C. R. Chimie 17 (2014) 1268–1275

Contents lists available at ScienceDirect

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Extraction of aroma compounds in blackcurrant buds by alternative solvents: Theoretical and experimental solubility study

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ARTICLE INFO

Article history:
Received 27 January 2014
Accepted after revision 24 March 2014
Available online 30 July 2014

Keywords:
Alternatives solvent
Extraction
Aroma
Blackcurrant buds
Hansen solubility parameter

ABSTRACT

This study was designed to evaluate the performance of nine alternative solvents (α-pinene, MeTHF, ethyl acetate, methyl acetate, ethyl lactate, butanol, isopropanol, ethanol and CO_2 supercritical fluid) for extracting aromas from blackcurrant buds (*Ribes nigrum* L) compared to that of *n*-hexane, commonly used. This study has been performed via experimentation and simulation using Hansen solubility methodology for the comprehension of the dissolving mechanism. Experimentally, the extracts were analysed to compare the solvents performance in terms of aroma compositions. The results indicated that an alternative solvent, i.e. MeTHF, could be the most promising one for *n*-hexane substitution with good yield and selectivity of aromas.

1. Introduction

Herbs and spices are invaluable resources and are useful in daily life as food additives, flavours, fragrances, pharmaceuticals, colors, or directly in medicine. This use of plants has a long history all over the world, and over the centuries, humanity developed better methods for the extraction of aromas from such materials. Aromas are complex mixtures of volatile substances generally present at low concentrations. Before such substances can be used or analysed, they have to be extracted from the matrix. Several extraction solvents or processes have been developed in order to obtain the best aromatic substance to satisfy the needs of the perfumer and of the flavourist, in accordance with the worldwide legislation governing the use of this product.

Currently, there are only two kinds of solvents that can be used in chemistry: solvents obtained from petroleum industry and solvents of agricultural origin, the so-called "bio-solvents". Hexane has been used for decades for extraction of aromas in the perfume industry [1]. It offers satisfactory performances due to its low boiling point added to its low polarity. However, many works dealt with the toxic and hazardous effects of this solvent [2–5], and several investigations were also achieved using alternative solvents with the aim of more effective and greener extraction procedures, safer for users and more environmentally friendly [1,6–11]. Nevertheless, and despite its ranking on top of the list of the hazardous solvent, *n*-hexane is still the solvent of choice for extraction of aromas.

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http://dx.doi.org/10.1016/j.crci.2014.03.013
1631-0748/

Because of negative effects on health and environment and of the recent REACH regulations, the need exists for replacing *n*-hexane. There are two possible solvents or alternative methods. A screening of non-polar or polar alternative solvent allows us to evaluate the best aromatic substance for the perfumer and the flavourist. Monoterpene hydrocarbons are less valuable than oxygenated compounds in terms of their contribution to the fragrance of the essential oil. Conversely, the oxygenated compounds are highly odoriferous and, hence, the most valuable. An alternative to these methods could be the extraction with supercritical carbon dioxide, since CO_2 is a green solvent, readily available, cheap, with low critical temperature. The supercritical fluid extraction (SFE) has been applied successfully to other species as Rosemary (*Rosemarinus officialis*) [12], oregano (*Origanum vulgare*), thyme (*Thymus zygis*), sage (*Salvia officinalis*) [13], and orange (*Citrus sinensis*) [14].

In this paper, the potential of alternative solvents has been compared with that of a conventional solvent, *n*-hexane, as the current solvents and commercial situation calls for research with new extraction media. We have applied nine alternative solvents (α-pinene, MeTHF, ethyl acetate, methyl acetate, ethyl lactate, butanol, isopropanol, ethanol and CO_2 supercritical fluid) and *n*-hexane to extract aroma from blackcurrant buds, largely used in perfumery. This study has been performed via experimentation and simulation using Hansen solubility methodology for the comprehension of the dissolution mechanism. We make appropriate comparisons in terms of extraction yields and aromatic profile.

2. Material and methods

2.1. Plants material

Frozen commercial blackcurrant buds (*Ribes nigrum* L.) were purchased from "Les côteaux bourguignons" cooperative, France. The initial moisture was 52.7 ± 1.1%. It was determined by a moisture analyser (MB35 by OHAUS).

2.2. Reagents

n-Hexane (analytical grade), ethyl acetate (purity 99%), ethanol (purity 96%), methyl acetate (purity 99%) were supplied by VWR International, Germany. (*S*)-Ethyl lactate (purity 99.9%) was purchased from Merck, Germany. 2-Propanol (purity 99.9%) α-pinene (purity 98%) and 1-butanol (99.4%) were provided by Sigma Aldrich, Germany. MeTHF was provided by Pannakem, USA.

2.3. Computational methods: HSPIP software

Hansen solubility parameters (HSP) are based on the concept that the total cohesive energy density is approximated by the sum of the energy densities required to overcome atomic dispersion forces (δ_d^2), molecular polar forces arising from dipole moments (δ_p^2), and hydrogen bonds (exchange of electrons, proton donor/acceptor) between molecules (δ_h^2), as given in the following equation:

$$\delta_{\text{total}^2} = \delta_d^2 + \delta_p^2 + \delta_n^2 \quad (1)$$

where δ_{total} is the Hansen total solubility parameter, which now consists of three HSPs in terms of dispersion (δ_d), polar (δ_p) and hydrogen bonding (δ_h).

The programme offers different ways to calculate HSPs: Yamamoto (Y-MB), Stefanis–Panayiotou, Van Krevelen, Hoy methods. The Yamamoto and Stefanis–Panayiotou methods are most recent [15,16]. The Stefanis–Panayiotou method is a new methodology for the calculation of groups' contributions to HSPs. The molecular structures are decomposed into two kinds of functional groups: the first groups corresponding to UNIFAC ones, which describe the overall structure, and the second groups, which improve description. Hiroshi Yamamoto adapted his neural network (NN) technique; this adaptive system changes its structure based on external and internal information that flows through the network. This method calculates, thus, parameters directly from the molecular structure in computational format. For the third version, Hiroshi carried out a huge analysis of results on a database of many thousands of molecules, including many pharmacological, cosmetic and fragrance chemicals. He was able to refine his list of group fragments and also to test novel NN and Multiple Regression (MR) fits. For the user, the only difference from previous editions is that the estimates are often improved–particularly for very large molecules where we acknowledged that the original Y-MB encountered problems. In addition to the HSP values, Y-MB provides estimates of many other important parameters such as MPt, BPt, vapour pressures, critical constants and environmental values. Finally, the Yamamoto method has been chosen for this study.

For HSP solvent optimization, a simple composite affinity parameter, the relative energy difference (RED) number, has been calculated using Eq. (2) to determine whether the alternative solvent and the solute are miscible,

$$RED = R_a/R_0 \quad (2)$$

where R_o is the radius of a Hansen solubility sphere, and R_a is the distance of a solvent from the centre of the Hansen solubility sphere, given by Eq. (3):

$$R_a^2 = 4(\delta_d A - \delta_d B)^2 + (\delta_p A - \delta_p B)^2 + (\delta_h A - \delta_h B)^2 \quad (3)$$

where *A* refers to the solute and *B* refers to the solvent.

The factor 4 in Eq. (3), based on Prigogine's Corresponding States Theory, has proved to effectively expand the dimensions in order to give spherical plots. In general, the parameters follow the classical "like dissolve like" rule: the smaller R_a is, the greater the affinity between solute and solvent. It means that potentially good solvents exhibit RED numbers smaller than 1, while inappropriate solvents have progressively higher RED numbers larger than 1. The chemical structures of the solvents and solutes discussed in this article could be mutually transformed by JChemPaint version 3.0.1 software to their simplified molecular input line entry syntax (SMILES) notations, which were subsequently used to calculate the solubility parameters of