Biocatalysis

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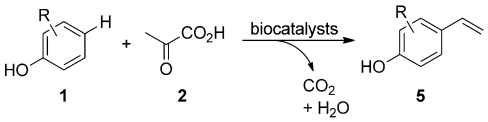
Vinylation of Unprotected Phenols Using a Biocatalytic System

Eduardo Busto, Robert C. Simon, and Wolfgang Kroutil**

Abstract: *Readily available substituted phenols were coupled with pyruvate in buffer solution under atmospheric conditions to afford the corresponding para-vinylphenol derivatives while releasing only one molecule of CO_2 and water as the by-products. This transformation was achieved by designing a biocatalytic system that combines three biocatalytic steps, namely the C–C coupling of phenol and pyruvate in the presence of ammonia, which leads to the corresponding tyrosine derivative, followed by deamination and decarboxylation. The biocatalytic transformation proceeded with high regioselectivity and afforded exclusively the desired para products. This method thus represents an environmentally friendly approach for the direct vinylation of readily available 2-, 3-, or 2,3-disubstituted phenols on preparative scale (0.5 mmol) that provides vinylphenols in high yields (65–83 %).*

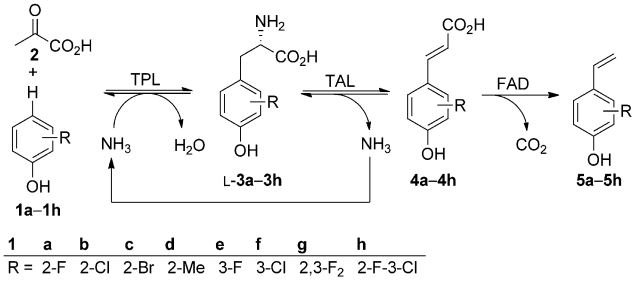
The preparation of vinyl arenes has become a major topic in synthetic organic chemistry[1] as they are in great demand for the preparation of polymers and fine chemicals.[2] Among them, *para*-hydroxystyrene derivatives represent privileged scaffolds that are widely found in advanced materials used for the preparation of chemical and biological sensors,[3] fire retardants, but also pharmaceuticals[4] and important organic compounds.[5] The vinylation of unprotected phenols has been scarcely reported, and only *ortho* functionalization has been achieved thus far.[6] Methods for the preparation of *para*-hydroxystyrene derivatives require a functional group in the *para* position and involve the transformation of *para*-halogenated phenols with transition-metal catalysts in Heck[5b] and Stille couplings,[7] or Knoevenagel[8] and Wittig reactions of the corresponding aldehydes.[9] Biotechnological approaches are limited to the decarboxylation of cinnamic acid derivatives prepared from the corresponding aldehydes.[10]

To the best of our knowledge, no single enzyme is able to catalyze the *para* vinylation of phenols; therefore, a biocatalytic system,[11,12] that is, an in vitro enzyme cascade combining enzymes from different organisms, was designed to achieve the vinylation of phenols in buffer solution. A biocatalytic retrosynthetic analysis[13] revealed that *para*-unsubstituted phenols **1** and pyruvate **2** are suitable starting materials for a synthesis of *para*-vinylphenols **5** where CO_2 and water are the sole by-products (Scheme 1).



Scheme 1. Biocatalytic *para*-selective vinylation of phenols with pyruvate.

In detail, the cascade process[14] was designed based on a combination of three enzymatic reactions: In the first step, the C–C coupling between a phenol and pyruvate catalyzed by a tyrosine phenol lyase (TPL)[15] leads to the formation of L-tyrosine derivatives **3** by ammonia incorporation (Scheme 2). The *para* selectivity is a result of the regioselectivity of the TPL. In the second concurrent step, deamination of **3** by a tyrosine ammonia lyase (TAL)[16] provides coumaric acid derivative **4** and ammonia. The ammonia is reused in the first step. Finally, decarboxylation of **4** catalyzed by a ferulic acid decarboxylase (FAD)[17] leads to the desired vinylated phenol **5**.



Scheme 2. Three-step cascade process for the *para* vinylation of phenols. FAD = ferulic acid decarboxylase, TAL = tyrosine ammonia lyase, TPL = tyrosine phenol lyase.

When testing possible enzymes we found that the recombinant tyrosine phenol lyase from *Citrobacter freundii* and its variant M379V[15c] were most suitable for the C–C coupling step; we chose to use the variant M379V for further experiments because of its broader substrate scope.[15c] This biocatalyst was employed as a cell-free extract. The most promising results for the deamination step were achieved with a TAL from *Rhodobacter spharoides* overexpressed in *E. coli*, which was used as a freeze-dried cell preparation.[16b] The ferulic acid decarboxylase from *Enterobacter* sp. was overexpressed in *E. coli* and also used as a freeze-dried cell preparation for the final decarboxylation step.[17a] We

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assumed that under our reaction conditions, this final step would shift the overall reaction sequence to completion.

To identify a suitable pH value for the three-step cascade process, the pH ranges of the three individual catalysts were compared (see the Supporting Information): The TPL as well as the TAL achieved the highest conversions at more alkaline pH values (pH 8–10 for TPL and pH 10 for TAL) whereas the decarboxylase preferred a pH range of 6–8. As the optimal pH values of the three enzymes are not the same, a compromise had to be found; For this purpose, we studied the dependence of the overall cascade process on the pH value using 2-fluorophenol (**1a**) as the substrate (Figure 1). The

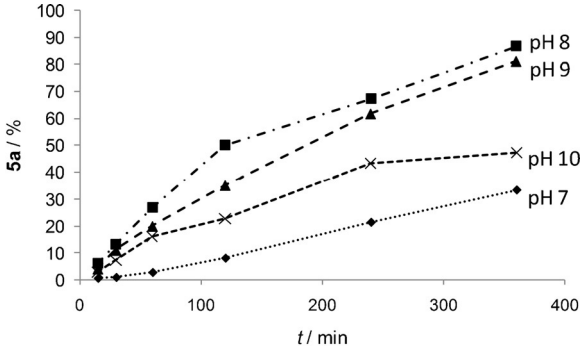


Figure 1. Conversion into vinylphenol **5a** at various pH values. Reaction conditions: **1a** (23 mM), pyruvate (46 mM), NH_4Cl (180 mM), buffer (50 mM; potassium phosphate for pH 7–8, CHES for pH 9–10), PLP (0.04 mM), TPL (M379V, 1.2 U, 4 mg cell-free extract), TAL (0.18 U, 20 mg freeze-dried *E. coli*/TAL), FAD (10.5 U, 5 mg freeze-dried *E. coli*/FAD), Et_2O (5% v/v), 30°C, 850 rpm.

highest concentrations of **5a** were obtained at pH 8 in phosphate buffer and at pH 9 in CHES buffer. Even though the two results are comparable, further experiments were performed at pH 8 in the phosphate buffer as this buffer is less expensive and thus more suitable for future applications. The slower product formation that was observed at pH 7 was most likely due to the lower activity of the two lyases (TPL, TAL) under these conditions (see the Supporting Information for a detailed reaction course). On the other hand, the slower formation of **5a** at pH 10 and the accumulation of coumaric acid **4a** are due to the low activity of the FAD at high pH (see the Supporting Information).

Reactions were performed in a solution containing Et_2O (5% v/v) as co-solvent[15c] as slightly better results were obtained compared with the reactions in the absence of this additive or with a water-miscible co-solvent such as DMSO (see the Supporting Information).

In the next optimization step, the equivalents of pyruvate and ammonium chloride were varied. When 0.5 equivalents of NH_4Cl were used, the cascade process led to the formation of vinylphenol **5a** in 55% within 16 hours (Table 1, entry 1). When the amount of NH_4Cl was increased to 180 mM (entries 2–4) at a pyruvate concentration of 46 mM, the desired product **5a** was formed in >99% conversion when measured after 16 hours. The formation of undesired side products, for example, by *ortho* vinylation, was not detected.

Table 1: Vinylation of 2-fluorophenol (**1a**) at various ammonium concentrations.[a]

Entry	NH_4^+ [mM]	**2** [mM]	**5a**[b] [%]
1	12	46	55
2	23	46	72
3	46	46	93
4	**180**	**46**	**>99**
5	180	23	88

[a] Reaction conditions: **1a** (23 mM), pyruvate, NH_4Cl, PLP (0.04 mM), TPL M379V (1.2 U, 4 mg cell-free extract), TAL (0.18 U, 20 mg freeze-dried *E. coli*/TAL), FAD (10.5 U, 5 mg freeze-dried *E. coli*/FAD), potassium phosphate buffer (50 mM, pH 8), Et_2O (5% v/v), 30°C, 16 h, 850 rpm. [b] Determined by reverse-phase HPLC analysis.

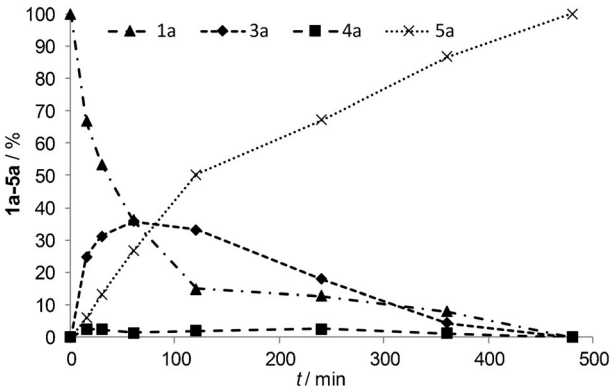


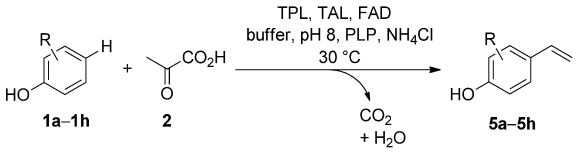
Figure 2. Time course for the biocatalytic vinylation of 2-fluorophenol (**1a**) into 2-fluoro-4-vinylphenol (**5a**). Reaction conditions: **1a** (23 mM), pyruvate (46 mM), NH_4Cl (180 mM), PLP (0.04 mM), TPL M379V (1.2 U, 4 mg cell-free extract), TAL (0.18 U, 20 mg freeze-dried *E. coli*/TAL), FAD (10.5 U, 5 mg freeze-dried *E. coli*/FAD), potassium phosphate buffer (50 mM, pH 8), Et_2O (5% v/v), 30°C, 850 rpm.

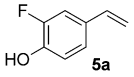
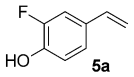
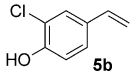
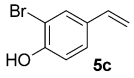
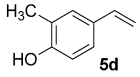
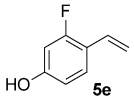
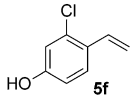
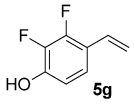
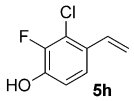
Furthermore, polymerization of the vinylphenols is not an issue under these reaction conditions.

Following the bio-vinylation of **1a** to **5a** over time at pH 8 and 30°C revealed that the concentration of tyrosine derivative **3a** reached a maximum after 60 min (Figure 2). The permanently low concentration of coumaric acid derivative **4a** indicated that the decarboxylation step is significantly faster than the previous step under the conditions employed. The concentration of the final vinylphenol **5a** increased linearly for the first three hours; then, its formation slowed down, and the reaction reached completion after eight hours. The reaction course indicates that the deamination reaction catalyzed by the TAL is the rate-determining step of the cascade process under these conditions as tyrosine derivative **3a** was accumulated in the reaction mixture. This is in agreement with the activity values measured for the three catalysts (see the Supporting Information).

The scope of the method was explored with a variety of 2- or 3-substituted phenols (Table 2). Aside from 2-fluorophenol (**1a**), phenols with a chloro (**1b**), bromo (**1c**), or methyl (**1d**) substituent in the 2-position were also successfully vinylated with >99% conversion (entries 1–5). The biovinylation was also successful for 3-substituted phenols such as 3-fluoro- (**1e**) or 3-chlorophenol (**1f**). Furthermore, 2,3-disubsituted phe-

Table 2: Preparative-scale experiments for the biocatalytic vinylation of phenols.[a]



Entry	Substrate	**1** [mM]	Product **5**	Conv.[b] [%]
1	**1a**	23	 **5a**	>99 (69)
2[d]	**1a**	46	 **5a**	>99 (71)
3	**1b**	23	 **5b**	>99 (68)
4	**1c**	10	 **5c**	>99[c]
5	**1d**	10	 **5d**	>99[c]
6[d]	**1e**	46	 **5e**	>99 (77)
7	**1f**	23	 **5f**	>99 (83)
8	**1g**	46	 **5g**	>99 (65)
9[d,e]	**1h**	23	 **5h**	>99 (65)

[a] Reaction conditions: Phenol **1**, pyruvate (2 equiv), NH_4Cl (180 mM), TPL (50 mg, 15 U, cell-free extract), TAL (200 mg, 1.84 U, *E. coli* whole cells), FAD (50 mg, 105 U, *E. coli* whole cells), potassium phosphate buffer (pH 8, 10 mL, 50 mM), Et_2O (5% v/v), 30°C, 120 rpm, 24 h. [b] Neither starting material **1** nor the intermediates L-**3** or **4** were detected. Conversions were determined by reverse-phase HPLC analysis. Yields after flash column chromatography are given in parentheses. [c] Experiment performed on analytical scale, see the Supporting Information. [d] Double amounts of the three biocatalysts were used. [e] Reaction time: 48 h.

nols, such as 2,3-difluoro- (**1g**) and 2-fluoro-3-chlorophenol (**1h**), were efficiently transformed into the corresponding *para*-vinylphenols (entries 8 and 9). Several of these vinylated phenols have not been prepared before (**5a** and **5c**) or have not even been described (**5f** and **5h**),[18] which clearly shows that the simple method presented in this manuscript expands the range of vinylphenols that can be prepared.

The *para* vinylation could also be carried out on preparative scale, leading, for instance, to the isolation of fluorinated product **5a** in 71% yield after filtration through silica gel when the reaction was performed at a phenol concentration of 46 mM (entry 2). Preparative transformations of 2-chlorophenol (**1b**), 3-substituted phenols (**1e** and **1f**), as well as 2,3-disubstituted phenols (**1g** and **1h**) corroborated the potential of our method, as the corresponding vinylated phenols were isolated in 65–83% yield (Table 2).

In conclusion, *para*-unsubstituted phenol derivatives were transformed into the corresponding *para*-vinylphenols in a three-step biocatalytic cascade process comprising a C–C coupling, deamination, and decarboxylation. The overall reaction required only pyruvate as a stoichiometric reagent, leading to the formation of CO_2 and water as the sole by-products. The transformations were performed at substrate concentrations of 10–46 mM leading to >99% conversion within 8–24 h and good yields of isolated products (65–83%). A novel method for C–C bond formation[19] and an environmentally friendly and mild route for the efficient preparation of *para*-vinylphenol derivatives, intermediates that are required for the synthesis of various advanced materials, have thus been developed.

Experimental Section

Representative procedure for the *para* vinylation of phenol **1a**: Recombinant TPL M379V from *C. freundii* (15 U, 50 mg cell-free extract), TAL from *R. spharoides* (3.68 U, 400 mg freeze-dried *E. coli*/TAL cells), and FAD from *Enterobacter* sp. (105 U, 50 mg freeze-dried *E. coli*/FAD cells) were rehydrated in a potassium phosphate buffer (50 mM, 180 mM NH_4Cl, 0.04 mM PLP, pH 8, 10 mL) for 10 min at 30°C and 120 rpm. Then, phenol **1a** (42 μL, 0.46 mmol, 46 mM) dissolved in Et_2O (500 μL) and pyruvate (101.2 mg, 0.92 mmol, 92 mM) were added to the mixture, and the reaction was incubated for 24 h at 21°C and 170 rpm. The reaction was stopped by the addition of an aqueous saturated NH_4Cl solution (5 mL) and extracted with EtOAc (3×15 mL). The combined organic phases were dried (Na_2SO_4), and the solvent was evaporated under reduced pressure (100 mmHg). The crude product was purified by flash chromatography on silica gel (20% EtOAc/hexane) to afford the corresponding vinylphenol **5a** as a colorless oil (45 mg, 71%).

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Keywords: biotransformations · cascade reactions · C–C bond formation · enzyme catalysis · vinylation

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