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Kinetic resolution of mandelate esters via stereoselective acylation catalyzed by lipase PS-30

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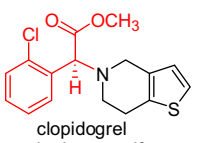
ABSTRACT

By using lipase PS-30 as catalyst, the kinetic resolution of a series of racemic mandelate esters has been achieved via stereoselective acylation. The value of kinetic enantiomeric ratio (*E*) reached up to 197.5. Substituent effect is briefly discussed.

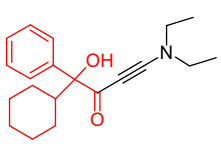
Enantiopure mandelate esters are one kind of the most versatile synthetic materials as they bear a hydroxyl group and a carbonyl group on one chiral carbon.[1,2] They provide a wide space for transformation into a large number of chiral molecules, especially in a wide range of pharmaceuticals and agrochemicals, such as oxybutynin, clopidogrel, and cefadole.[3–7] Mandelic acid is also used as a chiral resolving agent.[8–10] Formation of these chiral building blocks or their analogues can roughly be divided into three major categories: (1) kinetic resolution (KR) or dynamic kinetic resolution (DKR) of the racemic substrates promoted by enzymatic and/or metallic catalysts (the best *E* value was up to 1892);[11–29] (2) enantioselective reduction of the keto group of keto acid esters by chiral boranes[30–32] with the help of chiral auxiliaries,[33–35] by chiral metal catalysts, [36–49]NADH[50–52] or bio-catalysts;[53–60] and (3) Alpha-carbon oxidative hydroxylation of phenyl acetates.[61–64]

In the bio-catalyzed KR, a mandelate ester racemate is treated by an acylating reagent in the presence of a lipase or an esterase to stereoselectively obtain an acylated enantiomer and an unreacted enantiomer,[64–66] or alternatively, an acylated mandelate ester racemate is stereoselectively hydrolyzed in the presence of a lipase or an esterase to give a hydrolyzed enantiomer and an unreacted enantiomer.[65,67–70] In ideal case, both of the enantiomers can be obtained simultaneously in high enantiopurity with a yield close to 50%, which is usually not good for final product but might be good in the case where both of the resolved enantiomers are useful as starting material in synthesis.

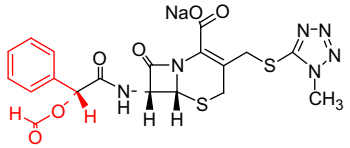
Following our previous investigation in the kinetic resolution of cyanohydrins, allylic alcohol, and propargylic alcohols catalyzed by lipases,[71–74] in this Letter, we wish to report our study on kinetic resolution of racemic mandelate esters.



clopidogrel hydrogensulfate



oxybutynin



cefadole

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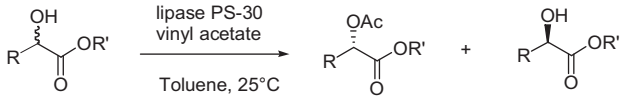
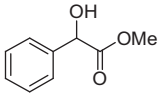
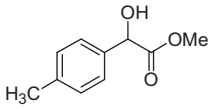
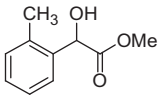
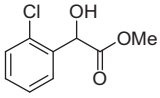
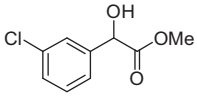
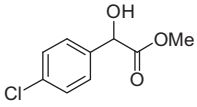
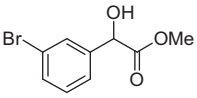
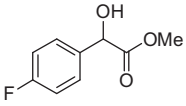
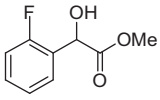
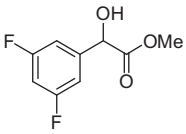
Table 1
Stereoselective acetylation of methyl mandelates **1a–q** with vinyl acetate catalyzed by lipase PS-30

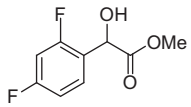
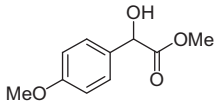
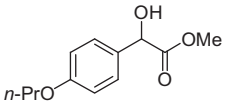
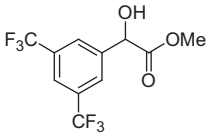
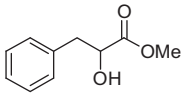
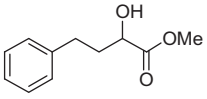
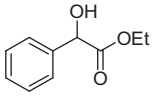


Rac-**1a~q** **2a~q**

Entry	Substrate	Ee_P[a] %	Ee_S[b] %	*E*[c]	C[d] %	C[e] HPLC %	Reaction time (day)
1	 **1a**	90.1	90.0	59.0	41	50	6
2	 **1b**	93.4	89.8	89.9	42	49.0	6
3	 **1c**	16.5	11.0	1.5	20	40.0	7
4	 **1d**	93.1	18.2	33.5	34	16.4	6
5	 **1e**	92.3	39.5	36.8	35	30.0	7
6	 **1f**	93.8	99.6	192.5	47	51.5	6
7	 **1g**	94.5	65.8	70.1	40	41.0	5
8	 **1h**	96.1	70.8	106.9	42	42.4	5
9	 **1i**	/	/	/	/	/	/
10	 **1j**	97.1	84.7	184.1	47	46.6	7

(*continued on next page*)

Table 1 (*continued*)

Entry	Substrate	Ee_P[a] %	Ee_S[b] %	E[c]	C[d] %	C[e] HPLC %	Reaction time (day)
11	 **1k**	/	/	/	/	/	/
12	 **1l**	97.1	34.2	95.0	42	74.0	6
13	 **1m**	63.6	93.7	15.0	37	59.6	5
14	 **1n**	96.0	2.5	50.2	39	2.5	5
15	 **1o**	93.8	39.2	57.8	40	70.5	4
16	 **1p**	96.4	94.3	197.5	45	49.4	5
17	 **1q**	92.7	6.1	28.0	39	6.2	7

[a] $ee_{(P)}$ stands for enantiomeric excess of methyl mandelate of the fast reacting enantiomer of the methyl mandelate. Analysis was performed on Chiralcel OJ-H or OD-H column with hexane/iPrOH in varying ratios to afford ee values.

[b] $ee_{(S)}$ stands for enantiomeric excess of the slow reacting enantiomer of the methyl mandelate which was obtained after the methyl mandelate was converted into the corresponding acetate then subjected to chiral HPLC analysis on Chiralcel OD-H column with hexane/*i*-PrOH in varying ratios.

[c] $E = \ln[(1 - C_{HPLC})(1 - ee_S)]/\ln[(1 - C_{HPLC})(1 + ee_S)]$, as defined in Ref. 75.

[d] Determined by isolated yield of **2**.

[e] $C_{HPLC} = ee_S/(ee_P + ee_S)$, as defined in Ref. 76.

In optimization of the reaction conditions, we chose LP-AK, LP-AS, and PS-30 due to their high efficiency and good accessibility. Screening using racemic ethyl mandelate as a model compound showed that lipase PS-30 was the best one among the three, which could give a value of kinetic enantiomeric ratio (E) up to 28.0 at 39% conversion. Therefore, lipase PS-30 was used throughout this study.

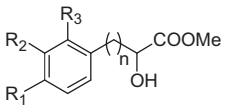
For the acyl reagent, vinyl acetate and vinyl butyrate were tested and vinyl acetate gave higher E value (up to 83.1 at 45% conversion after 7 days), while using vinyl butyrate as the acyl donor, the E value was only 1.7. Therefore, we used vinyl acetate as the acylating reagent in the following study.

Various esters formed by mandelic acid and different alcohols were tested. Higher enantioselectivity ($E = 59$) at 41% conversion could be obtained with methyl mandelate as the substrate. The kinetic resolution of the mandelate esters with alkoxy groups larger than ethoxy could not proceed.

Therefore, we could establish our reaction conditions: Racemic methyl mandelates were treated with vinyl acetate in the presence of lipase PS-30 (the immobilized form of *Burkholderia cepacia* lipase, purchased from Sigma–Aldrich) and 4A molecular sieves in toluene at 25 °C to afford *O*-acetyl (*S*)-methyl mandelate and the unreacted (*R*)-methyl mandelate. The reaction was stopped and worked up for enantiomeric excess (ee) value evaluation. From the ee values, the values of kinetic enantiomeric ratio (E), which is defined in Ref. 75,76, were calculated.

Table 1 summarizes our results. Some substrates shown in Table 1 (compounds shown in entries 4, 7, 10, 13, and 15) are for the first time subjected to enzymatic KR. The E values of ten substrates (entries 1, 2, 6–8, 10, 12, 15–17) are larger than 50. According to Schneider et al.,[67] value of $E > 50$ would be sufficient for production of the desired enantiomer in good yield and enantiomeric purity.

For discussion of data shown in Table 1, we take **1a** (entry 1, $E = 59.0$) as the parent compound for comparison with the others. We can see the phenomena as follows:



(1) Compounds **1b**, **1f**–**1h**, **1j**, and **1l** (entries 2, 6–8, 10 and 12, $E = 70.1$ to 192.5), which bear a substituent of moderate size on *meta*- or *para*-position of the phenyl group ($n = 0$, $R_3 = H$, R_1 or R_2 with moderate size), gave higher E values, while compounds **1m** (entry 13, $E = 15.0$) and **1n** (entry 14, no reaction), which bear a substituent of larger size on *para*-position ($n = 0$, $R_2 = R_3 = H$, R_1 with large size), gave significantly lower E values. This fact implies that size of substituent (i.e. the size of R group) has an influence on the interaction of the substrate with the enzyme.

(2) When the size of substituents on the phenyl group is small enough, such as F and Br (whose atomic radius is 42 and 94 pm, respectively, while that of H is 53 pm),[77] steric hindrance would not be a key factor for the interaction of the substrates and the enzyme, while electron-withdrawing effect would make some positive contribution to the E values (entries 6–8, and 10, $E = 70.1$ to 192.5, while in entry 1, $E = 59.0$). However, no reaction occurred when the mandelate substrates have a fluorine substituent on *ortho*-position ($n = 0$, $R_3 = F$) (entries 9 and 11). This might be attributed to that a six-membered ring intramolecular hydrogen-bond structure was formed between F and the α-hydroxyl group of the methyl mandelate (Fig. 1), which inhibited the acylation of the hydroxyl group.

(3) Substitution on *ortho*-position of the phenyl group ($n = 0$, $R_1 = R_2 = H$, R_3 with large size) (entry 3, compound **1c**, $E = 1.5$) causes stereo-hindrance to the hydroxyl group, leading to dramatical decrease of E values.

(4) In compounds **1p** and **1q** ($n = 1$ and 2, $R_1 = R_2 = R_3 = H$, R_1) (entries 16 and 17, $E = 57.8$ and 197.5, respectively), the phenyl group is relatively far away from the hydroxyl group, leading to the decrease of stereo-hindrance around the hydroxyl group, which is in favor of the interaction of the substrate with the enzyme thus giving the best resolution.

(5) Ethyl mandelate (entry 18, compound **1r**) gave lower E value (28.0) than that of methyl mandelate (entry 1, $E = 59.0$). No reaction occurred when the mandelic esters have alkoxyl groups larger than ethoxy, therefore they could not be used as the substrate of this enzymatic kinetic resolution reaction.

Configuration of some acylated products (**2a**, **2h**, **2o**, and **2q**) and the unreacted alcohols (**3b**, **3d**, and **3p**) is further confirmed by comparison of the observed optical rotations with those reported in the literatures (Table 2). Some other products have been reported in the references (**2b–f**, **2q** in Ref. 85; **2l**, **2p** in Ref. 13, respectively), but their $[\alpha]_D$ data could not be found in the corresponding references.

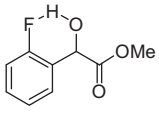


Figure 1. A proposed intramolecular hydrogen-bond between F and α-hydroxyl group of methyl 2-fluoro-mandelate.

Table 2
Configuration assignment of **2a**, **2h**, **2o**, **2q**, **3b**, **3d**, and **3p** by comparison with the reported $[\alpha]_D$ data

Compound	Measured values		Reported values		Ref.
	$[\alpha]_D$	ee (%)	$[\alpha]_D$	ee (%)	
2a	+100.04 (c 0.75, $CHCl_3$)	90.1	+124.6 (c 0.82, $CHCl_3$)	71 (*S*)	16
2h	+115.7 (c 0.98, $CHCl_3$)	96.1	+101.6 (c 1.09, $CHCl_3$)	100 (*S*)	78
2o	−6.21 (c 0.5, $CHCl_3$)	93.8	-7.5 (c 1.3, $CHCl_3$)	>99 (*S*)	79
2q	+110.4 (c 0.97, $CHCl_3$)	92.4	+124.6 (c 0.82, $CHCl_3$)	71 (*S*)	86
3b	−93.1 (c 0.74, $CHCl_3$)	89.8	−82.6 (c 1.00, $CHCl_3$)	90 (*R*)	80
3d	−57.2 (c 0.59, $CHCl_3$)	18.2	−45 (c 4.0, $CHCl_3$)	62 (*R*)	81
3p	−23.6 (c 1.07, $CHCl_3$)	94.3	−28.7 (c 1.61, $CHCl_3$)	99 (*R*)	82

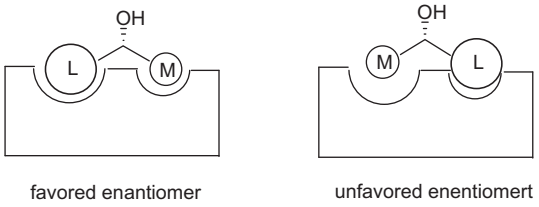


Figure 2. A schematic presentation of Kazlauskas' rule.

Configuration of the other products (**2c**, **2e**, **2f**, **2g**, **2j**, **2l**, **2m**, **2n**), where the aryl groups stand for the large size group and the ester groups stand for the middle size group, was proposed to have the same designation as the known ones based on Kazlauskas' rule (Fig. 2).[83,84]

In summary, we have achieved the KR of seventeen racemic methyl mandelic esters via stereoselective acylation using lipase PS-30 as the catalyst. Majority of the substrates gave values of E close to or larger than 50, the best one achieves 197.5.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.02.095.

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