Biomimetic oxidation of $\alpha$-pinene with tetrakis(1-methyl-4-pyridyl)porphyrin immobilized in sol-gel matrix

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The hydrocarbone $\alpha$-pinene is an attractive precursor substrate for bioconversion into valuable natural flavour and fragrance compounds (such as verbenone and pinocarvone), because of its widespread and low price. Pinenes ($\alpha$- and $\beta$-) are major component of turpentine, a by-product of the pulp making industry. One of the approaches in controlled and selective biotransformation of monoterpenes (under mild conditions) is the use of porphyrins as biomimetic catalysts. It would allow to overcome problem of the traditional biocatalysts sensitivity to toxic terpenes. Therefore elaboration of biomimetic catalysis using enzymes or porphyrins imitating enzymes on the column with immobilized biocatalyst is desirable.

The work is aimed at investigation of a novel method of $\alpha$-pinene biotransformation to pinocarveol and pinocarvone, using water-soluble porphyrins immobilized in sol-gel matrix. We have concerned on the optimal conditions of $\alpha$-pinene oxidation by tetrakis(1-methyl-4-pyridyl)porphyrin ($H_2TMePyP$). During our initial studies, we have examined and compared the ability of four commercially available porphyrins to catalyse oxidation of $\alpha$-pinene in chloroform. Analysis of terpenes was performed using a GC and GC-
MS techniques. The best catalyst for \( \alpha \)-pinene biotransformation was \( \text{H}_2\text{TMePyP} \) which gave the highest accumulation of \textit{trans}-pinocarveol, pinocarvone and a mixture of mytrenol and mytrenal. The impact of several parameters on this biotransformation has been investigated and optimized, including: the selection of appropriate organic solvent, substrate concentration, convenient acceptor/donor of electrons and oxygenating agent. It was shown that immobilized \( \text{H}_2\text{TMePyP} \) does not change its activity during ten photo catalytic cycles, without addition of any cocatalyst or cosubstrate. No oxidative products were detected in the absence of light. A water-soluble cationic porphyrin immobilized in sol-gel matrix acts as biomimetic catalyst in the oxygenation of cheap and readily available natural precursor, \( \alpha \)-pinene and would be a mild and clean method of pinocarveol, pinocarvone and myrtenol production, which are the components of the aggregating pheromones of the woodworms, and due to that can be used in the fight with the pests of the conifer trees.

\textbf{H}_2\text{TMePyP, sol-gel catalyst, }\alpha\text{-pinene, oxidation}