 1 h; a small amount of the dicarbonyl compound (benzyl, intermediate of the redox-racemisation) was also identified.

Before studying the scaling up to higher volume processes, the DKR of (*R,S*)-1 in 1 mL of 2-MeTHF was tested, coupling the action of Lipase TL® and Shvoĭs catalyst. As it is well known, the use of vinyl esters as acyl donors for the transesterification reaction can interfere with the activity of the racemisation catalyst [36]. Therefore, as the suitability of trifluoroethyl butyrate was already proved [13], it was chosen as acyl donor. In a first attempt, a low

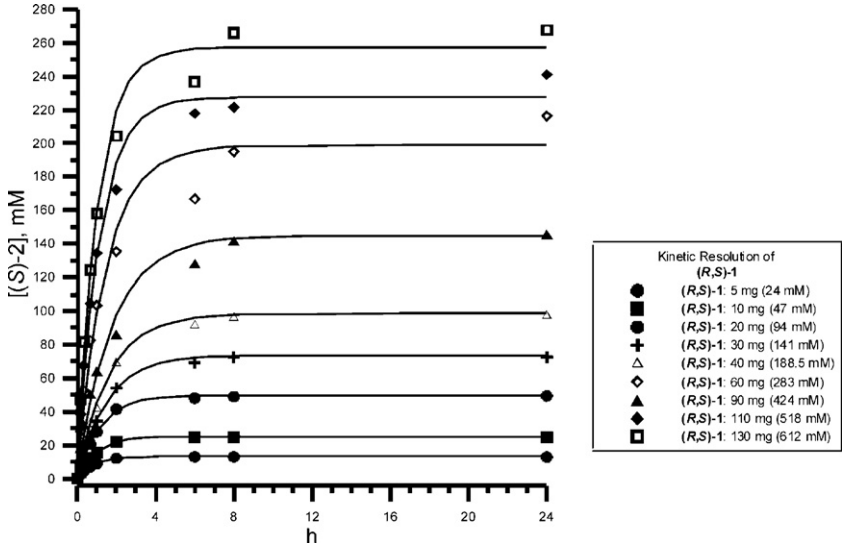


Fig. 2. Kinetic Resolution progress of different 1 mL assays starting from increasing substrate concentrations.

substrate concentration was employed (94 mM) in 1 mL of 2-MeTHF, and lipase (20 mg), ruthenium catalyst (5% mol) and trifluoroethyl butyrate (3 equiv.) were added and stirred at 55 °C under argon atmosphere. After 24 h 70% conversion was reached. Although all substrate had been converted, a great amount of the residual dicarbonyl compound had been accumulated in the medium. We had already described how this lipase shows a gradual deactivation over 50 °C [13], but also the organometallic catalyst had become deactivated during the process.

Bogár et al. had previously pointed out that the decomposition of the ruthenium catalyst in DKR processes, caused by the presence of traces of molecular oxygen, may be avoided by running the reaction on larger scales, which also allowed the decrease in the catalyst loading [23]. Following this idea, the DKR of (*R*,*S*)-1 was carried out increasing the reaction volume up to 10 mL of 2-MeTHF, with the aim of minimizing the deactivation of the catalyst and reducing the catalyst loading. In our previously reported protocol [13], lipase loading was carried out in three steps in order to avoid the reduction of its activity, so we decided to follow a similar procedure. Optimised KR in 2-MeTHF parameters were applied, increasing substrate concentration and lowering the amount of acyl donor. Therefore, the 10 mL scale was run as described in Section 2.3. After 24 h, 75% of product was detected, as well as some traces of the dicarbonyl product. At that step, the rest of the lipase (50 mg) was added and the reaction was stirred for 24 h more at 55 °C, finding a final conversion of 85% and enantiomeric excess higher than 99%.

Effectively, just the scale up from 1 mL to 10 mL allowed a decrease on the ruthenium catalyst loading from 5% mol to 0.5% mol, and no deactivation was observed during the first 24 h. Furthermore, apart from raising substrate concentration and decreasing the acyl donor loading, a more effective DKR process has been developed just in one-pot, avoiding the three steps of the previously described methodology [13].

4. Conclusions

In this article different parameters for the optimisation of the DKR process of benzoin were investigated. It has been found that the replacement of THF by 2-MeTHF allows not only a more sustainable process but also a more effective and productive reaction. Substrate loading was increased and acyl donor and Shvoĭs catalyst were employed in very highly reduced quantities, yielding enantiomeric pure (*S*)-benzoin in short reaction time in one step.

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