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Application of ultrasonic Ohmic hydrodistillator system in production of essential oil from Zenyan

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Abstract

In this study, two methods of *Carum copticum* essential oil extraction were examined. Traditional hydrodistillation (TH) and innovative Ultrasonic Ohmic Hydrodistillator (UOH) methods have been compared and evaluated for their effectiveness in the isolation of essential oil. The UOH offers main advantages over TH, namely: shorter isolation time (20 min against 2.5 h for TH), higher quality and quantity of essential oil, higher antioxidant activity and somewhat lower operating and energy cost. Based on the present study, the UOH process may be considered to have a significant potential in the field of extraction of essential oils from seeds and herbs.

Introduction

Carum copticum is an aromatic, grassy and annual plant which grows in the east of Iran, India and Pakistan with white and small flowers and brownish seeds (Boskabady and Shaikhi, 2000). Zenyan is the Persian name for seeds of *C. copticum* and were used for its therapeutic effects such as antivomiting, analgesic and anti-asthma (Goudarzi *et al*., 2011). In addition, Zenyan essential oil (EO) was reported to have antioxidant activity (Hashemi *et al.*, 2011) and antibacterial activity (Goudarzi *et al*., 2011).

Essential oils as secondary metabolites play a main role in the protection of the plants as antibacterials, antifungals and insecticides. They are extracted from different parts of the aromatic plants such as; flowers, seeds, leaves and fruits. There are numerous methods for extraction of essential oil. These methods include use of liquid carbon dioxide, microwave and distillation by boiling water or hot steam (Bakkali *et al.*, 2008). Many of these methods are more over time consuming and energy intensive (Presti *et al*., 2005).

Ohmic heating occurs when alternating current is passed through a food sample, and heat is generated by virtue of the samples electrical resistance (Lakkakula *et al*., 2008). This processing enables to heat materials at extremely rapidly rates which could save energy. Besides, ohmic processing is cleaner than the other heating methods (Lei *et al*., 2007). Besides, Ultrasound treatment is a food processing technology, which posses various applications when applied alone or in combination with other food processing methods (Yildirim *et al*., 2013). Sonication treatments have been reported to be effective for extraction. This treatment is considered to be beneficial due to its reduced processing time with lower energy consumption and being environmental friendly (Annegowda *et al*., 2012). In this study, quality and quantity of EO obtained by UOH has been compared with those obtained by TH.

Materials and Methods

Plant material

C. copticum seeds (28% initial moisture) were collected from the Khanzenyan city, Fars province, Iran. The species was identified and authenticated (Voucher specimen (no. 24985)) by A.R. Khosravi, a plant taxonomist, at Shiraz University, Herbarium, Shiraz, Iran. The seeds were then dried under ambient conditions (30–40°C) for three days on a large screened tray. Plant seeds were then kept in a

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dark and cold room until used shortly after that for the experiments.

Traditional hydrodistillation method

Dried matured seeds of the plant (20 g, 8% moisture) were hydrodistilled for 2.5 h in an all-glass Clevenger apparatus in accordance with the description of the British Pharmacopoeia (1998). Heat was supplied to the heating mantle (0.72°C/min temperature rate) and the essential oil was extracted with 500 mL of distilled water for 2.5 h (until no more essential oil was recovered). Essential oil sample was dried over anhydrous sodium sulphate and stored in sealed vials at 4°C until used.

Ultrasonic Ohmic Hydrodistillator method

Extraction of essential oil from *C. copticum* was performed with the newly designed UOH. The extractor unit consisted of a cylindrical chamber (0.07 m internal diameter and 0.25 m length) made with Teflon. It was equipped with two Titanium electrodes. The system was fully automated for which the voltage (0–300 V) and current (0–16 A) and temperature could be controlled, monitored and recorded to a data sheet through out the experiment. A Hielscher ultrasonic device (UP100H, 100 W, 30 kHz) with a titanium sonotrode (tip diameter10 mm) was used to sonicate the sample containing the plant materials. The extraction unit was also equipped with an all-glass clevenger-type apparatus. For each experimental run, 20 g (8% moisture) of the plant material was charged in to the chamber together with 500 mL brine (NaCl) solution (0.3% w/v). (Sodium chloride will provide sufficient electrical conductivity between two electrodes for the heat up process to be swift.) Prior to heating process, the plant materials which were fully immersed in brine solution was sonicated for 3 min in order to improve the EO release from the cell. The ohmic system was then switched on. A constant voltage of 150 V was applied between the two electrodes to increase the solution temperature from initial value of 21.8ºC right up to boiling. The temperature rise was recorded at about 20.8ºC/min. The extraction of EO was continued for 20 min. The EO was collected, dried under anhydrous sodium sulphate and stored in sealed vials at 4°C until used.

Electrical conductivity

Electrical conductivity (S/m) was calculated from voltage and current data using the following equation (Zell *et al*., 2009):

$$\sigma = LI/VA$$

where σ is electrical conductivity (S/m); I is the current intensity (A), V is the voltage (V), L is the gap between the electrodes (m) and A is the electrode surface area (m^2).

Essential oil analysis

The essential oil was analyzed by GC-MS. The analysis was carried out on a Thermoquest- Finnigan Trace GC-MS instrument equipped with a DB-5 fused silica column (60 m ×0.25 mm i.d., film thickness 0.25 μm). The oven temperature was programmed to increase from 60 to 250°C at a rate of 4°C/min and finally held for 10 min; transfer line temperature was 250°C. Helium was used as the carrier gas at a flow rate of 1.1 mL/min with a split ratio equal to 1/50. The quadrupole mass spectrometer was scanned over the 35–465 amu with an ionising voltage of 70 eV and an ionisation current of 150 mA.

GC-FID analyses of the oil were conducted using a Thermoquest-Finnigan instrument equipped with a DB-5 fused silica column (60 m ×0.25 mm i.d., film thickness 0.25 μm). Nitrogen was used as the carrier gas at the continuous flow of 1.1 mL/min; the split ratio was the same as for GC-MS. The oven temperature was raised from 60 to 250°C at a rate of 4°C/min and held for 10 min. The injector and detector (FID) temperatures were kept at 250 and 280°C, respectively. Semi quantitative data were obtained from FID area percentages without the use of correction factors.

Retention indices (RI) were calculated by using retention times of n-alkanes (C6–C24) that were injected after the oil at the same temperature and conditions. Compounds were identified by comparison of their RI with those reported in the literature (Adams, 2007) and their mass spectrum was compared with the Wiley Library (Wiley 7.0).

Antioxidant activity of essential oil

The radical scavenging capacity of EO for DPPH was monitored according to the method described by Burits and Bucar (2000). Fifty microlitres of different concentrations of the essential oil samples in methanol (15, 25, 35, 45 and 55 μg/mL) were added to 5 mL of a 0.004% methanol solution of DPPH. After a 30 min incubation period at room temperature under dark condition, the absorbance of the samples was read against a blank at 517 nm. Inhibition of free radical DPPH in percent (I%) was calculated in following way:

$$I\% = (A_{blank} - A_{sample}) / A_{blank} \times 100,$$

where A blank is the absorbance of the control

reaction (containing all reagent except the test compound), and A sample is the absorbance of the test compound. EO concentration providing 50% inhibition (IC_{50}) was calculated from the graph plotting inhibition percentage against EO concentration. BHT was used as a control and all tests were carried out in triplicates.

Statistical analysis

The results were analyzed using one-way ANOVA, and significant differences between groups were determined by the Duncan's multiple range test and t-test. All statistical analyses were performed using the SPSS package program version 20 and Minitab 16. Differences were considered significant at $P<0.05$.

Results and Discussion

Kinetics extraction

Time–temperature profiles of samples were recorded for all three thermocouples. Typical time–temperature profiles for extraction process (TH and UOH) appear in Figure 1. The time required to heat the sample from 19 to 97ºC at traditional hydrodistillator was approximately 6.5 times longer than OUH. Therefore, OUH is the rapid method for reaching to boiling point of the sample and beginning of the extraction.

The yields of essential oil extracted from Zenyan with the different extraction methods are respectively 21 ± 0.8% and 18 ± 0.6% (v/w) for the OUH and TH. As is shown in Figure 2a and b, an extraction time of 20 min with OUH provides more yields than those obtained after 150 min by means of TH, which is one of the reference methods in essential oil extraction.

Figure 2a and b show the difference of the extraction yield according to the extraction time. Three phases are observed in the process of the OUH (Figure 2a). Step 0 represents the heating phase from ambient temperature to 97°C. The first step is represented by an increasing line which characterizes the first quantities extracted, located at the surface of plant particles representing about 60% of the yield obtained into10 min. This phase is followed by a second increasing line (Step 2) representing diffusion of the imprisoned essential oil from the midst of the particles towards the external medium involved by the intern warming of the water located in the vegetable cells. In this phase, the oil amount extracted represents almost 40% of the total yield. The third part corresponds to a horizontal line which marks the end of the isolation process. The profile of the conventional extraction technique TH presents

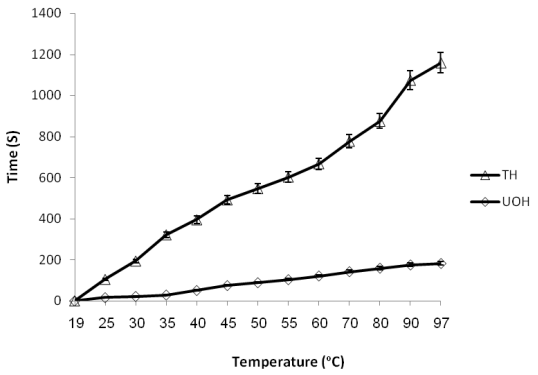

Figure 1. Time-temperature profiles of Traditional hydrodistillation(TH) and Ultrasonic Ohmic Hydrodistillator (UOH). All values are means of three determinations

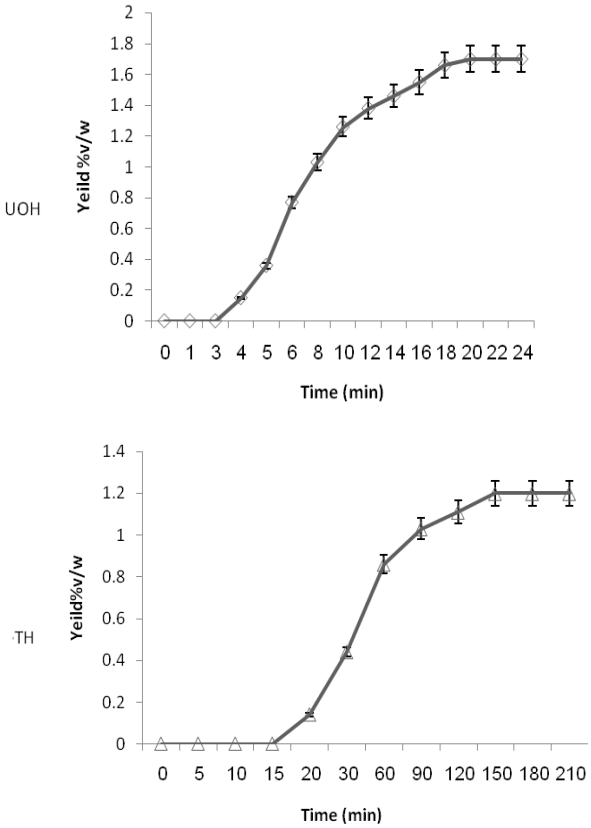

Figure 2. Yield profiles as a function of time for the OUH (a) and TH (b) isolations of essential oil from Zenyan. OUH: Ultrasonic Ohmic Hydrodistillator and TH: Traditional hydrodistillation. All values are means of three determinations

three similar aspects but different phases to those obtained with OUH; the first step leading to 72% of the yield obtained into 90 min. The end of the extraction process is reached after 150 min.

Electrical conductivity

Figure 3 shows the amperage values of the Zenyan sample in UOH. Results indicated amperage increased during ohmic heating. As shown in Figure 4, the electrical conductivity increased as the temperature

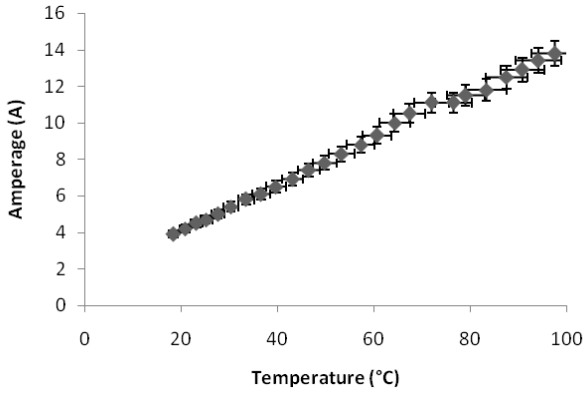

Figure 3. Amperage values of Zenyan sample in Ultrasonic Ohmic Hydrodistillator. All values are means of three determinations

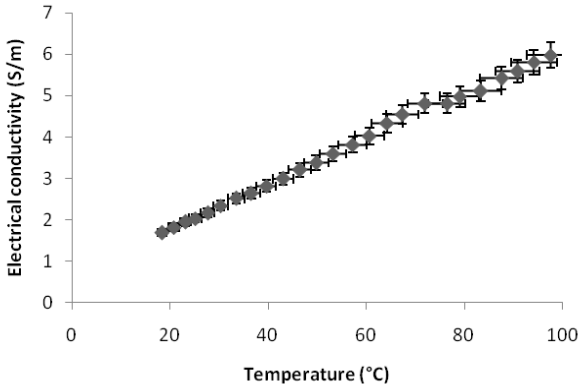

Figure 4. Electrical conductivity values of Zenyan sample in Ultrasonic Ohmic Hydrodistillator. All values are means of three determinations

increased during ohmic heating. The results indicated that that amperage and temperature significantly altered (increased) the electrical conductivity value of Zenyan in UOH. During ohmic heating, electrical energy is converted to thermal energy within a conductor by applying an alternating current across the material. The energy is almost entirely dissipated within the heated material; therefore, there is no need to heat intervening heat exchange walls, thus the process has close to 100% energy transfer efficiency (Shim *et al*., 2010).

Quality and quantity of essential oil

A total of 18 compounds (Table 1) were identified in Zenyan essential oils using the two techniques. UOH and TH enabled the finding of most volatile active compounds in Zenyan essential oil such as thymol, γ- terpinene and p-Cymene, but their proportions depend on the extraction technique. Slightly higher amounts of these compounds are present in the essential oils of the aromatic plant isolated by UOH in comparison with TH.

The content of monoterpene hydrocarbon (α-Terpinene) in TH essential oil was higher than in UOH essential oil, whereas TH essential oil didn't has linalool (Oxygenated monoterpene). Monoterpene hydrocarbons are less important than oxygenated compounds in terms of their contribution to the aroma of the essential oil. On the other hand, the oxygenated compounds are highly odouriferous and, hence, the most valuable. In general, results of EO extracted by UOH and TH showed that UOH system was a better reproduction of natural aroma of the herb essential oil than the hydrodistilled essential oil.

The difference between quality and quantity of two isolated essential oil is probably due to thermal duration and ultrasound application (Herrera *et al*., 2005; Bendahou *et al.*, 2008). Ohmic heating has a high energy efficiency and lower degradation of sample ingredients; therefore, increase extraction rate. Moreover, it has shown (Herrera *et al.*, 2005) that the herbs and spices cell wall in ultrasonic systems can be broken with the ultrasound treatment; therefore, this treatment also increases efficiency of UOH for extraction of essential oil.

Antioxidant activity

The antioxidant activity of the EO extracted by two extraction methods, against DPPH free radicals showed that UOH essential oil was more active than TH essential oil) UOH: IC_{50}=23 ±1.2 µg/mL and TH: IC_{50}=27 ±1.4 µg/mL) because of more thymol content (Hashemi *et al.*, 2014).Therefore, UOH could be a good alternative for the extraction of essential oils from Zenyan.

Cost considerations

The reduced cost of extraction is obviously useful for the proposed UOH method in terms of time and energy. Hydrodistillation required an extraction time of 90 min for heating of 500 mL water and 20 g aromatic plants to the extraction temperature followed by evaporation of the water and essential oil for 150 min. The UOH method required electrically heating for 3 min only and hydrodiffusion for 17 min of the in situ water and essential oil of the same material. In addition, the UOH process is uncomplicated and can be readily understood in terms of the operating steps to be performed.

Conclusion

In this study, we describe a new method for extracting essential oil from aromatic plants in comparison with conventional TH. The proposed method of UOH is an original combination of ultrasonic, ohmic heating and hydrodistillation. It provides more valuable EO. Additionally, the UOH

Table 1. Component of Zenyan essential oil extracted by two methods

Component	RI	UOH%	TH%
α- Thujen	931	0.33±0.02	0.32±0.01
α –Pinene	941	0.12±0.01	0.12±0.01
Sabinene	979	0.19±0.03	0.19±0.02
β-Pinene	986	0.42±0.05	2.42±0.07*
Myrcene	990	0.52±0.03	0.51±0.03
α—Terpinene	1022	0.02±0.009	3.16±0.06*
p-Cymene	1030	22.9±0.13	20.2±0.0.07*
1,8- Cineole	1038	0.52±0.08	0.5±0.06
Ocimene	1047	0.05±0.009	0.04±0.005
γ- Terpinene	1064	23.92±0.09	22.32±0.1*
is-Sabinene hydrate	1072	0.04±0.001	0.04±0.001
Linalool	1098	0.06±0.001	-
ms-Sabinene hydrate	1105	0.04±0.001	0.03±0.001
Cyclocitral	1171	0.13±0.02	0.13±0.03
Terpinen-4-ol	1185	0.13±0.03	0.11±0.01
α –Terpineol	1198	0.1±0.008	0.09±0.002
Thymol	1295	50.07±0.21	48.01±0.13*
Carvacrol	1301	0.14±0.01	0.13±0.009

method offers important advantages over traditional alternatives, namely: shorter extraction times, higher processing throughput, and increased rate of extraction. All these advantages make UOH a good alternative for the extraction of essential oil from herbs and seeds.

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