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Enantioselective reduction of fluorenones in surfactant-aqueous solution by fruits and vegetables

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ABSTRACT

Various fruits and vegetables have been evaluated as biocatalysts in the enantioselective reduction of substituted fluorenones under mild and eco-friendly conditions. Grape exhibited the best results with 99% ee and 97% conversion. The conversion rate varies in the presence of different surfactants, but the enantioselectivity remains unchanged. That is, enantiomeric selectivity is from biocatalysts and the conversion is related to the aqueous solubility of substrates. The surfactant, Triton X-100, is the best for improving the biotransformation and behaved in a concentration-dependent manner. The high enantioselectivity of halogen substituents is attributed to halogen electron-withdrawing effects rather than electron-donating effects like $-CH_3$, but the yield is not dependent on the size of the halogens. It is interesting that the absolute configuration of the product, 2-chloro-fluorenol, is *R* not *S*, indicating its biocatalytic reduction following anti-Prelog's rule. This study provided a useful method for the reduction of rigid macro-cyclic aromatic ketones.

1. Introduction

Enantiomerical molecules are applied in pharmaceuticals, pesticides, and as intermediates in the preparation of advanced materials such as liquid crystals [1]. Chiral alcohols can be obtained from the corresponding ketones by biocatalytic reductions [2–17], e.g., bioreduction of acetophenone derivatives, camphorquinones and steroidal ketones using red algae or various vegetables reported by Horiuchi and co-workers [18,19], *Daucus carota* and *baker's yeast* mediated reduction of indanone, tetralone and hydroxyl trimonoterpene ketones reported by Rao and co-workers [20].

We also noticed that many ketones and aldehydes could be reduced using plant cell in water as solvent in very good yields, but with low or moderate enantiomeric excesses value when aromatic ketones and α-ketoesters were used as substrates [21]. Therefore, we are interested in the high enantiomerical bioreduction of ring-fused aromatic ketones by plant cells.

As matter of fact, the asymmetric reduction of rigid polycyclic-fused aromatic ketones is still a big challenge in organic synthesis. The synthesis of chiral substituted fluorenols via the asymmetric reduction of fluorene ketones, for example, has attracted much attention because they are building blocks of liquid crystals [1], and the intermediate of benflumetol, one of the key components of widely applied antimalarial agents. However, obtaining these compounds is very difficult due to the following reasons: (1) the steric hindrance caused by the rigid structure of substituted fluorenone prevents the approach of asymmetric catalysts; (2) two side aromatic rings along the prochiral central carbon atom bear similar steric conformation leading to difficulties in the group recognition; (3) the poor solubility of substituted fluorenones is another problem to effect yields; and (4) the current applied reductant, KBH_4 or $NaBH_4$, is so reactive that it cause safety problems in storage and operation [22,23]. Many methods including metal hydride reduction [24,25], catalytic hydrogenation [26,27] and hydrogen transfer reactions have been developed to achieve this transformation. Compared with chemical methods, biotransformation has attracted much attention due to relatively benign reaction conditions and high chemo- and regio-selectivities [28]. However, the asymmetric reduction of rigid cyclic and aromatic ketones is also a big challenge in biotransformation, as these compounds have very low solubility in water, which is suitable for whole cell. Li et al. have previously tried baker's yeast to accomplish enantioselective reduction of several substituted fluorenones in water with DMSO as solvent [29]. But the low yield (32–78%), the high concentration of DMSO (10%) and the requirement of large quantity of yeast cells as well as mechanical stirring leave a large space for methodological improvement [29].

The plant cell is easily available and cheap, and using plant cell for biocatalysis and biotransformation has been tried for many years. Unlike microbial biocatalysts like baker's yeast, information in association with enzymes from plants is very less [30]. Recent

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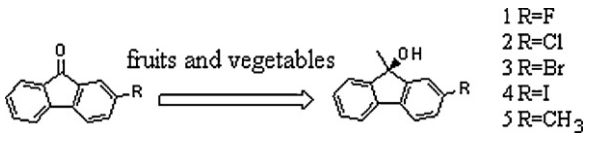


Scheme 1.

expansion of genomic knowledge in model plants *Arabidopsis* makes it possible to discover genes related to chemical/xenobiotic transformation. However, taking advantage of this information is too early because the putative enzyme resources are very large and lack of genomic knowledge of other plants. For example, over 130 genes in *Arabidopsis* genome are presumed to belong to short-chain dehydrogenase/reductase (SDR) [31]. Besides, plant enzymes are often produced in minute quantities [32], which make their purification difficult. In the view of biotechnology, the plant cells that catalyze regio- and enantioselective reactions have many advantages over traditional chemical synthesis [32–36].

We herein report highly efficient synthesis of chiral substituted fluorenols as rigid polycyclic-fused aromatic ketones by biocatalysts of fruits and vegetable cells under mild conditions in water without mechanical stirrers (Scheme 1).

2. Experimental

2.1. General procedures

The substituted fluorenones in Scheme 1 were synthesized in our laboratory and the structure and molecular weight were verified by ^{1}H NMR, ^{13}C NMR and MS, respectively. The purity was determined by RP-HPLC. The solvents including methanol, ethanol, ethyl acetate, and dimethylsulfoxide (DMSO) were all of HPLC-grade. Milli-Q water was used in all experiments. All other analytical or HPLC-grade chemicals and solvents were purchased from Sigma and Fluka as well as the local suppliers.

2.2. Conversion rate determined by RP-HPLC

RP-HPLC analysis of substrates and products was performed on Agilent 1100 system (USA) with a UV detector and a Kromasil C18 column (4.6 mm × 250 mm i.d.; 5 μm, 80 Å). The separation conditions included CH_3OH:H_2O = 70:30, UV detection at 254 nm, and the flow rate at 0.8 mL min^{-1}.

2.3. Product collection by semi-preparative RP-HPLC

The product was isolated from the reaction mixture by semi-preparative RP-HPLC, which was performed on Shim-pack PREP-ODS (H) KIT, 20 mm × 250 mm (Shimadzu). The separation conditions included CH_3OH:H_2O = 85:15, UV detection at 254 nm, and the flow rate at 8.0 mL min^{-1}.

2.4. Enantioselectivity determined by chiral HPLC

Chiral HPLC analysis of enantio-products was performed on the chiral column (chiralcel AD-H). The separation conditions included n-hexane:isopropyl alcohol = 98:2, UV detection at 254 nm and the flow rate at 1.0 mL min^{-1}.

2.5. Reducing the substituted fluorenones by plants

Fresh fruits and vegetables, including Apple (*Malus pumila* Mill.), Banana (*Musa balbisiana* Colla), Orange (*Citrus reticulata* Blanco.), Potato (*Solanum tuberosum* L.), Strawberry (*Fragaria ananassa* Duch.), Scallion (*Allium fistulosum* L. var.), Plum (*Prunus* spp.), Garlic (*Allium saticum* L.), Onion (*Allium cepa* L.), Cherry (*Prunus pseudocerasus* Lindl.), Jujube (*Zizyphus jujuba* Mill.), Topinambur (*Jerusalem artichoko*) and Grape (*Vitis* spp.), were purchased from a local market at typical maturity period between June 2008 and October 2008.

Fresh, undamaged, firm fruits and vegetables were chosen and firstly cleaned with detergent and rinsed under running tap water, and then were surface disinfected by immersing in 70% ethanol for 3 min, and in 0.5% NaClO for 5 min followed by three rinses with sterile distilled water. The fruits were peeled off and ground into fine powder in liquid nitrogen. Forty gram of each powder sample was put into flasks individually with 200 mL of sterile buffer (20 mM Tris–HCl, pH 7.5).

The reaction was initiated by the addition of 1 mL of 50 mM substituted fluorenones dissolved in DMSO. The reaction was allowed for 2 d at 30 °C, 170 rpm. For optimal solvents, SDS, Tween-20 and Triton X-100 were applied at various concentrations 0% (w/v), 0.5% (w/v), 1% (w/v), 2% (w/v), 4% (w/v), respectively. For optimal reaction time, 0 d, 0.5 d, 1 d, 2 d, 3 d, 4 d were evaluated. For optimal temperature, 20 °C, 25 °C, 30 °C, 37 °C, 40 °C and 45 °C were compared. For optimal pH studies, buffer at different pH was applied, which included 20 mM Tris–HCl (pH 7, 7.5, 8, 8.5) and 20 mM sodium phosphate (pH 6, 6.5, 7, 7.5). Blank assays without substrates and without biomass were carried out as control. The results are repeated three times.

2.6. Determination of substituted fluorenols

After the completion of reaction, ethyl acetate was added to the reaction mixture. The separated organic phase was filtered through a column filled with anhydrous sodium sulfate. Then, after filtration followed with the removal of organic solvent by vacuum concentration, the crude mixture was purified by semi-preparative HPLC.

2-Fluoro-fluorenol: yield: 92%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82–7.75 (m, 2H), 7.58 (d, J = 7.6 Hz, 1H), 7.38(m, 2H), 7.30 (dd, J = 7.6, 7.2 Hz, 1H), 7.21 (t, J = 10.0 Hz, 1H), 5.50 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.8, 138.5, 128.5, 127.1, 125.0, 121.5, 121.4, 119.8, 115.3, 115.1, 112.4, 112.2, 73.4; HRMS-EI (70 eV) m/z calcd for $C_{13}H_9OF$ [M] 200.0637, found 200.0638; mp 131.4–132.1 °C; $[\alpha]_D^{23} = +3.17$ (c 0.25, C_2H_5OH); retention time: $t_{(-OH)}$ = 12.67 min, $t_{(-C=O)}$ = 26.87 min. $t_{(-)}$ = 27.51 min, $t_{(+)}$ = 30.47 min.

2-Chloro-fluorenol: yield: 93%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81–7.79 (m, 2H), 7.60–7.58 (m, 2H), 7.45–7.32 (m, 3H), 5.50 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.1, 146.7, 138.3, 131.9, 128.5, 128.3, 127.8, 125.1, 121.5, 120.2, 73.3; HRMS-EI (70 eV) m/z calcd for $C_{13}H_9OCl$ [M] 216.0342, found 216.0304; mp 139.2–141.0 °C; $[\alpha]_D^{23} = +17.84$ (c 0.85, C_2H_5OH); retention time: $t_{(-OH)}$ = 12.15 min, $t_{(-C=O)}$ = 21.42 min. t_R = 29.33 min, t_S = 31.81 min.

2-Bromo-fluorenol: yield: 88%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.80 (d, J = 7.6 Hz, 1H), 7.76–7.72 (m, 2H), 7.59–7.56 (m, 2H), 7.41–7.33 (m, 2H), 5.50(s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.4, 146.6, 138.7, 138.3, 131.2, 128.6, 128.0, 127.9, 125.1, 122.0, 120.4, 120.2, 73.3; HRMS-EI (70 eV) m/z calcd for $C_{13}H_9OBr$ [M] 259.9837, found 259.9831; mp 138.4–139.0 °C; $[\alpha]_D^{23} = +9.60$ (c 0.30, C_2H_5OH); retention time: $t_{(-OH)}$ = 12.06 min, $t_{(-C=O)}$ = 20.67 min. $t_{(+)}$ = 30.97 min, $t_{(-)}$ = 34.99 min.

2-Iodo-fluorenol: yield: 83%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (s, 1H), 7.80–7.72 (m, 2H), 7.63–7.57 (m, 2H), 7.41–7.33 (m, 3H), 5.49 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.4, 146.3, 139.1, 138.5,137.0, 133.8, 128.5, 128.0, 125.0, 122.1, 120.2, 93.1, 73.3; HRMS-EI (70 eV) m/z calcd for $C_{13}H_9OI$ [M] 307.9698, found 307.9707; mp 141.7–142.5 °C; $[\alpha]_D^{23} = +2.81$ (c 0.20, C_2H_5OH); retention time: $t_{(-OH)}$ = 17.27 min, $t_{(-C=O)}$ = 30.19 min. $t_{(-)}$ = 52.45 min, $t_{(+)}$ = 60.67 min.

2-Methyl-fluorenol: yield: 92%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (d, J = 7.6, 1H), 7.64 (d, J = 7.6, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.40 (s, 1H), 7.36 (dd, J = 7.2, 7.6 Hz, 1H), 7.28 (dd, J = 7.6, 7.2 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 5.44 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.1, 146.8, 139.5, 136.8, 128.9, 128.3, 126.9, 125.7, 125.0, 119.7, 119.5, 73.5, 21.2; HRMS-EI (70 eV) m/z calcd for $C_{14}H_{12}O$ [M] 196.0888, found 196.0887; mp 140.2–141.1 °C; $[\alpha]_D^{23} = +10.82$ (c 0.20, C_2H_5OH); retention time: $t_{(-OH)}$ = 14.11 min, $t_{(-C=O)}$ = 20.56 min. $t_{(+)}$ = 23.11 min, $t_{(-)}$ = 24.84 min.

3. Results and discussion

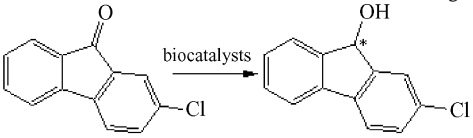
3.1. Exploiting of plant biocatalysts

In the attempt of exploiting plant biocatalysts for enantioselectively reducing substituted fluorenones and several plants were evaluated by using 2-chloro-fluorenone as substrate. DMSO was applied as solvent and shaking replaced mechanical stirrers. The enantiomeric excess, % ee, and % conversion were determined by RP-HPLC.

As shown in Table 1, except garlic (*Allium saticum* L.) was inactive under the reaction conditions, all other plant species were able to reduce 2-chloro-fluorenone. But the ee value and the conversion rate varied a lot. Among the tested plants, the Grape (*Vitis* spp.) exhibited both the highest conversion rate (97%) and the highest enantioselectivity (ee > 99%), indicating that Grape (*Vitis* spp.) had advantages over other plants in enantioselective reduction, which was else reported by Li et al. in the production of hydroxylamines [37].

Based on the knowledge of microbial biocatalysts, we assume that two enzyme systems include an asymmetric reduction system and a cofactor regeneration system might be responsible for the reduction of ketones in plants, e.g., NAD(P)H dependent carbonyl reductases/aldo-keto reductases/dehydrogenases [38]. Whole-cell biocatalysts are usually stable, and many of them offer internal cofactor regeneration that can be used without any additives or by adding cosubstrates, reducing sugar or simply light [39]. As for this work, since there is no external addition of the source of reducing power and the cofactor, and there are a large amount of endogenous reducing sugars in grape and other plants, the regeneration of NADH or NAD(P)H may possibly be supplied through the oxidation of the reducing sugars catalyzed by sugar reductases [38,40,41].

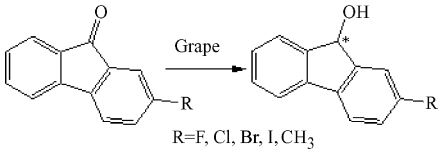
Table 1
Enantioselective reduction of 2-chloro-fluorenone using biocatalysts.



Species	Conversion/%[a]	Ee/%[b]
Apple (*Malus pumila* Mill.)	69	90
Banana (*Musa balbisiana* Colla)	30	46
Orange (*Citrus reticulata* Blanco.)	15	43
Potato (*Solanum tuberosum* L.)	7	50
Strawberry (*Fragaria ananassa* Duch.)	37	93
Scallion (*Allium fistulosum* L. var.)	13	72
Plum (*Prunus* spp.)	100	50
Garlic (*Allium saticum* L.)	–	–
Onion (*Allium cepa* L.)	8	26
Cherry (*Prunus pseudocerasus* Lindl.)	4	87
Jujube (*Zizyphus jujuba* Mill.)	88	28
Topinambur (*Jerusalem artichoko*)	100	76
Grape (*Vitis* spp.)	97	>99

[a] The conversion rate was determined by reverse phase HPLC.
[b] The ee was determined by normal phase HPLC using a chiralcel AD-H column.

Table 2
Enantioselective reduction of different substituted fluorenones by Grape (*Vitis* spp.).



Compound	Conversion/%[a]	Yield/%[b]	Ee/%[c]	$[\alpha]_D^{23}$[e]
1	>98	92	>99	+3.17
2	>97	93	>99 (*R*)[d]	+17.84
3	95	88	>99	+9.60
4	91	83	92	+2.81
5	>98	92	74	+10.82

[a] The conversion was determined by reverse phase HPLC.
[b] Yield was determined by semi-preparative HPLC.
[c] The ee value was determined by normal phase HPLC using a chiralcel AD-H column.
[d] The absolute configuration was determined to be *R* by comparing its optical rotation with the literature data.
[e] *c*, 0.20–0.85; C_2H_5OH, 23 °C.

3.2. Effect of nonionic surfactant

The extractive biotransformation using nonionic surfactant in two-phase systems has been investigated extensively [42–44]. However, reports of the effect of surfactant on biotransformation by whole cells in aqueous solution were very few. Effects of surfactants on biotransformation kinetics of anthracene and pyrene, which have significant implications in the bioremediation of PAHs-contaminated sites, were reported [45].

DMSO as regular solvent to improve the solubility of substrates, is also well known for its toxicity at higher concentration (>0.1%) to bioactivities. We firstly applied DMSO as solvent, but the concentration of it was hardly lowed down to 10% to give good yield. To optimize the reaction in water and to decrease the amount of DMSO to minimum, several surfactants were investigated. As shown in Fig. 1A, the conversion rate was largely influenced by various surfactants whereas the ee value remained the same. This suggested enantiomeric selectivity was from biocatalysts and the % conversion was related to the aqueous solubility of substrates. Comparing with SDS and Tween-20, Triton X-100 was the best. Triton X-100 improving the biotransformation was in a concentration-dependent manner (Fig. 1A) and low (1%) rather than high (4%) concentration was preferred. Triton X-100 enhanced the conversion but did not change the enantioselectivity, suggesting it was an ideal surfactant in this case. Further investigation indicated the reduction efficiency was affected by reaction time, temperature and pH. The optimal conditions included 2 d (Fig. 1B), 30 °C (Fig. 1C) and pH 7.5 (Fig. 1D).

3.3. Substrate specificity

In order to explore the substrate specificity of the biocatalyst Grape (*Vitis* spp.), a series of substituted fluorenones were applied as substrates. As shown in Table 2, the reduction of 2-fluoro-fluorenone, 2-bromo-fluorenone and 2-iodo-fluorenone yielded >83% of the corresponding fluorenols with >92% ee. The reduction of 2-methyl-fluorenone yielded >98% of the corresponding fluorenol but with the lowest ee value (74%). Therefore, we presumed that electronic effects might play an important role in the enantioselectivity. The high enantioselectivity of halogen substituents could be attributed to the electron-withdrawing groups rather than electron-donating groups like $-CH_3$ group in the recognition of the chiral center by the biocatalysts, which was in accord with *baker's yeast* applied by Li et al. before [29]. However, unlike *baker's yeast* by the selectivity order, I > Br > F > CH_3, the grape did in another

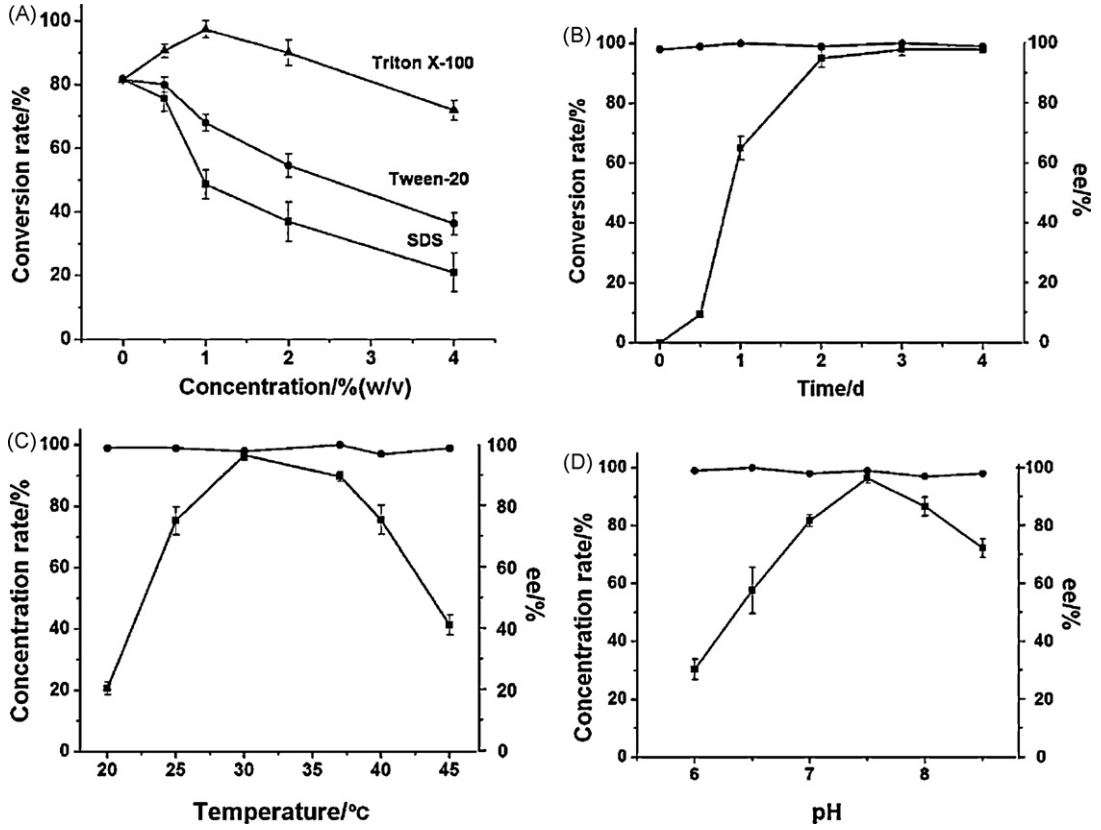


Fig. 1. Factors affecting the conversion rate of substituted 2-chlorofluorenone by Grape (*Vitis* spp.). (A) Nonionic surfactants; (B) reaction time; (C) temperature; (D) pH. The conversion rate was determined by reverse phase HPLC. The ee was determined by normal phase HPLC using a chiralcel AD-H column.

way, $F \approx Cl \approx Br > I > CH_3$. We have noticed, in case of bioreduction of acetophenone by red algae or various vegetables, Horiuchi and coworkers [19] reported that the yields increased with increasing size of halogens, and the reduction of methyl and methoxy acetophenones was observed in low yields (7–38%) and enantioselectivity (2–41%). In the case of methoxy groups, there was a substantial drop in the enantioselectivity of the product. In these cases, it seems that the mesomeric effect of the substituents was superior to their inductive effect [18,19], which is very similar to our observation on relationship between yields and groups' electron properties.

3.4. Absolute configuration

The absolute configuration of the reduced product, 2-chlorofluorenol was determined to be *R* by comparing its optical rotation with documentary data [46]. It indicated that this biocatalytic reduction of 2-chloro-fluorenone followed anti-Prelog's rule and the hydrogen transfer took place preferentially from the prochiral *Si*-face. The absolute configurations of the other enantiomerically pure substituted fluorenols were not determined because the well diffracting crystals have not been obtained.

During bioreduction of aromatic ketones, in most case the product was (*S*)-configuration, for example, for bioreduction of acetophenone derivatives, camphorquinones and steroidal ketones using red algae or various vegetables, the alcohol products had the (*S*)-configuration, which is consistent with Prelog's rule [18,19]. Also, the carrot or *baker's yeast* mediated reduction of carbonyl groups followed Prelog's rule to produce (*S*)-alcohols products [20].

To our knowledge, bioreduction of aromatic ketones following anti-Prelog's rule was seldom reported. There are only few examples, i.e. Sanz's bioreduction of ketones using both cell cultures and tissues of various endemic plant species in an anti-Prelog manner [30].

This at least implied that it is possible to selectively prepare the *S* and *R* chiral isomers of an alcohol by reduction of the corresponding ketone by appropriate biocatalysts.

4. Summary

Biocatalysts have been recognized and widely used in production of variety of chemicals for many years. With the help of molecular biological techniques, a number of enzymes with high efficiency and selectivity have been exploited and characterized. Most of these enzymes are from bacterium and fungi, in particular those with open-accessed genomic database. These scientific advances reveal that enzymes from different species may exhibit different catalytic characteristics, which include substrate or stereochemistry selectivities. This is why it is still of research interest to exploit enzymes belonging to the same family but deriving from different sources. Compared with microbial biocatalysts, plants have much more complex metabolic pathways, which are far less understood. One opinion is that they may have unknown and unique enzymes [2,32]. Since most genomic DNA sequences of fruits and vegetables are not available, it may be not easy to dig out the enzymes involved. Under this circumstance, exploiting plant cells with highly catalytic activities is of significance.

In this work, we developed a highly efficient method for the preparation of enantiomerically pure substituted fluorenols in water by plants. Under mild and eco-friendly conditions including 30 °C, shaking at 170 rpm, 1% Triton X-100, pH 7.5, 97% of prochiral substituted fluorenone was reduced into the corresponding chiral fluorenols within 2 d in the presence of Grape (*Vitis* spp.) with 99% ee and at 97% conversion, which might expand

the scope of the biocatalysts in asymmetric organic synthesis. The enantiomeric selectivity was from biocatalysts and the conversion was related to the aqueous solubility of substrates, and nonionic surfactant Triton X-100 was the best for improving the biotransformation in a concentration-dependent manner. The high enantioselectivity of halogen substituents is presumed to be attributed to their electron-withdrawing effects rather than electron-donating effects like $-CH_3$, and the yield is not depended on the size of the halogens. However, it is interesting that the absolute configuration of the reduced product, 2-chloro-fluorenol is *R* rather than *S*, indicating its biocatalytic reduction followed anti-Prelog's rule. This study provided a useful method for the reduction of rigid polycyclic-fused aromatic ketones. And also, no organic solvents as well as mechanic stirrer requirement suggested superior advantages of Grape (*Vitis* spp.) over commonly applied biocatalysts.

Acknowledgments

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References

[1] J.A. McCubbin, X. Tong, R. Wang, Y. Zhao, V. Snieckus, R.P. Lemieux, J. Am. Chem. Soc. 126 (2004) 1161–1167.
[2] T. Matsuda, R. Yamanaka, K. Nakamura, Tetrahedron: Asymm. 20 (2009) 513–557.
[3] K. Nakamura, R. Yamanaka, Tetrahedron: Asymm. 13 (2002) 2529–2533.
[4] T. Utsukihara, W. Chai, N. Kato, K. Nakamura, C.A. Horiuchi, J. Mol. Catal. B: Enzym. 31 (2004) 19–24.
[5] N.A. Salvi, S. Chattopadhyay, Tetrahedron 57 (2001) 2833–2839.
[6] S.M. Roberts, J. Chem. Soc. Perkin Trans. (2000) 611–633.
[7] K. Ishihara, H. Yamaguchi, N. Nakajima, J. Mol. Catal. B: Enzym. 23 (2003) 171–189.
[8] F. Baldassarre, G. Bertoni, C. Chiappe, F. Marioni, J. Mol. Catal. B: Enzym. 11 (2000) 55–58.
[9] W.K. Ma czka, A. Mironowicz, Tetrahedron: Asymm. 15 (2004) 1965–1967.
[10] B. Baskar, S. Ganesh, T.S. Lokeswari, A. Chadha, J. Mol. Catal. B: Enzym. 27 (2004) 13–17.
[11] D. Caron, A.P. Coughlan, M. Simard, J. Bernier, Y. Piche, R. Chenevert, Biotechnol. Lett. 27 (2005) 713–716.
[12] R. Bruni, G. Fantin, S. Maietti, A. Medici, P. Pedrini, G. Sacchetti, Tetrahedron: Asymm. 17 (2006) 2287–2291.
[13] N. Blanchard, W. Pierrevande, Org. Biomol. Chem. 4 (2006) 2348–2353.
[14] I. Kira, T. Suzuki, N. Onishi, K. Watanabe, E. Nakanishi, J. Mol. Catal. B: Enzym. 56 (2009) 283–287.
[15] J.S. Yadav, P.T. Reddy, S. Nanda, A.B. Rao, Tetrahedron: Asymm. 12 (2001) 3381–3385.
[16] J.S. Yadav, S. Nanda, P.T. Reddy, A.B. Rao, J. Org. Chem. 67 (2002) 3900–3903.
[17] J. S. Yadav, S. Nanda, P.T. Reddy, A.B. Rao, US Patent 20,040,082,043 (2004).
[18] T. Utsukihara, O. Misumi, N. Kato, T. Kuroiwa, C.A. Horiuchi, Tetrahedron: Asymm. 17 (2006) 1179–1185.
[19] T. Utsukihara, S. Watanabe, A. Tomiyama, W. Chai, C.A. Horiuchi, J. Mol. Catal. B: Enzym. 41 (2006) 103–109.
[20] J.S. Yadav, G.S.K.K. Reddy, G. Sabitha, A.D. Krishna, A.R. Prasad, H.U.R. Rahaman, K.V. Rao, A.B. Rao, Tetrahedron: Asymm. 18 (2007) 717–723.
[21] L.L. Machado, F.J.Q. Monte, M.C.F. Oliveira, M.C. Mattos, T.L.G. Lemos, V.G. Fernández, G. Gonzalo, V. Gotor, J. Mol. Catal. B: Enzym. 54 (2008) 130–133.
[22] Z. Yu, F.L. Calahorra, D. Velasco, Tetrahedron: Asymm. 11 (2000) 3221–3225.
[23] Z. Yu, F.L. Calahorra, D. Velasco, Tetrahedron: Asymm. 11 (2000) 3227–3230.
[24] E.J. Corey, C.J. Helal, Angew. Chem. Int. Ed. 37 (1998) 1986–2012.
[25] P. Daverio, M. Zanda, Tetrahedron: Asymm. 12 (2001) 2225–2259.
[26] A. Hu, G.T. Yee, W. Lin, J. Am. Chem. Soc. 127 (2005) 12486–12487.
[27] T. Ohkuma, C.A. Sandoval, R. Srinivasan, Q. Lin, Y. Wei, K. Muniz, R. Noyori, J. Am. Chem. Soc. 127 (2005) 8288–8289.
[28] W. Kroutil, H. Mang, K. Edegger, K. Faber, Curr. Opin. Chem. Biol. 8 (2004) 120–126.
[29] F. Li, J. Cui, X. Qian, W. Ren, X. Wang, Chem. Commun. (2006) 865–867.
[30] A.A. Orden, F.R. Bisogno, O.S. Giordano, M.K. Sanz, J. Mol. Catal. B: Enzym. 51 (2008) 49–55.
[31] Y. Kallberg, U. Oppermann, H. Jörnvall, B. Persson, Protein Sci. 11 (2002) 636–641.
[32] A. Giri, V. Dhingra, C.C. Giri, A. Singh, O.P. Ward, M.L. Narasu, Biotechnol. Adv. 19 (2001) 175–199.
[33] M.A. Longo, M.A. Sanromaín, Food Technol. Biotechnol. 44 (2006) 335–353.
[34] R. Bruni, G. Fantin, A. Medici, P. Pedrini, G. Sacchetti, Tetrahedron Lett. 43 (2002) 3377–3379.
[35] K. Ishihara, H. Hamada, T. Hirata, N. Nakajima, J. Mol. Catal. B: Enzym. 23 (2003) 145–170.
[36] R. Villa, F. Molinari, J. Nat. Prod. 71 (2008) 693–696.
[37] F. Li, J. Cui, X. Qian, R. Zhang, Y. Xiao, Chem. Commun. (2005) 1901–1903.
[38] M. Kataoka, K. Kita, M. Wada, Y. Yasohara, J. Hasegawa, S. Shimizu, Appl. Microbiol. Biotechnol. 62 (2003) 437–445.
[39] K. Goldberg, K. Schroer, S. Lütz, A. Liese, Appl. Microbiol. Biotechnol. 76 (2007) 249–255.
[40] M. Kataoka, L.P.S. Rohani, K. Yamamoto, M. Wada, H. Kawabata, K. Kita, H. Yanase, S. Shimizu, Appl. Microbiol. Biotechnol. 48 (1997) 699–703.
[41] J.D. Stewart, Curr. Opin. Biotechnol. 11 (2000) 363–368.
[42] Z. Wang, Appl. Microbiol. Biotechnol. 75 (2007) 1–10.
[43] A. Malaviya, J. Gomes, J. Ind. Microbiol. Biotechnol. 35 (2008) 1435–1440.
[44] Z. Wang, J.H. Xu, W. Zhang, B. Zhuang, H. Qi, Biotechnol. Prog. 24 (2008) 1090–1095.
[45] C. Sartoros, L. Yerushalmi, P. Béron, S.R. Guiot, Chemosphere 61 (2005) 1042–1050.
[46] A.C. Darby, M.K. Hargreaves, D.A. Raval, J. Chem. Soc. D (1970) 1554–1555.