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Flavors and fragrances produced from the biocatalytic oxidation of α -pinene

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PURPOSE OF THE ABSTRACT

Alpha-pinene is the main component of the monoterpenoidic fraction in some essential oils (mastic oil) and turpentine (residue from paper and pulp industry) [1]. We present here two routes for its valorization following the biocatalytic oxidation of alpha-pinene to valuable flavors and fragrances (e.g. alpha-pinene oxide, camphene, campholenal, verbenol and verbenone).

In the first one, alpha-pinene was oxidized to α -pinene oxide and other derivatives such as campholenal, camphene, carveol, verbenol and verbenone. The investigated biocatalytic system consisted of a lipase-based cross-linked aggregates design (i.e. cross-linked enzyme aggregates (CLEA) and cross-linked enzyme aggregates onto magnetic particles (CLEMPA)) [2]. Additionally, a bifunctional biocatalyst (lipase/biopolymer catalyst) was successfully tested for the alpha-pinene oxidation followed by product isomerisation [3]. For both cases, lipase catalyzed an efficient oxidation of alpha-pinene using H₂O₂ as oxidation reagent and ethyl acetate as both acetate-supplier and solvent (maximum 60 % conversion of alpha-pinene with the main selectivity of 40 % alpha-pinene oxide, 15 % camphene and 20 % campholenal).

The second route followed the alpha-pinene valorization in a biphasic enzyme-based catalytic system allowing the allylic oxidation of alpha-pinene with the production of verbenole and verbenone [4]. The two phases consisted of: i) an organic solvent (e.g. pentane) hosting alpha-pinene (substrate) and its derivatives (the reaction products), and ii) a buffer phase with the peroxidase enzyme as biocatalyst and H₂O₂ as oxidation reagent. Alpha-pinene was oxidized at the allylic position via a radical mechanism. The biphasic design of the biocatalytic system avoided the inconvenience of the poor substrate/product solubility in the aqueous phase. Also, faster kinetic and promising perspectives of the process efficiency were provided using only one enzyme instead of whole cell (multi-enzyme complex), very commonly for actual biotechnologic processes.

New perspectives on using biocatalysis as synthetic alternative to flavors and fragrances industry will be also considered: (i) for the production of carvacrol, campholenal, alpha-pinene oxide, verbenol and verbenone; (ii) to enhance the efficiency of the enzyme systems; (iii) to enable "green strategies" for chemical processes; and (iv) to design versatile systems for the valorization of monoterpenes.

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS

biocatalysis | enzyme | α -pinene | flavors/fragrances

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