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Abstract

Biocatalytic Preparation of Perillic Derivatives as an Alternative to Limonene Valorization †

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Perillic-type derivatives of limonene from the class of the oxygenated derivatives have not been effectively utilized to date, despite the large number of applications that they can fulfill based on their phytochemical properties [1,2]. Perillyl derivatives (e.g., alcohol, aldehyde, and acid) are plant compounds designed as monoterpenes with low toxicity and prominent biological action, called phytochemicals, which are considered valuable intermediates for functional foods and novel therapies. They are increasingly important for their flavors, antimicrobial properties, and anticancer properties [3,4]. The aim of this study was the development of an alternative for the biocatalytic preparation of perillic acid from perillic aldehyde. Aldehyde dehydrogenase will catalyze the biocatalytic transformation of perillic aldehyde.

The tests were performed in 2 mL Eppendorf tubes. The sample contained 1mM perillic aldehyde, 1 mM NAD^+, biocatalyst (aldehyde dehydrogenase such as F-ALDH, ALD-S1, and ALD-S2), and buffer, until a volume of 1000 µL was reached in each reaction vessel. The mixture was vortexed for 10 minutes and then incubated in the thermoshaker for 24h, 1000 rpm, at a temperature of 25 °C. After reaction, the sample content was monitored using an HPLC-DAD system. Before analysis, the sample was mixed with the mobile phase (1:1, v/v). An analysis was performed in an isocratic regime using 20:20:60 acetonitrile/sulfuric acid/water as a composition of the mobile phase, 1 mL/min of flow rate, a reaction time of 30 min, and 10 µL of injected volume, at a temperature of 60 °C of the detector.

The oxidation reaction of perillic aldehyde to perillic acid was studied. The reaction was catalyzed by aldehyde dehydrogenase in the presence of a NAD^+ cofactor. The screening of the enzyme biocatalyst was performed initially in the presence of three different enzymes, aldehyde dehydrogenase type (F-ALDH, ALD-S1, ALD-S2). Moreover, the experimental parameters of the biocatalytic system have been optimized in order to increase the process efficiency. The performance of the system was evaluated by calculating the conversion of perillic aldehyde and selectivity to perillic acid. The biocatalysts ALD-S1 and ALD-S2 showed a similar behavior. A substrate conversion of 80% has been achieved, with a total selectivity in perillic acid. We developed a biocatalytic approach for the efficient conversion of perillic aldehyde into acid derivatives, which is a valuable alternative to limonene valorization from the biomass residues.

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