Biocatalytic redox reactions of allylic alcohols catalysed by microorganisms

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Abstract

Study of the allylic alcohols behavior in biocatalysis reactions employing whole cells of the yeasts *Candida albicans* and *Saccharomyces cerevisiae* as well as the enantioselective reduction of substituted double bonds.

Key words: Allylic alcohols, biocatalysis, enantioselective reduction.

Introduction

Allylic alcohols are abundant in natural products such as essential oils and are widely used as components of industrial food, fragrance and pharmaceutical. Biocatalysis uses free enzymes or whole cells as catalysts in organic chemistry reactions and it is a great tool of green chemistry.¹

Results and Discussion

The first substrate studied was cinnamyl alcohol (**1**), 50 mg, 3g of *C. albicans* (CCT 5847) and 10 mL of water, after 24 hours it was obtained the compound **4**:

2 and **3** are probably reaction intermediates because the aldehyde works as an activating group to reduce the double bond. The biocatalysis of cinnamyl alcohol (**1**) catalyzed by *S. cerevisiae* gave distinct results depending of substrate matrices. Dihydrocinnamic acid (**4**) was the only product detected after 7 days when **1** was adsorbed in XAD-7 resin, while the dihydrocinnamyl alcohol (**5**) was the major product observed when substrate was dispersed in cellulose (fragments of filter paper), and cinnamic acid (**6**) was also detected with 10% conversion after 72 hours of reaction.

The biocatalysis of cinnamaldehyde (**2**) was studied with *C. albicans* and *S. cerevisiae*. **2** was totally converted into dihydrocinnamic acid (**4**) after 113 hours when the substrate was dispersed in cellulose. But when the resin is applied the reaction did not complete, **4**, **5** and **6** was still observed after 6 days of reaction (**Table 1**).

Table 1. Biocatalysis of cinnamaldehyde (**2**) with *C. albicans*

Time	Cellulose		Resin XAD-7		
	5 (%)	4 (%)	5 (%)	4 (%)	6 (%)
113 h	--	100	72	23	5
144 h	--	100	81	15	4

Studies with α -methyl cinnamyl alcohol (**7**) adsorbed in XAD-7 resin provided interesting results about enantioselective reduction of the double bond, yielding the acid (*S*)-**8** with 100% of conversion, 83% ee, $[\alpha]_D^{20} = +21^\circ$, lit. $[\alpha]_D^{20} = -35,3^\circ$ (*R*)² after 8 days of reaction:

The use of *S. cerevisiae* as biocatalyst promoted an enantioselective hydrogenation higher than *C. albicans*, 60 % of (*S*)-**8** was observed with >99% ee after 6 days of reaction, when the substrate **7** was adsorbed in XAD-7 resin. α -Methyl dihydrocinnamyl alcohol was the major product when the substrate **7** was dispersed in cellulose and reacted with *S. cerevisiae*, what shows the differences of products caused by which matrix the substrate is dispersed.

Conclusions

The yeast *C. albicans* was able to oxidize cinnamyl alcohol (**1**) to its hydrogenated acid **4** in 24 hours, while *S. cerevisiae* did it in 7 days, both using XAD-7 resin as adsorbent matrix. The use of *S. cerevisiae* and substrate **1** dispersed in cellulose furthered the formation of **5** instead of its acid **4**. The oxidation of **1** to **2** is a fast process step based in the fact of biocatalysis of **2** did not occur any faster compared to reaction of **1**. Biocatalysis of α -methyl cinnamyl alcohol (**7**) with whole cells of *C. albicans* furnished the acid **8** with 83% ee while the yeast *S. cerevisiae* provided the same acid with elevated ee (>99%).

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¹ Sheldon, R. A. *Chem. Soc. Rev.*; **2012**, 41, 1437

² Colpaert, F.; Manginckx, S.; Verniest, G.; De Kimpe, N.; *Journal of Organic Chemistry*; **2009**, 79(10), 3792-3797