Research note

Subcritical water extraction of essential oils from coriander seeds (*Coriandrum sativum* L.)

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Abstract

Subcritical water extraction (SCWE), hydrodistillation and Soxhlet extraction were compared for the extraction of essential oil from coriander seeds (*Coriandrum sativum* L.). The extraction efficiencies of different temperatures (100, 125, 150 and 175 °C), mean particle sizes (0.25, 0.50 and 1 mm), and water flow rates (1, 2 and 4 ml/min) were investigated. Separation and identification of the components were carried out by GC–FID and GC–MS. The results showed that the optimum temperature, mean particle size, and flow rate were 125 °C, 0.5 mm, and 2 ml/min. The SCWE was compared with both conventional methods in terms of the efficiency and the essential oil composition. Hydrodistillation and Soxhlet extraction showed higher extraction efficiencies, but the SCWE resulted to the essential oils more concentrated in valuable oxygenated components.

Keywords: Subcritical water extraction; *Coriandrum sativum* L.; Coriander seeds; Essential oil

1. Introduction

Coriander (*Coriandrum sativum* L.) is widely distributed and mainly cultivated for the seeds. The seeds contain an essential oil (up to 1%) and the monoterpenoid, linalool, is the main component. The coriander seed is a popular spice and finely ground seed is a major ingredient of curry powder. The seeds are mainly responsible for the medical use of coriander and have been used as a drug for indigestion, against worms, rheumatism and pain in the joints (Wangensteen, Samuelsen, & Malterud, 2004). The coriander seeds have a pleasant flavour owing to the particular composition of the essential oil. The fruits are used in the preparation of fish and meat, but also for baking. The first factory for the steam distillation of the essential oil of coriander was built in Russia in 1885 in the Voronež district. The extracted essential oil is used in the flavouring of a number of food products and in soap manufacturing. It is principally used as a flavouring agent in the liquor, cocoa and chocolate industries. Like the fruits, it is also employed in medicine as a carminative or as a flavouring agent. It has the advantage of being more stable and of retaining its agreeable odour longer than any other oil of its class (Diederichsen, 1996).

Subcritical or superheated water extraction (SCWE) of essential oils is a new technique based on the use of water, at temperatures between 100 °C and 374 °C and pressure high enough to maintain the liquid state (Ayala & Luquede Castro, 2001). It is also called pressurized hot water extraction (PHWE) or pressurized low polarity water extraction (PLPWE). Under these conditions it is much less polar and organic compounds are much more soluble than at room temperature. The most important advantages of SCWE over traditional extraction techniques are shorter extraction time, higher quality of the extract, lower costs of the extracting agent, and an environmentally compatible technique (Herrero, Cifuentes, & Ibanez, 2006). The SCWE is rapidly emerging as an alternative for the extraction of

essential oils compounds (Luquede Castro, Jimenez-Carmona, & Fernandez-Perez, 1999).

The SCWE was used for the extraction of rosemary (*Rosmarinus officinalis*) leaves essential oil for the first time by Basile, Jimenez-Carmona, and Clifford (1998). Since that time, the SCWE of essential oils from the several other plants has been investigated (Ong, Cheong, & Goh, 2006; Smith, 2002).

The aim of this work was to investigate the SCWE and identification of coriander (*Coriandrum sativum* L.) essential oil. The results are compared with those obtained by conventional techniques such as hydrodistillation and Soxhlet extraction.

2. Material and methods

2.1. Materials

The coriander seeds (*C. sativum* L.) were collected in September 2005 (Sabzevar, Iran). *n*-nonane (Merck) was used as an internal standard. NaCl, Na_2SO_4 (both from Merck) and HPLC grade hexane (Aldrich Chemical Co., USA) were used as demulsifier, drying agent and extractant, respectively, in the liquid–liquid extraction step of the aqueous extracts. Doubly distilled, de-gassed water purified through a Milli-Q de-ionizing unit (Millipore, Bedford, MA, USA) was used as extractant.

2.2. Sample preparation

Fresh *C. sativum* seeds were stored in polyethylene bags at −70 °C until analysis. 4.0 g of samples were used for SCWEs and Soxhlet extractions and 40.0 g for hydrodistillations. The samples were ground immediately prior to extraction in order to avoid losses of volatiles. Two replications of the extraction and analysis procedure were performed for each of the runs.

2.3. Subcritical water extraction system

The subcritical water extractions were carried out in a laboratory-built apparatus shown in Fig. 1. De-ionized water filled into a 5 L stainless steel feed tank was first purged for 2 h with N_2 to remove dissolved O_2. A Dosapro Milton Roy (H9 series, USA) high pressure metering pump was used to deliver the water through the system at a constant flow rate of 1, 2 and 4 ml/min. The pump output could be adjusted by stroke knob at the required flow rates and be checked using a burette equipped in the inlet pipelines. A coil made from 3 m length stainless steel tubing (3 mm i.d. × 6.35 o.d.) was used for preheating the water. The extractor consisted of a stainless steel cylindrical extraction chamber (103 mm × 16 mm i.d.). The solid bed inside the extractor was fixed with ring screws at both ends in order to permit the circulation of the water through it. Input and output of the water was carried out through two side-connected quick-open high pressure valves. The

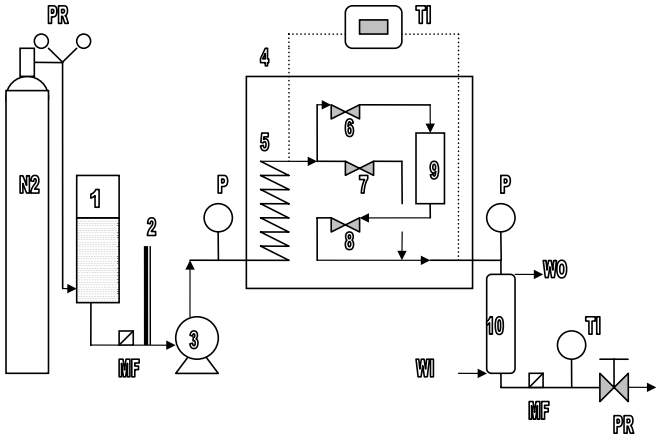

Fig. 1. Schematic diagram of superheated water extraction system: 1, water reservoir; 2, burette; 3, pump; 4, oven; 5, preheater; 6, inlet water; 7, bypass stream; 8, outlet water; 9, extraction cell; 10, heat exchanger; MF, micro filter; P, pressure indicator; PR, pressure regulator; TI, temperature indicator; WI, cooling water in; WO, cooling water out.

main body of the extractor was closed with screw caps at both ends. The flow direction was top to bottom. After the preheating coil, a three way line was made by using three 1/4 inch (6.35 mm) high-pressure heat-resistant needle valves. The needle valves 6 and 8 were inserted on the inlet line to the extractor and outlet line from it, respectively. The needle valve 7 was used as by-passing line. In this manner, the water flow stream could be selected either to the extractor or by-passing it. The preheating coil, the extractor and the needle valves were placed in a fan-equipped temperature-controlled oven (Teb Azma Co., Tehran, Iran), designed to work at up to 200 °C. In order to avoid heat losses of essential oils, a double pipe heat exchanger (tube side: 10.20 mm i.d. × 13.22 mm o.d., cooling surface area: 240 cm^2) cooled with water with about 15 °C and 3 l/min flow rate was used to cool the extract coming out from the oven to a temperature close to 20 °C. A 1 m length stainless steel tube (1 mm i.d. × 3.2 mm o.d.) was applied before a 1/8 inch (3.18 mm) pressure regulator (Hoke Co., USA). In this manner, maintaining the desired pressure in the system was performed precisely. The outlet was inserted in a collection vial. All parts which were in contact with the extractant water made from stainless steel 316.

Two 140 μm microfilter (SS 316, Nupro Co., USA) were used to protect the high pressure pump and pressure regulator, respectively. After the pump, a safety valve (50 bar, SS 316) was used to control the maximum allowable pressure in the system.

2.4. Subcritical water extractions

For all subcritical water extractions, the extractor was filled with 4.0 g ground *C. sativum*. To prevent moving of the particles from the fixed bed, fiber glass wool sandwiched in between two stainless steel filter was inserted in both sides of the fixed bed. The extractor was assembled

in the oven and pressurized by closing the valves 6 and 8, closing the end line regulator, and opening the valve 7. Then, the valve 6 was opened and pumping the water continues to pressurize the system again up to 20 bar. After that, the pump was turned off, the valve 7 was closed, the valves 6 and 8 were fully opened and the oven was brought up to the required temperature, a process that required 20 min. At that time, the pressure regulator was opened, the pump was turned on, and the flow rate was adjusted at the desired rate. Regarding to the selected flow rate and a system void volume between the extractor and collection vessel (~60 ml), in the all runs, around 30 ml of the water coming out of the system was discarded. Using GC analysis, it was observed that this amount of the extracts was clean and no peak was detected. After that, the collection of the extract in a separating funnel was started. The extraction process was supposed to be started at that time (extraction time = 0). After collecting the required volume of extract, a liquid–liquid extraction step using hexane was carried out. The volumetric ratio of hexane to extract was 1:2 in all experiments and extractions were completed by two equal volume of solvent in two step. Around 1 g NaCl was added to facilitate the breaking of the emulsion. The organic phases were concentrated under a N_2 stream to about 0.5 ml volume. An appropriate amount of nonane (0.6 μl) was added to the concentrate as an internal standard. The mixture (0.5 μl) was directly injected into the GC. For the kinetic experiments, the collection vial was replaced at appropriate time intervals.

2.5. Hydrodistillation

An amount of 4.0 g of *C. sativum* seeds were ground and placed in the flask of the Clevenger extractor (British Pharmacopoeia, 1999) and extracted with 150 ml of water steam for 3 h. Low essential oil collected made it difficult to read the amount of oil in the measuring tube of the extractor accurately. So, it was decided to use 40.0 g of the sample with 300 ml of water and applying appropriate dilution ratio before the GC. In this case, around 0.15 ml of essential oil was obtained after hydrodistillation. The extracted essential oil was transferred into a volumetric flask, using three rinses of hexane. The extract was dried over anhydrous Na_2SO_4. The solution was concentrated under a N_2 stream to around 0.5 ml and diluted to 5 ml using hexane. 0.6 μl of nonane was added as an internal standard to 0.5 ml of this solution prior to the GC.

2.6. Soxhlet extraction

Traditional Soxhlet extraction was carried out in standard apparatus by standard methods (Furniss, Hannaford, Smith, & Tatchell, 1989) for 12 h on 4.0 g *C. sativum* with 200 ml hexane. The extract was concentrated under a N_2 stream until around 0.5 ml volume remained and 0.6 μl of nonane was added to the concentrate as an internal standard prior to the GC.

2.7. Analysis

Separation and identification of the components were carried out using GC–FID and GC–MS. The GC apparatus was Phillips model PU-4500, equipped with FID detector. The GC operated under temperature program conditions from 50 to 240 °C at 3 °C/min, an injection volume of 0.5 μl of the hexane extracts was employed using manual injection. The carrier gas was Helium (99.999%, Roham Gas Co., Tehran, Iran). The column head pressure was 0.27 bar. The detector and injector temperatures were 250 °C and 240 °C, respectively. The column was DB1 (25 m × 0.53 mm, film thickness 1.0 μm) bonded phase fused silica capillary.

GC–MS analysis was conducted on a Varian Saturn model 3400 GC–MS system equipped with a DB-5 fused silica column (30 m × 0.25 mm, film thickness 0.25 μm) and interfaced with a Varian ion trap detector. The GC conditions were: oven temperature from 60 °C to 240 °C at 3 °C/min; injector and transfer line temperature, 250 °C and 260 °C; carrier gas, helium at a flow rate of 1 ml/min; splitting ratio, 1:60. The detector temperature was maintained at 240 °C. The MS conditions were: ionization energy, 70 eV; mass range, 40–400 amu and scan mode EI. The percentage composition of the identified components was computed from the GC peak area. The components were identified by comparing their retention times and mass spectra with those of pure reference components. Mass spectra were also compared with those in the NIST (National Institute of Standards and Technology), WILEY5 and TERPENOIDES mass spectra libraries and our own created library.

3. Results and discussion

In using SCWE, hydrodistillation and Soxhlet extraction methods to isolate essential oils from *C. sativum*, the 18 components representing over 90% of the total components detected, were identified, Table 1. The mean relative standard deviation per peak was calculated to be 15%. As can be seen in Table 1, the main component of *C. sativum* is linalool. The concentration of linalool was between 78% and 83% and so, it was chosen as the key component to find the best SCWE operating conditions.

Among the operating conditions that may affect the extraction efficiencies, the pressure is of minor importance. For all subcritical water extractions, the extraction pressure was selected to be 20 bar to maintain the water as a liquid at the extraction temperatures. The main operating conditions to be optimized were selected to be extraction temperature, mean particle size and water flow rate in the range of 100–175 °C, 0.25 to 1.0 mm, and 1 to 4 ml/min, respectively. The univariate method was used in all experiments. Two extraction yields including linalool extraction yield (area ratio of linalool/IS) and total essential oil yield (area ratio of all components/IS) were defined. For the mentioned extraction yields percentage relative standard

Table 1
The percentage composition of essential oil of *C. sativum* L. extracted by SCWE, hydrodistillation and Soxhlet extraction

Components	SCWE[a]	Hydrodistillation[b]	Soxhlet extraction[c]	RI[d]
α-Thujene	nd	7.875	3.976	928
Sabinene	nd	0.267	0.241	975
β-Pinene	nd	0.762	0.687	980
Myrcene	nd	0.322	0.486	993
p-Cymene	3.766	3.617	0.841	1028
Limonene	t	0.330	0.250	1031
Z-β-Ocimene	t	0.177	t	1038
γ-Terpinene	0.421	4.544	7.286	1065
Terpinolene	0.271	t	0.180	1092
Linalool	82.916	77.977	79.619	1102
Camphor	t	0.153	0.232	1146
Citronellal	t	0.189	0.333	1157
Trpinene-4-ol	t	0.193	0.587	1180
Decanal	1.879	0.240	0.574	1202
Cumin aldehyde	5.280	1.053	0.359	1242
Terpinene-7-al ⟨α⟩	t	t	t	1286
Terpinene-7-al ⟨γ⟩	4.757	0.196	t	1291
Geranyl acetate	0.224	2.117	4.365	1387

t = trace (<0.1), nd = Not detected.
[a] Temperature = 125 °C, particle size = 0.5 mm, flow rate = 2 ml/min, pressure = 20 bar.
[b] Extraction time = 3 h.
[c] Extraction time = 12 h.
[d] Retention indices on the DB-5 column.

deviation (% RSD) values were calculated on the basis of the obtained peak areas. The % RSD values were ranged from 5.5% to 14.9%.

3.1. Effect of temperature

One of the most important parameters in SCWE process is temperature. Subcritical water extraction must be carried out at the highest permitted temperature. Regarding to extraction of essential oils, it has been shown that temperatures between 125 and 175 °C will be the best condition. The extraction temperature for *C. sativum* was optimized in order to maximize linalool extraction yield as a key component. Its influence was studied between 100 °C and 175 °C and mean particle size, flow rate, extraction time and pressure were selected to be 0.5 mm, 2 ml/min, 45 min and 20 bar pressure, respectively. As can be seen in Fig. 2, the linalool extraction yield increased generally with increase in temperature up to 125 °C. At 150 and 175 °C, it decreased and an extract with burning smell was produced. It is may be the result of degradation of some of the constituents, e.g., linalool, at the higher temperatures (Kubatova, Lagadec, Miller, & Hawthorne, 2001). Because of the highest amount of linalool at 125 °C and disagreeable odor of the extract at higher temperatures, the further experiments were carried out at this temperature.

3.2. Effect of particle size

The *C. sativum* seeds were ground and screened by standard sieves. The mean ground seed particles were 0.25, 0.5, and 1.0 mm. The effect of mean particle size on the linalool extraction yield as cumulative area ratio (linalool/IS) at 125 °C temperature, 2 ml/min flow rate, 20 bar pressure, and 120 min extraction time has been shown in Fig. 3.

As seen, the extraction efficiencies of linalool for 0.25 mm and 0.5 mm size particles were relatively the same. The final amount of linalool extracted from 0.25 mm size particles was slightly lower than that for 0.50 mm particles. It may be the result of vaporization of some of the essential oils, including linalool, from the smaller particles during

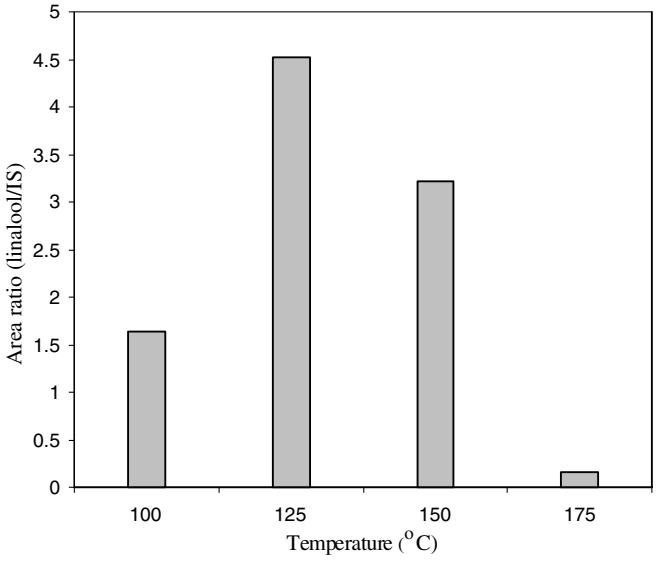

Fig. 2. Effect of temperature on the SCWE (linalool/IS) from 4.0 g of *C. sativum* L. seeds. Operating conditions: flow rate = 2 ml/min, particle size = 0.5 mm, pressure = 20 bar, extraction time = 45 min.

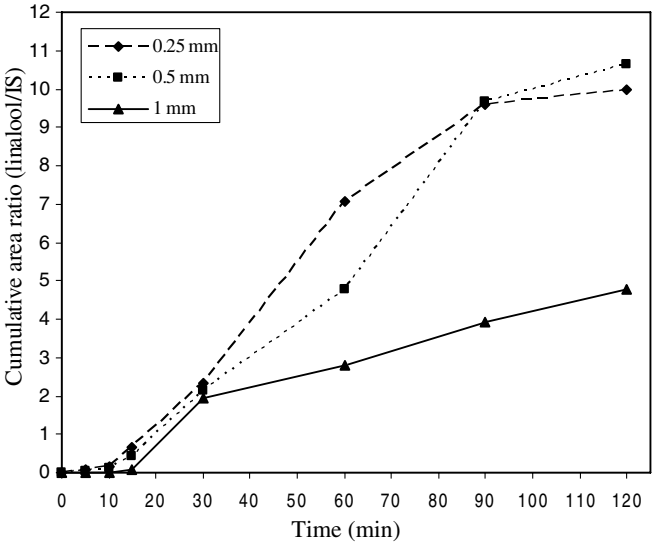

Fig. 3. Effect of particle size on the SCWE (linalool/IS) from 4.0 g of *C. sativum* L. seeds. Operating conditions: temperature = 125 °C, flow rate = 2 ml/min, pressure = 20 bar.

the grinding process. Regarding to the larger 1.0 mm size particles, the efficiency is substantially lower. It shows that the process may be controlled by mass transfer of linalool for larger particle sizes. For further experiments, the optimum value for the mean particle size was selected as 0.50 mm. The total extraction yields found for the total essential oil in terms of cumulative area ratio (all components/IS) were 14.5, 14.1, and 8.8 for 0.25, 0.5, and 1 mm, respectively. It shows that total amount of the essential oils extracted were nearly the same for 0.25 and 0.5 mm and substantially lower for 1 mm.

3.3. Effect of flow rate

The effect of water flow rate on the linalool extraction yield at 125 °C temperature, 0.5 mm particle size, 20 bar pressure, and 120 min extraction time has been shown in Fig. 4. The water flow rate was studied in the range of 1 to 4 ml/min.

As can be seen, the rate of linalool extractions was very faster at the higher flow rates. It is in accordance with previous works (Kubatova, Jansen, Vaudoisot, & Hawthorne, 2002). The rate is slower at 2 ml/min and even slower at 1 ml/min. It means that the mass transfer of linalool component from the surface of the solid phase into the water phase regulated most of the extraction process. Increase of flow rate resulted in increase of superficial velocity and thus quicker mass transfer (Cacace & Mazza, 2006). The main disadvantage of applying higher water flow rates is increasing the extract volume and consequently, lower concentration of the final extracts. In practice, the best flow rate must be selected considering two important factors including extraction time and extract concentration. It is clear that shorter extraction time and more concentrated extracts are desirable. Fig. 5 shows the same data for the linalool extraction yields plotted against extraction volume. As can be seen, up to 120 ml extraction volume, (up to water-to-seed ratio of 30 ml/g) there was a significant difference among the linalool extraction yields obtained by 1, 2, and 4 ml/min flow rates and extraction times of 120, 60, and 30 min, respectively. However, at the higher extraction volumes, the yields obtained were close to each other. To prevent slower extraction rate and longer extraction times (at the flow rate of 1 ml/min), and large amount of final dilute extracts (at the flow rate of 4 ml/min), flow rate of 2 ml/min was selected as the optimum value for the extraction of linalool, as the key component, from 4.0 g of *C. sativum* seeds at 125 °C temperature, 0.5 mm particle size, 20 bar pressure, and 120 min extraction time at the range of flow rate examined.

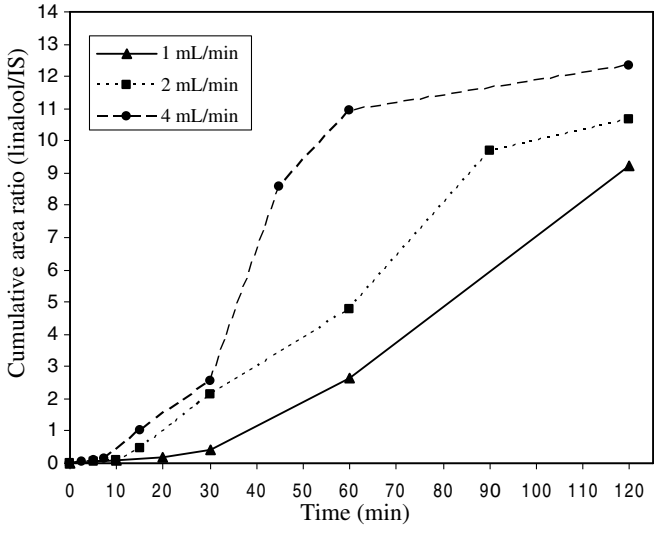

Fig. 4. Effect of flow rate on the SCWE (linalool/IS) from 4.0 g of *C. sativum* L. seeds. Operating conditions: temperature = 125 °C, particle size = 0.5 mm, pressure = 20 bar.

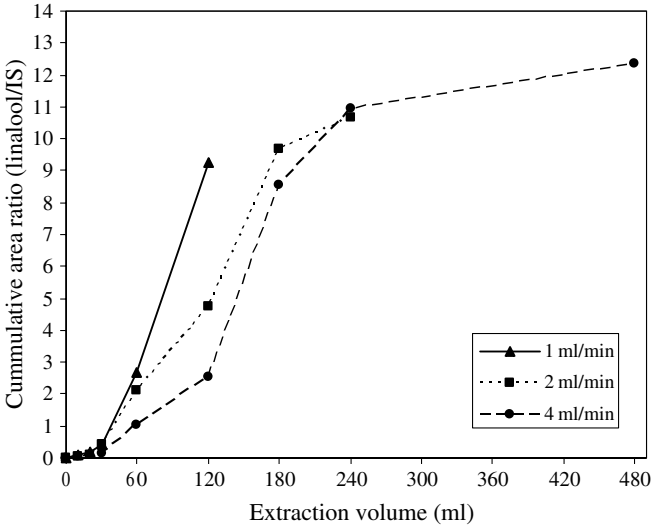

Fig. 5. Effect of extraction volume on the SCWE (linalool/IS) from 4.0 g of *C. sativum* L. seeds. Operating conditions: temperature = 125 °C, particle size = 0.5 mm, pressure = 20 bar, extraction time = 120 min.

The total extraction yields found for the total essential oil in terms of cumulative area ratio of *C. sativum* seeds were 12.0, 14.1, and 17.2 at 1, 2, and 4 ml/min, respectively. It shows that total amount of the essential oils extracted were higher at higher flow rates.

3.4. Comparison with conventional techniques

The comparison among the SCWE, hydrodistillation and Soxhlet extraction has been shown in Table 1. The total extraction yields found for the total essential oil of *C. sativum* seeds were 14.1, 21.7, and 19.4 for SCWE, hydrodistillation, and Soxhlet extraction, respectively. The lower value for the total extraction yields was for the SCWE method and the highest value was for hydrodistillation. Hydrodistillation has a distinct mechanism of extraction (mainly distillation), whereas SCWE and Soxhlet extraction are mainly dissolution and/or solubilization of the essential oil in the solvent (extraction process). As the hexane is a non-polar solvent, non-oxygenated components

are enhanced compared to subcritical water. On the other hand, in general non-oxygenated components present lower vapor pressures compared to oxygenated components, and in this sense, its content in hydrodistillated extracts are increased. Despite of the lower total extraction yields for SCWE (65% and 73% of hydrodistillation and Soxhlet extraction yields, respectively), the presence of the hydrocarbons in the subcritical water extracted essential oil were very low and from quality point of view, because of the significant presence of the oxygenated components, the final extract using SCWE method was relatively better and more valuable.

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