Study of the biorreduction of halogenated enones by supported microorganisms
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Abstract
The catalytic efficiency of enzymes from *Saccharomyces cerevisiae* can be applied to biocatalysis. The main enzymes found in *S. cerevisiae* are Alcohol Dehydrogenases (ADH) and Old Yellow Enzymes (OYE). ADH and OYE rapidly reduce compounds such as 3-bromo-4-phenyl-3-buten-2-one thus complicating the acquisition of their reaction intermediates, such as α-bromoketone. Through the use of biphasic systems and immobilisation techniques it is possible to increase the chemoselectivity of these reactions in order to obtain α-bromoketone by preferential olefin reduction by OYE.

Key words: Immobilisation, *Saccharomyces cerevisiae*, 3-bromo-4-phenyl-3-buten-2-one.

Introduction

Biocatalysis involving *S. cerevisiae* is largely employed in organic synthesis due to the efficiency of the enzymes ADH and OYE. Carbonyl compounds with an electron-withdrawing group, e.g. 3-bromo-4-phenyl-3-buten-2-one (1), are rapidly reduced by the actions of ADH and OYE, which complicates the process of obtaining the α-bromoketone intermediate (2). Immobilisation of the *S. cerevisiae* in a calcium alginate gel allows for the confinement of the cells inside a physical structure which not only decreases the amount of available 3-bromo-4-phenyl-3-buten-2-one, but also isolates the reduction pathway and the number of purification steps of the product.

Results and Discussion

Biphasic systems of water-solvent resulted in the best rates of olefin reduction and decreased the reaction velocity of ketone reduction (Fig. 1). In order to optimise the production of α-bromoketone, the following conditions were optimised: mass of cells, proportion water-solvent and volume of solvent.

![Figure 1. Reduction of 3-bromo-4-phenyl-3-buten-2-one by *Saccharomyces cerevisiae*](image)

The optimum condition was that of a biphasic system of water-ionic liquid [bmim(PF6)] at a ratio of 5:1 with 5g of cells. This resulted in an increase of α-bromoketone and near total consumption of 3-bromo-4-phenyl-3-buten-2-one in 24 hours (Fig. 2). These data were tested by scaling up the reaction (5x) to assess its reproducibility. The substrate and products were analysed by gas chromatography–mass spectrometry.

![Figure 2. Profile of 3-bromo-4-phenyl-3-buten-2-one reduction by *S. cerevisiae* immobilized in calcium alginate gel using water-[bmim(PF6)] (5:1) as solvent](image)

Conclusions

The desired α-bromoketone was obtained through immobilisation of the yeast in calcium alginate gel using water-[bmim(PF6)] (5:1) as solvent, allowing the isolation of α-bromoketone in appropriate quantity for analyses.

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