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Research paper

Extraction of green absolute from thyme using ultrasound and sunflower oil

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Abstract

Absolute is the plant aroma isolate mostly used in the food and fragrance sectors. The use of organic solvents constitutes the most commonly used method for obtaining this aroma. However, this technique may leave trace amounts of solvents which are considered undesirable for these industries. In this work, a new green extraction approach was implemented using ultrasound (US) with sunflower oil (SO) as a natural solvent to produce green absolute from thyme (*Thymus vulgaris*). US optimal conditions for absolute yield were investigated using response surface methodology (RSM) and compared to conventional SO (SO-CV) and hexane (Hex-CV) extractions. The absolutes were analyzed by GC–MS for their chemical composition and tested for their antioxidant activities (total phenols, DPPH and frying test).

Optimized conditions obtained by RSM for absolute yield were T = 50 °C, t = 22 min, P = 98 W. The US using SO as solvent offers important advantages: shorter extraction time, increase of 47% in absolute yield compared to SO-CV extraction. Although the absolute obtained by hexane extraction provided improved yield (8.64 g/100 g DW), it contained around 75% of waxy materials. GC–MS analysis showed no remarkable variation of the chemical composition of the absolutes compared to those obtained by hexane extraction. Moreover, the US extraction allowed the highest recovery of monoterpene phenols thymol and carvacrol (86.2%). The absolute obtained by SO-US was free from waxes and organic solvent residues and exerted the highest antioxidant activity. Results show that ultrasound extraction using SO is a good alternative. It suggests the possibility of the production of green absolutes on pilot and industrial scale.

Keywords: Green extraction; Ultrasound; Natural solvent

1. Introduction

The food and fragrance industries are interested in the plant aroma compounds such as concrete and absolute. The concrete is the plant extract with characteristic odor and flavor; it consists mainly of volatile compounds and non-volatile waxy substances obtained by petroleum solvents such as hexane or pentane. Then, the concrete is dissolved in ethanol solution to reduce the waxy components which disturb the formulation, allowing the formation of the absolute, the most faithful aroma to the plant scent [1]. However, this extraction method may leave trace amounts of organic solvents, which are considered undesirable for these industries, because they are harmful to human health and the environment [2].

At the same time, there is a big interest in green chemistry to seek out for green extraction techniques that may reconcile the challenges set by the economics, the society and the environment. The green chemistry is intended to develop extraction processes, which reduce the energy consumption, allow the use of natural solvents and ensure a safe and high quality product [3,4].

Different absolute extractions using petrochemical solvents have been reported for flowers such as *Narcissus pseudonarcissus*

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Nomenclature

Abbreviations

Abs	Absolute
CV	Conventional
EO	Essential oil
Hex	Hexane
OC	Oleo-concrete
RSM	Response surface methodology
SE	Soxhlet extracts
SO	Sunflower oil
US	Ultrasound

[5], *Michelia Champaca* Linn [1], *Tagetes patula* L. [6], and *Mimusops elengi* L. [7].

Thyme (*Thymus vulgaris*) is a perennial herbaceous shrub belonging to the Lamiaceae family. It is widespread throughout the Mediterranean region [8]. This aromatic plant is extensively used for food flavoring and is well known for its various beneficial effects, e.g., antiseptic, carminative, antimicrobial, and antioxidative properties [9]. Most of these biological properties are mediated by thymol and carvacrol, the main monoterpene phenol components of the thyme.

Different extraction techniques were conducted on thyme. The essential oil was obtained by steam distillation [10,11] and hydrodistillation [12,13]. The aroma active compounds of thyme were obtained by other extraction methods such as microwave assisted hydrodistillation [14], supercritical fluid extraction [15], solid phase microextraction, pressurized liquid extraction, Soxhlet extraction [16] and by the use of different solvents [17].

Although the different characteristics of thyme extracts were extensively studied, so far no reported works on absolute of thyme have been conducted yet for food application.

Ultrasound (US) has been used for various processes in the food industry. The technique is fast and allows the reduction of solvents, thus resulting in a more pure product and higher yields. This method has been applied to extract food components such as antioxidants [18], aromas [19] and other organic and mineral components from a variety of matrices [20–23]. The extra vibration of US improves the cavitation process and the contact surface that occurs between sample matrix and liquid solvent phase causing the rupture of cell walls, consequently enhancing the recovery yield of available extractable cell material [24,25]. The US was used for the recovery of aromatic compounds from thyme by ultrasound-assisted dynamic extraction [26]. It was also used in the thyme drying process [27] and in the steam distillation of thyme EO [28].

In this work, a new green procedure using ultrasound, an inexpensive and easy-to-use method for green absolute extraction from thyme (*Thymus vulgaris*), was conducted. Sunflower oil (SO) was used as a substitute to organic solvents: a process which is in line with green extraction concepts. The US extraction method was optimized using response surface methodology (RSM) and compared to conventional SO and hexane extractions. The chemical compositions of the absolutes were analyzed by gas chromatography–mass spectrometry (GC-MS). The total phenolic compounds Folin-Ciocalteu, the antioxidant test 2,2-diphenyl-1-picrylhydrazyl (DPPH) and total polar material tests (TPM) were also conducted on absolutes obtained by different extraction methods. The objective of this study was the implementation for the first time of a new green approach to produce green absolute from thyme for food industry using ultrasound apparatus and sunflower oil as an environmentally friendly solvent.

2. Materials and methods

2.1. Plant material and chemicals

Sunflower oil was obtained from a local supermarket in Avignon province (France), *Thymus vulgaris* (chemotype thymol) was purchased from Flore en thym, SAS (south of France). Ethanol (high purity 99.8%) and hexane were obtained from VWR, (EC), Folin Ciocalteu phenol reagent was purchased from chem-lab (Belgium), DPPH reagent and thymol were supplied by Sigma Aldrich (Germany), methanol was bought from Merck (Germany), and ethanol (96%) was supplied by Brenntag (Belgium).

2.2. Extraction procedures

Solid–liquid ratio: The different ratios (plant material/solvent) vary with the type of solvent and plant material used. In this work, a ratio of 1/10 (w/w) was selected for the different absolute extraction techniques. For a ratio above 1/10, the dry matter absorbed all of the available solvent and increased in volume resulting consequently in a lower yield. The combination of high absolute yields and higher amount of available solvent was chosen since the ultrasound apparatus requires a minimum amount of free solvent for extraction procedures.

Conventional extraction of absolute with hexane and ethanol (Fig. 1a): Ten grams of thyme dry matter were soaked in hexane (100 ml) and submitted to heating reflux for 2 hours. The solution was filtered. The hexane was evaporated on a rotary evaporator at 40 °C giving the waxy residue called concrete. Ethanol (high purity 99.8%) (20 ml) was added to the concrete, warmed at 50 °C for 5 min to get a homogeneous mixture. Filtration of the precipitate followed by evaporation of ethanol at 40 °C gave a green absolute. Extractions were performed in triplicates and mean yield values, expressed in g/100 g of thyme dry weight (DW), were reported.

Extraction of absolute with sunflower oil and ethanol (Fig. 1b): Ten grams of thyme dry matter were soaked in 100 ml sunflower oil, so-called "oleo concrete (OC)". The OC was then extracted by US and Conventional methods (CV). Then, the oleo concrete was filtered; ethanol (high purity 99.8%) (250 ml) was added to the solution, agitated vigorously and allowed to stand for 1 hour. The ethanolic solution was collected, partly evaporated and refrigerated at −14 °C for 12 hours to eliminate SO residue. The supernatant was collected and evaporated at 40 °C giving a yellow extract, the absolute. Extractions were

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