J. of Supercritical Fluids 61 (2012) 191–198

Contents lists available at SciVerse ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Combination of supercritical carbon dioxide and ionic liquid in a novel assembly of carvacrol

Catarina I. Melo[a], Rafał Bogel-Łukasik[a,b], Ewa Bogel-Łukasik[a,*]

[a] REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[b] Laboratório Nacional de Energia e Geologia, I.P., Unit of Bioenergy, Estrada do Paço do Lumiar 22, 1649-038 Lisbon, Portugal

ARTICLE INFO

Article history:
Received 2 September 2011
Received in revised form 4 October 2011
Accepted 5 October 2011

Keywords:
Hydrogenation
Separation
Extraction
Carvacrol
Supercritical carbon dioxide
Ionic liquids

ABSTRACT

Exploitation of neoteric solvents in the efficient total synthesis of carvacrol, an antimicrobial reagent, has been accomplished. The first reaction aimed supercritical mediated heterogeneous hydrogenation of carvone catalysed by palladium. The second step guided to an application of great salvation capacity of ionic liquids in separation of carvacrol from the post-hydrogenation mixture. The process has been completed by use of a high pressure CO_2 potential to extract carvacrol from the ionic liquid reservoir.

1. Introduction

Carvacrol is a natural plant chemical, one of the major components of oregano and thyme essential oils. Due to its antimicrobial properties and low toxicity accompanied by odour of oregano and a pizza-like taste, carvacrol is a food additive to prevent bacterial contamination [1]. Among antimicrobials, carvacrol has been applied to potato puree, table grapes, chicken and sprouts [2]. An incorporation of carvacrol into the *Gelidium corneum* film used for processed food and pharmaceutical products improved an antimicrobial activity as well as a mechanical property of the film. Due to its specific properties, carvacrol is an important chemical and methods of synthesis different than extraction from the natural plants are studied extensively. Up to now, the moderate to high temperature methods for production of carvacrol have been reported. Carvacrol was produced by Friedel–Crafts alkylation of o-cresol with isopropanol using superacidic catalysts at 180 °C within 2 h with selectivity of 82% at almost complete conversion [3]. In aromatization of carvone, in presence of 6 M H_2SO_4 with Amberlyst 15 acid catalyst started at 75 °C and proceeded by an exothermic effect of the reaction at 180 °C within 1 min, carvone was completely converted into carvacrol [4]. In other acid catalysed isomerisation of carvone to carvacrol, use of 6 M sulphuric acid was reported [5,6]. The isomerisation of carvone in water at 250 °C yielded a 95% of carvacrol [7]. All of the mentioned methods of carvacrol synthesis are characterised by relatively high yields of the reaction (60–100%), but unfortunately their drawbacks are the use of hazardous chemicals, of moderate or high temperature and the production of wastes' stream.

Supercritical CO_2, a promising solvent for organic synthesis [8], applied as a medium in hydrogenation facilitates reaction [9] due to total miscibility of gases and reduction in mass transfer limitations and viscosities of the obtained mixtures. The favourable solubilities of CO_2 in terpenes [10–12] and terpenoids [13] allowed executing the hydrogenation reaction in the high-pressure CO_2 [14].

Ionic liquids (ILs) are other solvents offering the flexible physical properties. They are characterised by near-zero vapour pressure [15], thermal stability [16] and widely tuneable properties as regards polarity, hydrophobicity and miscibility with other solvents [17,18] through appropriate modification of the cation and anion. The negligible vapour pressure of ILs is an interesting feature which makes them easily recyclable and reusable. Furthermore, a very low vapour pressure of ILs reduces the risk of explosion that is a clear advantage over the use of the classical volatile solvents [15]. Ionic liquids have found an application in many chemical reactions [19–22] and processes including extraction and separation [23–27].

In this work, we attempted to produce carvacrol for the first time in mild conditions using alternative solvents in a three-step process aiming at: (1) synthesis of desired carvacrol in the heterogeneously catalysed hydrogenation of cheap carvone occurred in $scCO_2$; (2) separation of carvacrol from the post-hydrogenation mixture using

* Corresponding author. Tel.: +351 212948500 ext. 10941; fax: +351 212948550.
E-mail address: ewa@dq.fct.unl.pt (E. Bogel-Łukasik).

0896-8446/$ – see front matter
doi:10.1016/j.supflu.2011.10.005