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Whole-Cell Photoenzymatic Cascades to Synthesize Long Chain Aliphatic Amines and Esters from Renewable Fatty Acids

Hee-Jeong Cha,[a] Se-Yeun Hwang,[a] Da-Som Lee,[a] Ravi Kumar Akula,[a,b] Yong-Uk Kwon,[b] Moritz Voß,[c] Eva Schuiten,[c] Uwe T. Bornscheuer,[c] Frank Hollmann,*[d] Deok-Kun Oh,*[e] and Jin-Byung Park*[a]

Abstract: Long chain aliphatic amines such as (*S,Z*)-heptadec-9-en-7-amine and 9-aminoheptadecane were synthesized from ricinoleic acid and oleic acid, respectively, by whole-cell cascade reactions using the combination of an alcohol dehydrogenase (ADH) from *Micrococcus luteus*, an engineered amine transaminase from *Vibrio fluvialis* (Vf-ATA), and a photoactivated decarboxylase from *Chlorella variabilis* NC64A (Cv-FAP) in a one-pot process. In addition, long chain aliphatic esters such as 10-(heptanoyloxy)dec-8-ene and octylnonanoate were prepared from ricinoleic acid and oleic acid, respectively, by using the combination of the ADH, a Baeyer-Villiger monooxygenase variant from *Pseudomonas putida* KT2440, and the Cv-FAP. The target compounds were produced at rates of up to 37 U/g dry cells with conversions up to 90%. Therefore, this study contributes to the preparation of industrially relevant long chain aliphatic chiral amines and esters from renewable fatty acid resources.

Introduction

There is an increasing demand for the preparation of chemical building blocks from biomass-derived starting materials. Renewable oils and fatty acids are particularly interesting because they are abundant in nature and can be derived from non-edible sources. Oils and fatty acids are already used for the synthesis of a variety of chemicals ranging from cosmetic esters to performance additives.[1] For instance, hydroxy fatty acids serve as starting materials to manufacture flavors, resins, waxes, lubricants, polymers and as additives in coatings and paintings.[1b, 2] More recently, hydroxy fatty acids have been used as starting materials in multi-enzyme cascades combining alcohol dehydrogenases (ADH) and amine transaminases (ATA) (Scheme S1).[3] The hydroxyl group can also be converted in a sequence of ADH-catalyzed oxidation followed by a Baeyer-Villiger monooxygenase (BVMO)-step; the resulting esters are hydrolyzed into alkanoic acids and ω-hydroxy fatty acids by an esterase.[4] The ω-hydroxy fatty acids can be oxidized into α,ω-dicarboxylic acids by an alcohol/aldehyde dehydrogenase[5] or converted into ω-amino fatty acids by an ADH and ω-transaminase.[5d, 6] Further synthetic possibilities comprise the transformation into α,ω-diols by combined reduction through carboxylic acid reductases and ADHs[7] or into α,ω-diamines using carboxylic acid reductases, ADHs and ω-transaminase.[6]

Another promising transformation of fatty acids includes the decarboxylation to the corresponding, C-1 shortened alkanes (Scheme S1). Established chemical methods, however, rely on rather harsh reaction conditions[8] under which additional functional groups are unlikely to remain un-altered. A very promising solution to this challenge was reported recently by Beisson and coworkers.[9] The photodecarboxylase from the algae *Chlorella variabilis* NC64A (Cv-FAP) catalyzes the selective, light-driven decarboxylation of (fatty) acids[10] and thereby possibly expands the scope of products derived from renewable oleochemicals significantly.

In this study, a novel fatty acid biotransformation pathway was investigated to produce long chain aliphatic amines and esters from renewable fatty acids, which can be used as active ingredients in cosmetic formulations and performance additives in oleochemicals.[1b, 1c, 2b] For instance, the biotransformation of ricinoleic acid (**1**) into (*S,Z*)-heptadec-9-en-7-amine (**5**) and 10-(heptanoyloxy)dec-8-ene (**7**) (Scheme 1) and the biotransformation of oleic acid ((*Z*)-octadec-9-enoic acid (**10**)) into 9-aminoheptadecane (**14**) and octylnonanoate (**16**) (Scheme 2) were investigated by using Cv-FAP as a key enzyme.

Results and Discussion

In a first set of experiments we created an *Escherichia coli*-based whole cell catalyst expressing Cv-FAP and tested it for the transformation of ricinoleic acid (**1**) into (*Z*)-heptadec-9-en-7-ol (**2**) (Scheme 1).

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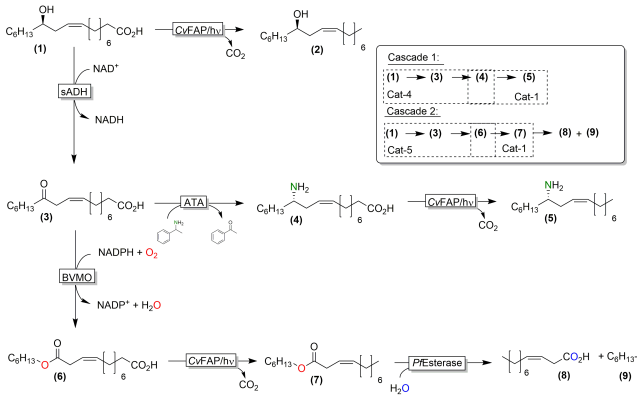


Scheme 1. Cascades for the transformation of ricinoleic acid **(1)** into secondary fatty alcohols **(2)** or amines **(5)**, fatty acid esters **(7)** or the corresponding acids **(8)** and alcohol **(9)**.[3, 5b, 11] Details about the catalysts used can be found in Table 2. Since the expression level of a long chain fatty acid transporter (FadL) in *E. coli* had previously been shown accelerate whole-cell biotransformation rates of long chain fatty acids,[1f, 12] two types of *E. coli*-based biocatalysts (Cat-1 and Cat-2 (Table 2)) were constructed. Cat-1 is the recombinant *E. coli* expressing the Cv-FAP in the cytoplasm while Cat-2 is the recombinant *E. coli* expressing Cv-FAP in the cytoplasm and FadL in the outer membrane.

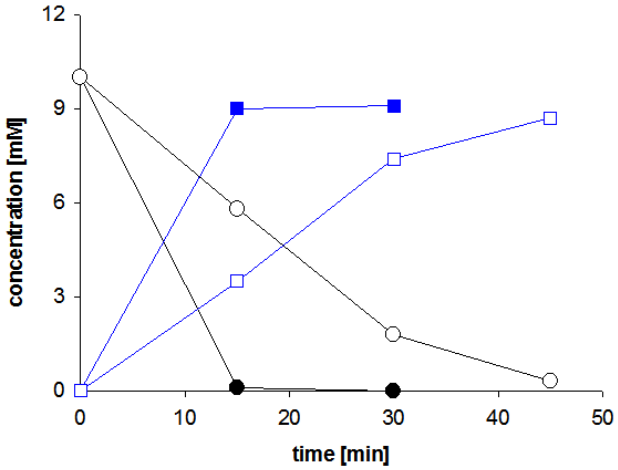


Figure 1. Biotransformation of ricinoleic acid (**1**, ●, ○) into (*Z*)-heptadec-9-en-7-ol (**2**, ■, □) using Cat-1 (closed symbols) or Cat-2 (open symbols). Conditions: c(**1**) = 10 mM, c(Cat-1) or c(Cat-2) = 3.6 g_{CDW} L^{-1}), illumination with blue light (λ=450 nm).

Cat-1 completely converted ricinoleic acid (**1**) into (*Z*)-heptadec-9-en-7-ol (**2**) within only 15 min (Figure 1 and Figure S1). The transformation took significantly longer (30 min) using Cat-2 under otherwise identical conditions (Figure 1**Fehler! Verweisquelle konnte nicht gefunden werden.**). Similar observations were also made for the transformations of oleic acid and linoleic acid (Figure S2). The lower rates might be due to a negative impact of the expression of FadL on the Cv-FAP expression (Figure S3). Therefore, we used Cat-1 as chassis for all further catalyst designs.

Next, we aimed at the conversion of ricinoleic acid (**1**) into (*S,Z*)-heptadec-9-en-7-amine (**5**) (Cascade 1, Figure 2). For this, we used a previously reported recombinant *E. coli* system (Cat-3)[3] comprising a secondary alcohol dehydrogenase (sADH) with a transaminase (Vf-ATA_H3-RA) and the long chain fatty acid transporter (FadL) with the aforementioned Cat-1. Though the transformation proceeded smoothly to full conversion (Figure S4a), the enantiomeric purity of the desired (*S,Z*)-heptadec-9-en-7-amine (**5**) was disappointingly low (27% ee, Scheme S3 and Figure S5). Therefore, Vf-ATA_H3-RA was subjected to structure-based rational engineering to improve its enantioselectivity. Substrate docking revealed that Lysine 163 may play a crucial role (Figure S6). Indeed, substitution of this amino acid by aspartic acid (Vf-ATA_H3-RA_K163D) resulted in a more active and more enantioselective (71% ee) catalyst (Cat-4) (Table S2 and Figure S4b). Overall, using the combination of Cat-1 and Cat-4 yielded in 78% conversion of ricinoleic acid (**1**) into (*S,Z*)-heptadec-9-en-7-amine (**5**) (71% ee, Table 2).

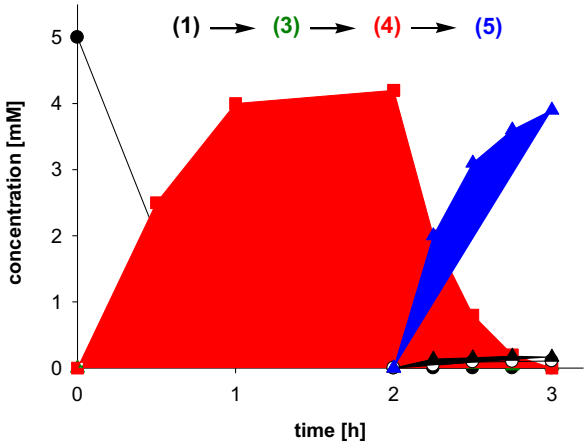


Figure 2. Cascade-1: Biotransformation of ricinoleic acid (**1**, ●) into (*S,Z*)-heptadec-9-en-7-amine (**5**, ▲) via (*Z*)-12-oxooctadec-9-enoic acid (**3**, ▲) and (*S,Z*)-12-aminooctadec-9-enoic acid (**4**, ■). Conditions: c(**1**) = 5 mM, c(Cat-1 = 3.6 g_{CDW} L^{-1}, c(Cat-4) = 7.2 g_{CDW} L^{-1}, c(methyl benzyl amine) = 10 mM, illumination with blue light (λ=450 nm) was initiated at t = 2h.

It is worth noting, that at the time the illumination was initiated not all starting material had been converted into (*S,Z*)-12-aminooctadec-9-enoic acid (**4**), therefore, also trace amounts of the decarboxylation products of the non-reacted starting material and intermediate were observed (Figure 2, symbols ○▲).

In another example we evaluated the conversion of ricinoleic acid (**1**) to (*Z*)-10-(heptanoyloxy)dec-8-ene (**7**) (Cascade 2, Figure 3). For this Cat-1 and Cat-5 were combined. The latter comprised recombinant *E. coli* expressing the FadL[4, 12-13], sADH and a Baeyer-Villiger monooxygenase variant from *Pseudomonas putida* KT2440 (E6BVMO_C302L). The biotransformation was initiated by adding ricinoleic acid (**1**, 15 mM) to the culture broth of Cat-5 (Figure 3). After 8 h the transformation of ricinoleic acid into 11-(heptanoyloxy)undec-9-enoic acid (**6**) was nearly complete and Cat-1 was added and

illumination was initiated for another 4 h. 9.7 mM of the desired product 10-(heptanoyloxy)dec-8-ene (**7**) were obtained (Figure 3 and Figure S8a). The overall isolated yield from ricinoleic acid was 52% with a purity of 92% (Figure S8b). Upon addition of the esterase from *Pseudomonas fluorescens* SIK WI (*Pf*-Esterase) the ester product (**7**) could also be hydrolyzed into *n*-heptanoic acid (**8**) and 2-decen-1-ol (**9**) from the ester compound (**7**) (Scheme 1 and Figure S8c).

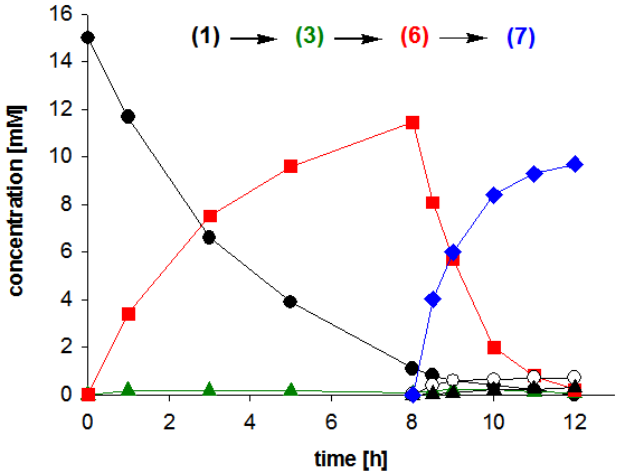
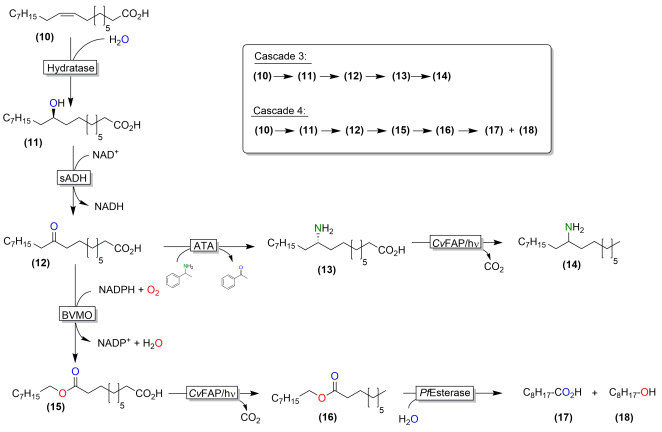


Figure 3. Cascade-2: Biotransformation of ricinoleic acid (**1,** ●) into 10-(heptanoyloxy)dec-8-ene (**7,** ◆) via (Z)-12-oxooctadec-9-enoic acid (**3**, ▲) and 11-heptanoyloxyundec-9-enoic acid (**6,** ■). Conditions: c(**1**) = 15 mM, c(Cat-1 = 3.6 g_{CDW} L^{-1}, c(Cat-5) = 3.6 g_{CDW} L^{-1}, illumination with blue light (λ=450 nm) was initiated at t = 8h. Minor amounts of the decarboxylation products of **1** (○) and **3** (▲) were observed as well.

A key element of the transformations shown above is the hydroxyl functionality present in ricinoleic acid. To broaden the substrate scope, we decided to enlarge the cascades by a C=C-double bond hydration step (Scheme 2). To achieve this, Cat-3 and Cat-5 were supplemented with a fatty acid double bond hydratase (OhyA) from *Stenotrophomonas maltophilia* generating Cat-6 and Cat-7 (Table 2).



Scheme 2. Cascades for the transformation of oleic acid **(10)** into fatty amines **(14)**, fatty acid esters **(16)** or the corresponding acids **(17)** and alcohol **(18)**.[1f, 3, 5b] Details about the catalysts used can be found in Table 2.

Combining Cat-6 with Cat-1 enabled us to transform oleic acid (**10**, 5.2 mM) into 9-aminoheptadecane (**14**) (Cascade 3, Figure 4a). In contrast to Cascade 1, the amine donor for the reductive amination step could not be added from the beginning of the reaction as it severely inhibited OhyA.[3] Nevertheless, the target product 9-aminoheptadecane (**14**) was obtained in an overall 58% conversion (at 3 mM).

Finally, we performed the transformation of oleic acid (**10**, 10.5 mM) into octylnonanoate (**16**) (Cascade 4, Figure 4b). Using a combination of Cat-7 and Cat-1, octylnonanoate (**16**) was obtained at an overall conversion of 69 % (7.2 mM) from ricinoleic acid (Table 2). The ester (**16**) was isolated in an overall yield of 48% with a purity of 90% (Figure S10c). Addition of *Pf*-esterase into the reaction medium resulted in complete hydrolysis of **16** into *n*-nonanoic acid (**17**) and *n*-octanol (**18**).

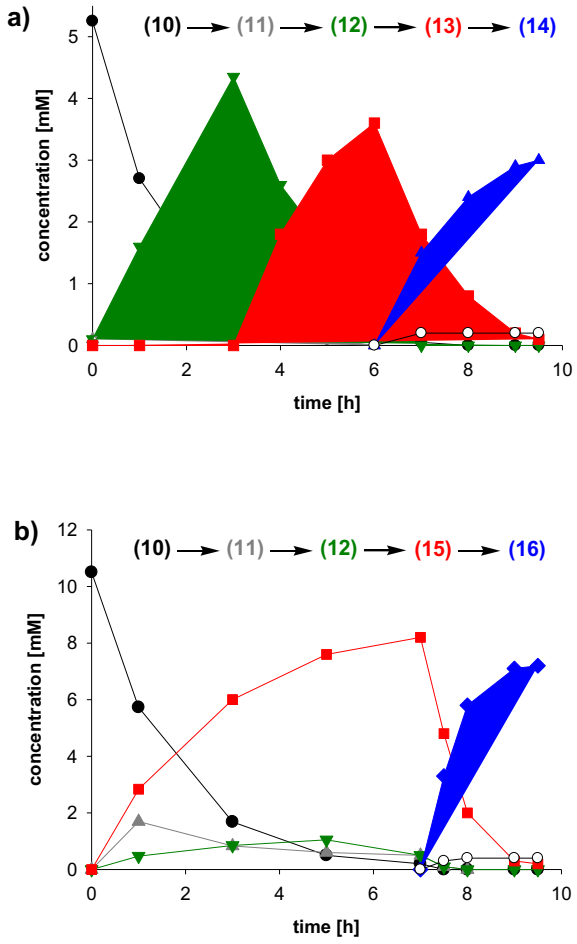


Figure 4. a) Cascade-3: Biotransformation of oleic acid (**10,** ●) into 9-aminoheptadecane (**14,** ▲) via (*R*)-10-hydroxyoctadecanoic acid (**11**, ▲), 10-oxooctadecanoic acid (**12**, ▼) and 10-aminooctadecanoic acid (**13,** ■). Conditions: c(**10**) = 5.2 mM, c(Cat-1 = 3.6 g_{CDW} L^{-1}, c(Cat-6) = 7.2 g_{CDW} L^{-1}, illumination with blue light (λ=450 nm) was initiated at t = 6h. **b) Cascade-4:** Biotransformation of oleic acid (**10,** ●) into octylnonanoate (**16,** ◆) via (*R*)-10-hydroxyoctadecanoic acid (**11**, ▲), 10-oxooctadecanoic acid (**12**, ▼) and 9-(nonanoyloxy)nonanoic acid (**15,** ■). Conditions: c(**10**) = 10.5 mM, c(Cat-1 = 3.6 g_{CDW} L^{-1}, c(Cat-7) = 3.6 g_{CDW} L^{-1}, illumination with blue light (λ=450 nm) was initiated at t = 7h.

Table 1. Summary of the products obtained through the presented photoenzymatic cascades.

Cascade	Products	Final product [mM]	Conversion [%]
-	(*R,Z*)-heptadec-9-en-7-ol (**2**)	9.1	91
1	(*S,Z*)-heptadec-9-en-7-amine (**5**)	3.9	78
2	10-(heptanoyloxy)dec-8-ene (**7**)	9.7	65
3	9-aminoheptadecane (**14**)	3	58
4	octylnonanoate (**16**)	7.2	69

Experimental

A full description of the experimental procedures, analytical details and additional experimental data can be found in the Supporting Information.

Table 2. List of the recombinant biocatalysts used in this study.

Name	Description	Remark
Cat-1	*E. coli* BL21 (DE3) pET28a-Cv-FAP	Photodecarboxylase (Cv-FAP)
Cat-2	*E. coli* BL21 (DE3) pACYC-FadL /pET28a-Cv-FAP	Photodecarboxylase (Cv-FAP) +Fatty acid transporter (FadL)
Cat-3	*E. coli* BL21 (DE3) pACYC-ADH-FadL /pET24b-Vf-ATA$_{_H3\text{-}RA}$	Secondary alcohol dehydrogenase (sADH)+Fatty acid transporter (FadL)+ Amine transaminase (Vf-ATA$_{_H3\text{-}RA}$)
Cat-4	*E. coli* BL21 (DE3) pACYC-ADH-FadL /pET24b-Vf-ATA$_{_H3\text{-}RA_K163D}$	Secondary alcohol dehydrogenase (sADH)+Fatty acid transporter (FadL)+ Amine transaminase (Vf-ATA$_{_H3\text{-}RA_K163D}$)
Cat-5	*E. coli* BL21 (DE3) pAPTm-E6BVMO$_{_C302L}$-ADH /pCon-FadL	Secondary alcohol dehydrogenase (sADH)+Fatty acid transporter (FadL)+ Baeyer-Villiger monooxygenase (E6BVMO$_{_C302L}$)
Cat-6	*E. coli* BL21 (DE3) pACYC-ADH-FadL-OhyA /pET24b-Vf-ATA$_{_H3\text{-}RA}$	Secondary alcohol dehydrogenase (sADH)+Fatty acid transporter (FadL)+ Fatty acid hydratase (OhyA)+Amine transaminase (Vf-ATA$_{_H3\text{-}RA}$)
Cat-7	*E. coli* BL21 (DE3) Δ*infA* harboring pACYC-ADH-FadL-OhyA and pSTAPL_E6BVMO$_{_C302L_M340L}$_Lv3	Secondary alcohol dehydrogenase (sADH)+Fatty acid transporter (FadL)+ Fatty acid hydratase (OhyA)+Baeyer-Villiger monooxygenase (E6BVMO$_{_C302L_M340L}$)

Cv-FAP: photodecarboxylase from *Chlorella variabilis* NC64A, FadL: long chain fatty acid transporter, sADH: secondary alcohol dehydrogenase from *Micrococcus luteus*, Vf-ATA$_{_H3\text{-}RA}$: amine transaminase variant from *Vibrio fluvialis*, Vf-ATA$_{_H3\text{-}RA_K163D}$: the engineered Vf-ATA$_{_H3\text{-}RA}$ to improve enantioselectivity, E6BVMO$_{_C302L}$: engineered variant of the Baeyer-Villiger monooxygenase from *Pseudomonas putida* KT2440, OhyA: fatty acid double bond hydratase from *Stenotrophomonas maltophilia*. See the Table S1 for details of the plasmids.

Acknowledgements

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Keywords: Enzyme catalysis • photodecarboxylase • long chain aliphatic amines and esters • fatty acids • *Escherichia coli*

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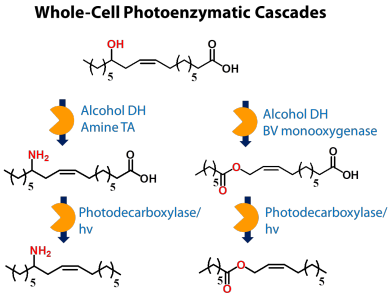
Entry for the Table of Contents

RESEARCH ARTICLE

Long chain aliphatic amines such as (*S,Z*)-heptadec-9-en-7-amine and 9-aminoheptadecane as well as long chain aliphatic esters such as 10-(heptanoyloxy)dec-8-ene and octylnonanoate were prepared at high yields from ricinoleic acid and oleic acid by the whole-cell enzyme cascades using a photoactivated decarboxylase from *Chlorella variabilis* NC64A (Cv-FAP) as a key enzyme in a one-pot process.



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Whole-Cell Photoenzymatic Cascade Transformation of Renewable Fatty Acids into Long Chain Aliphatic Amines and Esters