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Supercritical CO_2 extraction from endemic Corsican plants; comparison of oil composition and extraction yield with hydrodistillation method

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ABSTRACT

Generally speaking, essential oils (EOs) and components of interest are extracted from plants using hydrodistillation (HD), steam distillation or organic solvent methods The Supercritical CO_2 (SC-CO_2) extraction technique is a good alternative to the three previously mentioned methods as it is able to be applied at temperatures close to ambient and shows no toxicity to humans or the environment. The aim of this study is to investigate the ability of supercritical CO_2 extraction to extract bioactive components from four Corsican endemic plants: *Rosmarinus officinalis*, *Juniperus communis ssp nana*, *Helichrysum italicum* and *Pistacia lentiscus*. After the extracts were analyzed by gas chromatography, it would appear that SC-CO_2 is the most adapted process for the extraction of such components of interest as verbenone, germacrene D, bornyl acetate, ferruginol, trans-caryophyllene, elemol, γ-cadinene, geraniol or β-eudesmol in higher quantity. The SC-CO_2 extraction curves were obtained using two models published by Sovová. These models give access to complementary information and help to estimate the values of some important data such as the possible maximal extraction yield for *Helichrysum italicum* and the end of the extraction period.

1. Introduction

EOs are complex and variable mixtures of organic and volatile components mainly composed of terpenes in addition to some aromatic components. Those compounds can be located in all parts of the plants: flowers, leaves, roots, stems, fruits and seeds. The EOs extracted from the different parts exhibit various biological properties and thanks to this feature, plants are used for applications in pharmaceuticals, food, cosmetics and fragrances [1–7]. On the island of Corsica (France), a wide variety of aromatic and medicinal plants can be found. These endemic plants are used in all the above-mentioned fields of applications as they have therapeutic, organoleptic and fragrance properties [8–16]. The EOs extracted from Corsican endemic plants are products with high added values mainly commercialized by local producers.

At industrial scale, EOs are extracted by classical hydrodistillation (HD) or steam distillation methods. Nevertheless, using these technics has an incidence of low extraction yields, high energy costs and the loss or degradation of some specific compounds, especially heat-sensitive compounds, by thermal or hydrolysis effects. The quality of EOs may consequently be impaired.

In fine chemistry applications, different groups of components are extracted from plants by applying organic solvent methods. However, a separation step is needed and traces of organic solvent can be found in the extracts. These disadvantages have led to the development of alternative separation techniques based on the use of supercritical fluids. In such processes, SC-CO_2 is most commonly used since it is non-toxic, relatively inert, non-flammable and readily available as a by-product of the chemical industry.

SC-CO_2 is considered as a GRAS (Generally Recognized As Safe) solvent. Due to its low critical temperature (304.21 K), SC-CO_2 can be used to extract heat-sensitive components, it can be quite selective and its solvent power can be improved by tuning temperature and pressure. Furthermore, no separation step is needed as CO_2 is gaseous under ambient conditions of temperature and pressure. Finally, CO_2 is recycled at industrial scale enabling a completely clean and compact process [17]. SC-CO_2 extraction has been used as an efficient process for extracting oil from different parts of plants, with extracts having interesting applications in pharmaceutical and food applications [18–24].

The comparison between SC-CO_2 and HD methods for the extraction of components of interest has been investigated for a huge diversity of plant species [5,25–35]. The results reported in these studies clearly show that SC-CO_2 extraction leads to the highest extraction yield, improved oil quality, and a higher selectivity of the extracted components. In the above-mentioned references, the experiments were performed at laboratory scale, the effects of the use of a co-solvent and the effects of the experimental SC-CO_2 extraction parameters (pressure, temperature)

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Nomenclature

a_s	Specific area between the regions of intact and broken cells (m^{-1})
C_1	BIC model parameter
C_2	BIC model parameter
C_u	Concentration of extract in the plant before extraction ($kg\ kg^{-1}{}_{plant}$)
D_e	Effective intraparticle diffusion coefficient ($m^2\ s^{-1}$)
e'	Mass loss ($kg_{\ extract}\ kg^{-1}{}_{\ plant}$)
G	Initial fraction of extract in open cells
k_f	Fluid-phase mass transfer coefficient (s^{-1})
K_m	Mass-related partition coefficient ($kg_{plant}\ kg^{-1}{}_{solvent}$)
k_s	Solid-phase mass transfer coefficient ($m\ s^{-1}$)
q_c	Relative amount of the passed solvent at the crossing point ($kg_{\ solvent}\ kg^{-1}{}_{\ insolublesolid}$)
q'	Specific flow rate ($kg_{solvent}\ kg^{-1}{}_{solid}\ s^{-1}$)
r	Grinding efficiency or fraction of broken cells
t	Extraction time (s)
$t_{comb,i}$	Combined characteristic time of mass transfer (s)
t_f	Characteristic time of the fluid phase mass transfer (s)
t_r	Residence time (s)
t_1	Time of the end of the first extraction period (s)
y_0	Initial fluid phase concentration ($kg_{\ solute}\ kg^{-1}{}_{\ solvent}$)

Greek letters

ε	*bed void fraction*
θ_f	Dimensionless external mass transfer resistance
ρ_s	Plant density ($kg\ m^{-3}$)

as well as the effect of sample pre-treatment and extraction time were studied in order to give the optimal conditions for extracting up to three specific components and/or leading to the highest extraction yield.

To our knowledge, no investigations have so far been conducted on the comparison of $SC\text{-}CO_2$ and HD methods in the extraction of components of interest from Corsican endemic plants. Considering the importance and the quality of the EOs from these types of plants and regarding the previous studies reported in the literature, this study aims to investigate $SC\text{-}CO_2$ extraction from four Corsican endemic plants and make a comparison with the HD method. The Corsican endemic plants species selected for this work are: *Rosmarinus officinalis*, *Juniperus communis ssp nana*, *Helichrysum italicum* and *Pistacia lentiscus*. These species were chosen because of their highly interesting biological properties and their various fields of applications in food, cosmetics and pharmaceutics.

Numerous studies dealing with the composition of EOs and their biological activities [36–43], and the $SC\text{-}CO_2$ extracts from plants [44–52] have been reported in the literature for similar species. Furthermore, it is well-known that various parameters such as geographical location [53], harvest period [54], extracting method [55] have non negligible effects on the chemical compositions of plants, which can lead to a different EO composition for the same plant species.

The main aim of this work is to investigate the feasibility of obtaining bioactive molecules which are either not or only slightly able to be extracted by HD, by applying the $SC\text{-}CO_2$ extraction method. Unlike previous studies, it was decided here not to determine the optimal operating extraction conditions but to make investigations at a specific pressure, temperature and flow rate using an easily applicable sample pre-treatment.

The operating pressure and temperature for $SC\text{-}CO_2$ extraction were chosen by taking into account the following criteria: easily applicable at industrial scale, pilot scale and laboratory scale applications, involving a solvent power comparable to typical organic solvents ($SC\text{-}CO_2$ density higher than 800 $kg\ m^{-3}$) [18,23] and allowing the extraction of volatile compounds. A pressure of 300 bar and a temperature of 313 K ($SC\text{-}CO_2$ density about 909.89 $kg\ m^{-3}$) were selected. The $SC\text{-}CO_2$ flow rate was set at 0.4 $kg\ h^{-1}$. The extracts and the EOs obtained by SC-CO2 extraction and HD respectively were analysed by gas chromatography. The effect of the extraction method on the extraction yields is also presented. The biological activities of the $SC\text{-}CO_2$ main extracted components were compared to those obtained by HD. The HD process was conducted at industrial scale whereas $SC\text{-}CO_2$ extractions were conducted at laboratory scale.

2. Materials and methods

2.1. Plant material

The four Corsican endemic plants *Rosmarinus officinalis*, *Juniperus communis ssp nana*, *Helichrysum italicum* and *Pistacia lentiscus*, were picked in Corsica. The samples were collected during the flowering period (between April and May 2012) in the middle of the island, next to the town of Corte. The leaves and flowers were separated from their stems and placed in glass vials surrounded by aluminum paper, to protect them from light and stored at 4 °C to avoid the loss of volatile compounds and/or degradation. Before the $SC\text{-}CO_2$ extraction experiments, the leaves and flowers were cut in order to increase the contact area. The average equivalent particle diameter was about 1 cm; no further pre-treatment was applied.

2.2. Chemicals

Supercritical CO_2 extractions were carried out with carbon dioxide of 99.7% purity supplied by Air Liquide Méditerranée (France). Anhydrous ethanol used for collecting the extracts was purchased from Carlo Erba (France).

2.3. HD and $SC\text{-}CO_2$ extraction

The classical HD process was performed on *Rosmarinus officinalis* and *Helichrysum italicum* at industrial scale on about 500 kg of dried plant mass for 3 h without any sample pre-treatment. The $SC\text{-}CO_2$ extractions of *Rosmarinus officinalis*, *Helichrysum italicum*, *Juniperus communis ssp nana* and *Pistacia lentiscus* were performed in a laboratory scale apparatus equipped with a 20 mL extraction autoclave provided by Separex (Champigneulles, France); the scheme of the set-up is shown in Fig. 1. All $SC\text{-}CO_2$ extractions were performed at 300 bar, 313 K at a CO_2 flow rate of 0.4 $kg\ h^{-1}$ on *Juniperus communis ssp nana* and *Pistacia lentiscus* leaves, on *Rosmarinus officinalis* leaves and flowers, and on *Helichrysum italicum* flowers. The sample mass introduced in the extraction autoclave for $SC\text{-}CO_2$ extraction, was 9.519 g for *Helichrysum italicum*, 6.356 g for *Juniperus communis ssp nana*, 6.674 g for *Pistacia lentiscus* and 6.257 g for *Rosmarinus officinalis.*

Fig. 1 The experimental setup is as follows:

Liquid CO_2 (1) is cooled in a cryogenic bath (2), filtered and pumped (3) to the extraction vessel (4). Before entering the extraction vessel, CO_2 is heated until the chosen temperature. The extraction vessel which contains the sample is also heated. Pressure is controlled by a pressure gauge (5). Downstream of the extraction vessel, CO_2 is released to gas state through an expansion valve (6). The extracted compounds are recovered in a collector (7). The flow is measured thanks to the flow meter (8) placed at the end of the extraction