



Full paper/Mémoire

Limonene as an agro-chemical building block for the synthesis and extraction of bioactive compounds



Utilisation du limonène comme synthon agrochimique pour la synthèse et l'extraction de produits naturels

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ABSTRACT

The objective of this study was to transform limonene as an agro-chemical platform for the production of a wide range of added-value compounds for pharmaceutical, cosmetic and food ingredients. This molecule was also evaluated as an alternative solvent for the extraction of several bioactive compounds compared to *n*-hexane. Limonene was extracted from the essential oils of orange peels through a solvent-free microwave extraction technique. Limonene was successfully transformed into products with industrial interest by catalytic oxidation using three different iron catalysts. The ability of limonene to be used as an alternative solvent was performed using two simulation tools, Hansen solubility parameters (HSPs) and the Conductor-like Screening Model for Real Solvents (COSMO-RS), and via experimentation. The results indicated that limonene could be a promising green solvent and synthon for petroleum substitution in the extraction or synthesis of bioactive compounds.

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R É S U M É

L'objectif de cette étude est de montrer les potentialités du limonène comme une plateforme agrochimique pour la production d'une large gamme de composés à valeur ajoutée pour les industries pharmaceutique, cosmétique et agroalimentaire. Cette molécule a été évaluée en tant que synthon pour la synthèse de molécules bioactives et comme solvant alternatif à l'hexane pour l'extraction de composés bioactifs. Deux outils de simulation solvant-soluté ont été utilisés pour simuler et optimiser les potentialités du limonène : les paramètres de solubilité Hansen (HSP) et le modèle « Conductor-like Screening Model for

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Real Solvents » (COSMO-RS). Les résultats indiquent que le limonène peut être un solvant vert et un synthon prometteur pour la substitution du pétrole dans l'extraction ou la synthèse de composés bioactifs.

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1. Introduction

D-Limonene belongs to the family of terpenes and is the major constituent of the essential oils resulting from citrus fruit skins. With a production of more than 50 million tons, the orange juice industry represents an important source for D-limonene and a challenging research pilot platform for the valorisation of by-products. It is considered as a GRAS (Generally Recognized as Safe) material by the U.S. Food and Drug Administration and plays an important role in flavors and fragrances as well as acts as a cleaning/degreasing agent in industrial and in household applications [1,2]. The growing interest in D-limonene has emerged since its cleaner and degreaser qualities were recognized and taken into consideration [3]. In this respect, this molecule has been designated as an efficient alternative for halogenated carbon hydrates or conventional degreasing agents used in industry and households. In their attempt to develop an industrial application for D-limonene, different authors [4–6] have indicated, recently, the high suitability of this molecule as a synthon and solvent for the synthesis and extraction of natural compounds to replace petroleum-based chemicals and solvents such as *n*-hexane. Likewise, D-limonene is a versatile compound that can be oxidized to produce diverse compounds used in the production of fragrances, perfumes and food additives.

Ever since the first reaction carried out by Bordenca in 1951 [7] using nitrosyl-chloride, background information on the catalytic oxidation of D-limonene can be found in many papers. In recent years, many attempts have been reported to transform D-limonene into high-added-value compounds. In this context, *Penicillium digitatum* was used to carry out the biotransformation of D-limonene to α -terpineol [8]. Likewise, Maróstica Jr. et al. [9] investigated the production of *R*-(+)- α -terpineol by the biotransformation of D-limonene from orange essential oils, using cassava waste water as a suitable substrate for mycelial growth medium. Moreover, the bioconversion of (+)-limonene to get (+)- α -terpineol using *Pseudomonas gladioli* as the biocatalyst was carried out [10].

α -Terpineol, or its acetate analog, has also been synthesized using various chemical methods [11] through different acids (chloroacetic acid, acetic acid, formic acid, etc.) using different catalysts (cation exchange resin, zeolite, ferric sulphate) and oxymercuration followed by reduction with sodium borohydride. Further, catalytic oxidation of D-limonene leads to oxidized compounds with more or less efficiency and selectivity, up to the catalyst, such as metal complexes [12]. Liquid-phase oxidation (LPO) of hydrocarbons is another important methodology for the manufacturing of valuable organic

compounds that has been developed in several industrial processes. LPO can be performed with different oxidants and, in the presence of a suitable catalyst, it can take place under relatively mild conditions of temperature and pressure. Pena et al. [13] carried out the LPO of limonene with molecular oxygen as the sole oxidizing agent under non-solvent conditions in the presence of three different nickel-aluminium hydrotalcites. Several oxygenated limonene derivatives such as endo- and exo-epoxides, carveol and carvone represented 45–60% of the whole amount of products obtained.

Due to the need for environmentally friendly processes and products, sustainable chemistry has prompted a great amount of research into the processing of renewable feedstock to obtain platform molecules and downstream end products [14]. In this context, the methodology applied in this study was focused on the biorefinery concept because D-limonene was obtained by solvent-free microwave extraction from orange peels, an agricultural by-product from the orange juice industry, followed by a deterpenation process (Fig. 1). Finally, D-limonene was used as feedstock in two different procedures. First, this compound was employed as the starting material (agro-synthon) to synthesize other high value products with industrial interest. This process was performed through an oxidation reaction using three iron supported catalysts, two mesoporous supports (Fe-SBA 15 and Fe-F16SM) and a double lamellar hydroxide support (Fe-LDH). This process works on the principle of generating free radicals (such as HO[•]).

Otherwise, alternatives to conventional extraction procedures or to conventional petroleum solvents may increase production efficiency and contribute to environmental preservation by replacing the use of petroleum solvents by bio-solvents and reducing fossil energy and generation of hazardous substances. The drive to reduce CO₂ and volatile organic compound (VOC) emissions, chemical and food industries are in search of new technologies in order to reduce energy and solvent consumption, to meet legal requirements on emissions, product/process safety and increased quality as well as functionality. Solvent extraction of natural products is one of the promising innovation themes that could contribute to the sustainable growth of chemical and food industries. So, D-limonene was used as an alternative solvent to substitute *n*-hexane in the extraction of bioactive natural products (carotenoids, oils and aromas). In addition, the study of the extraction of bioactive compounds combines an experimental procedure with a theoretical approach carried out by means of two computational simulation methods, Hansen solubility parameters (HSP) and predictive computational COSMO-RS (Conductor-like Screening Model for Real Solvents) software.

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