Cascade Redox Reactions with allylic alcohols in biocatalysis

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Abstract
Study of the allylic alcohols behavior in biocatalysis reactions employing whole cells of the yeast Candida albicans as well as the enantioselective reduction of C = C substituted bonds.

Key words: allylic alcohols, biocatalysis, cascade reactions.

Introduction

Allylic alcohols are abundant in natural products such as essential oils and are widely used as majoritarian 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 cinnamic 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. Studies with α-methyl cinnamic alcohol (5) provided interesting results about enantioselective reduction of the double bond, yielding the acid (S)-6 with 100% of conversion, 83% ee, [α]₀⁺₂₀ = +21°, lit. [α]₀⁺₂₀ = -35,3° (R)² after 8 days of reaction:

It was also studied some terpenes like geraniol (7) and its isomer (Z) nerol (12).

For an experiment done with 50 mg of 7, we obtained the following reaction behavior:

Image 1. Study of geraniol biocatalysis catalyzed by C. albicans. 10 and 11 are intermediates.

It was obtained 93% of (R)-3, derivatized to methyl ester, 70% ee, [α]₀⁺₂₀ = +2°, lit. [α]₀⁺₂₀ = +8.4°.³ For 12, the same (R) enantiomer was obtained:

Conclusions

C. albicans was effective to reduce the double bond and to oxidate primary alcohols to its acids α or β-substituted enantiomerically enriched. It is an unprecedented fact in literature.

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³ Flachsbart, B.; Fritzche, M.; Weldon, P., J.; Schulz, S.; Chemistry & Biodiversity 2009, 6 (1), 1-37