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Review

Isolation of essential oil from different plants and herbs by supercritical fluid extraction

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ABSTRACT

Supercritical fluid extraction (SFE) is an innovative, clean and environmental friendly technology with particular interest for the extraction of essential oil from plants and herbs. Supercritical CO_2 is selective, there is no associated waste treatment of a toxic solvent, and extraction times are moderate. Further, supercritical extracts were often recognized of superior quality when compared with those produced by hydro-distillation or liquid–solid extraction. This review provides a comprehensive and updated discussion of the developments and applications of SFE in the isolation of essential oils from plant matrices. SFE is normally performed with pure CO_2 or using a cosolvent; fractionation of the extract is commonly accomplished in order to isolate the volatile oil compounds from other co-extracted substances. In this review the effect of pressure, temperature and cosolvent on the extraction and fractionation procedure is discussed. Additionally, a comparison of the extraction yield and composition of the essential oil of several plants and herbs from *Lamiaceae* family, namely oregano, sage, thyme, rosemary, basil, marjoram and marigold, which were produced in our supercritical pilot-plant device, is presented and discussed.

Contents

1. Introduction

Essential oils extracted from a wide variety of plants and herbs have been traditionally employed in the manufacture of foodstuffs, cosmetics, cleaning products, fragrances, herbicides and insecticides. Further, several of these plants have been used in traditional medicine since ancient times as digestives, diuretics, expectorants, sedatives, etc., and are actually available in the market as infusions, tablets and/or extracts.

Essential oils are also popular nowadays due to aromatherapy, a branch of alternative medicine that claims that essential oils and other aromatic compounds have curative effects. Moreover, in the last decades, scientific studies have related many biological properties (antioxidant, anti-inflammatory, antiviral, antibacterial, stimulators of central nervous system, etc.) of several plants and herbs to some of the compounds present in the essential oil of the vegetal cells [1–5]. For example, valerenic acid, a sesquiterpenoid compound, and its derivatives (acetoxyvalerenic acid, hydroxyvalerenic acid, valeranone, valerenal) of valerian extract are recognized as relaxant and sedative; lavender extract is used as antiseptic and anti-inflammatory for skin

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care; menthol is derived from mint and is used in inhalers, pills or ointments to treat nasal congestion; thymol, the major component of thyme essential oil is known for its antimicrobial activity; limonene and eucalyptol appear to be specifically involved in protecting the lung tissue. Therefore, essential oils have become a target for the recovery of natural bioactive substances. For example, nearly 4000 articles in which "essential oil" or "volatile oil" appears as keyword were published in the literature since year 2000 up today (http://www.scirus.com/); around 3000 also include the word "bioactive" or "bioactivity" in the article text.

Essential oils are composed of lipophilic substances, containing the volatile aroma components of the vegetal matter, which are also involved in the defense mechanisms of the plants. The essential oil represent a small fraction of plant composition, and is comprised mainly by monoterpenes and sesquiterpenes, and their oxygenated derivatives such as alcohols, aldehydes, ketones, acids, phenols, ethers, and esters. The amount of a particular substance in the essential oil composition varies from really high proportions (e.g. around 80–90% (w/w) of δ-limonene is present in orange essential oil) to traces. Nevertheless, components present in traces are also important, since all of them are responsible for the characteristic natural odor and flavor. Thus, it is important that the extraction procedure applied to recover essential oils from plant matrix can maintain the natural proportion of its original components [6].

New effective technological approaches to extract and isolate these substances from raw materials are gaining much attention in the research and development field. Traditional approaches to recover essential oil from plant matrix include steam- and hydro-distillation, and liquid–solvent extraction. One of the disadvantages of steam-distillation and hydro-distillation methods is related with the thermolability of the essential oil constituents, which undergo chemical alteration due to the effect of the high temperatures applied (around the normal boiling temperature of water). Therefore, the quality of the essential oil extracted is extremely damaged [6].

On the other side, the lipophilic character of essential oils requires solvents such as paraffinic fractions (pentane and hexane) to attain an adequate selectivity of the extraction. Further, liquid solvents should have low boiling points, in order to be easily separated from the extract and re-utilized. In this sense, the main drawback is the occurrence of organic toxic residues in the extracted product.

Among innovative process technologies, supercritical fluid extraction (SFE) is indeed the most widely studied application. In practice, SFE is performed generally using carbon dioxide (CO_2) for several practical reasons: CO_2 has moderately low critical pressure (74 bar) and temperature (32 °C), is non-toxic, non-flammable, available in high purity at relatively low cost, and is easily removed from the extract. Supercritical CO_2 has a polarity similar to liquid pentane and thus is suitable for extraction of lipophilic compounds. Thus, taking into account the lipophilic characteristic of plant essential oils, it is obvious that SFE using CO_2 emerged as a suitable environmentally benign alternative to the manufacture of essential oil products.

The commercial production of supercritical plant extracts has received increasing interest in recent decades and has brought a wide variety of products that are actually in the market. As mentioned before, supercritical plant extracts are being intensively investigated as potential sources of natural functional ingredients due to their favorable effects on diverse human diseases, with the consequent application in the production of novel functional foods, nutraceuticals and pharmacy products. The reader is referred to several recent works [7–10] in which is reviewed the supercritical extraction and fractionation of different type of natural matter to produce bioactive substances. The general agreement is that supercritical extracts proved to be of superior quality, i.e. better functional activity, in comparison with extracts produced by hydro-distillation or using liquid solvents [11–14]. For example, Vági et al. [11] compared the extracts produced from the extraction of marjoram (*Origanum maorana L.*) using supercritical CO_2 (50 °C and 45 MPa) and ethanol Soxhlet extraction. Extraction yields were, respectively, 3.8 and 9.1%. Nevertheless, the supercritical extract comprised 21% of essential oil, while the alcoholic extract contained only 9% of the volatile oil substances. Furthermore, studies related with the antibacterial and antifungal properties of the extract revealed better activity for the supercritical product. Another example of improved biological activity exhibited by supercritical extracts was reported by Glisic et al. [14], demonstrating that supercritical carrot essential oil was much more effective against *Bacillus cereus* than that obtained by hydro-distillation.

Indeed, numerous variables have singular effect on the supercritical extraction and fractionation process. Extraction conditions, such as pressure and temperature, type and amount of cosolvent, extraction time, plant location and harvesting time, part of the plant employed, pre-treatment, greatly affect not only yield but also the composition of the extracted material.

Knowledge of the solubility of essential oil compounds in supercritical CO_2 is of course necessary, in order to establish favorable extraction conditions. In this respect, several studies have been reported [15–18]. Nevertheless, essential oils are readily adsorbed on vegetal matrix, the solid-solute equilibrium can be described by a linear relationship with only one parameter (partition coefficient K) and then, the equilibrium concentration in the supercritical fluid is much lower than the solubility of essential oil in the fluid. Therefore, pretreatment of the plant becomes crucial to break cells, enhancing solvent contact, and facilitating the extraction. In fact, moderate pressures (9–12 MPa) and temperatures (35–50 °C) are sufficient to solubilize the essential oil compounds [15–18]. Yet, in some cases, higher pressures are applied to contribute to the rupture of the vegetal cells and the liberation of the essential oil. However, other substances such as cuticular waxes are co-extracted and thus, on-line fractionation can be applied to attain the separation of the essential oil from waxes and also other co-extracted substances.

In this review, on the basis of data reported in the literature and own experience, a detailed and thorough analysis of the supercritical extraction and fractionation of plants and herbs to produce essential oils is presented. Furthermore, the supercritical CO_2 extraction of several plants (oregano, sage, thyme, rosemary, basil, marjoram and marigold) from *Lamiaceae* family was accomplished in our supercritical pilot-plant at 30 MPa and 40 °C. High CO_2 density was applied in order to ensure a complete extraction of the essential oil compounds. Then, on-line fractionation in a cascade decompression system comprising two separators was employed to isolate de essential oil fraction. Yield and essential oil composition was determined and compared.

2. The essential oil of plants and herbs

Essential oils could be obtained from roots and rhizomes (such as ginger), leaves (mint, oregano and eucalyptus), bark and branches (cinnamon, camphor), flowers (jasmine, rose, violet and lavender) and fruits and seeds (orange, lemon, pepper, nutmeg). In general, essential oil represents less than 5% of the vegetal dry matter. Although all parts of the plant may contain essential oils, their composition may vary with the part of the plant employed as raw material. Other factors such as cultivation, soil and climatic conditions and harvesting time can also determine the composition and quality of the essential oil [19,20]. For example, Celiktas et al. [21] studied different sources of variability in the