

A Study on Oil Extraction from Albanian Chamomile and Characterization by IR Spectroscopy

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Abstract: Albania is recognized for its natural bio-resources such as medicinal and aromatic plants. It is a considerable producer of herbs including common sage, raspberry leaf, thyme, oregano, and chamomile. The mountainous relief and Mediterranean climate are the main factors for having such an ecosystem diversity and biodiversity. Extraction of essential oil from *M. recutita* L. is carried out using a Soxhlet technique. Carbon dioxide (CO₂) is used as a solvent for the extraction under near critical conditions, since it is physiologically harmless, environmentally safe and it can be easily removed from products. Additionally, hexane is used as well for the Soxhlet extraction and the yield of the obtained extract is compared with yield of the extract obtained with liquid CO₂. FTIR analysis indicated presence of matricine, dicycloether and α -bisabolol as organic components present in the essential oil of *M. recutita* L.

Keywords: Extraction, essential oil, chamomile, Soxhlet technique, IR spectroscopy

Introduction

Usually, the extraction of essential oils from herbs can be performed by hydro-distillation technique (Andoni *et al.*, 2015). Nevertheless, low yield, long extraction time, and degradation of thermo-sensitive compounds are involved when using such technique. These drawbacks can be avoided by using a Soxhlet technique (Dama *et al.*, 2015). As a solvent can be utilized carbon dioxide (CO₂) which is the most extensively used solvent in supercritical fluid extraction or near critical fluid extraction, since it is physiologically harmless, environmentally safe and it can be easily removed from products (Taraj *et al.*, 2013; Andoni *et al.*, 2014).

Albania is recognized for its natural bio-resources such as a large number of herbs, medicinal, cosmetic and aromatic plants (Metaj, 2007 and Vaso, 1998). In particular, it is a large producer of salvia species such as *Salvia Officinalis* L. (common sage) and *Salvia Fruticosa* Mill. Furthermore, Albania is the main exporter of *Salvia Officinalis* L. to US (Schmiederer *et al.*, 2013). The Chamomile (*Matricaria recutita* L.) is also a well-known aromatic and medicinal herb in Albania (Andoni *et al.*, 2015 and Taraj *et al.*, 2013). It belongs to the *Asteraceae* family and it is generally known as German chamomile, Roman chamomile and English chamomile (Gupta *et al.*, 2010). German chamomile is an annual plant that is native to Southern and Western Europe, North and West Asia. Chamomile (*Matricaria chamomilla* L.) is traditionally used as a medicinal and pharmaceutical preparation, due to its anti-inflammatory properties. The main constituents of *Matricaria recutita* L. are the terpenoids α -bisabolol and its oxides (75 %) (Reverchon & Senatore 1994, Ghasemi *et al.*, 2013, Salamon *et al.*, 2010), dicycloethers (13 %) (Reverchon & Senatore 1994; Gupta *et al.*, 2010), matricine (Reverchon & Senatore 1994, Gupta *et al.*, 2010, Ghasemi *et al.*, 2013), and apigenin-7-glucoside.

Following our previous work on extraction of essential oils from Albanian aromatic and medicinal herbs (Taraj *et al.*, 2013; Andoni *et al.*, 2014; Andoni *et al.*, 2015; Dama *et al.*, 2015; Ciko *et al.*, 2016), we further extended this work by utilizing a Soxhlet extractor to extract essential oil from *Matricaria recutita* L. Liquid CO₂ was used as a friendly environment solvent during the Soxhlet extraction. Additionally, for comparison reasons hexane was incorporated as well, as solvent during the Soxhlet extraction of the essential oils from Albanian chamomile. FTIR analysis indicated presence of matricine, α -bisabolol, and dicycloether as organic components present in the essential oil of *M. recutita* L.

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Materials and Methods

Sampling methodology and extraction methods

The origin of the flower heads of *M. recutica* L. used in this work is from local Albanian herbs. The herb was dried at 40°C and subjected afterwards to grinding process and then used such as for the extractions with liquid CO₂ (subcritical conditions) and hexane. Figure 1 exhibit a photo of Albanian chamomile. Albanian chamomile has a green color characterized by fluffy stems and white flowers with a yellow disc in center. The stem of the Albanian chamomile is in the upright position.



Figure 1. Photo of Albanian chamomile (*M. recutica* L.)

All the chemicals were of analytical grade. Instrumental grade carbon dioxide was supplied in a high pressure cylinder. The extraction with liquid CO₂ under near critical conditions occur in vapor-liquid equilibrium at the temperature of 33⁰C (306 K) and the pressure of 61 bars. Figure 2, a) exhibits phase diagram of carbon dioxide. A supercritical or near critical fluid exhibit intermediate properties between those of a liquid and a gas, but has the solvating property of liquids (Taraj *et al.*, 2013). The extraction with subcritical CO₂ was carried out in an autoclave, as shown in the Figure 2, b) and c) (Taraj *et al.*, 2013). In the present work extraction of *M. recutica* L. essential oil was carried out at 40⁰ C (temperature of oil bath) and at pressure of 65 bars (CO₂ pressure). The extraction was allowed to run up to ~12 hours, which accounts for 50 cycles. A cycle ends when liquid CO₂ reaches the maximum level at Soxhlet recipient (Figure 2, c) and starts to spill over, down to the collection beaker. The amount of CO₂ used was 230 g. The crude extract was taken after the evaporation of the solvent (CO₂) and dissolved afterwards in hexane.

In the Soxhlet extraction, *M. recutica* L. is placed inside thimble in similarity with the extraction with liquid CO₂ (Figure 2, d). The thimble is positioned in the main chamber of the Soxhlet extractor. The Soxhlet is slotted onto a flask which contains hexane up to 300 mL. While the Soxhlet part is fitted in a condenser, the hexane is heated and allowed to reflux (Ciko *et al.*, 2016). The hexane vapor runs up to the distillation arm and overflows back to the chamber where the plant is located. The condenser provides the vapor of the hexane to cool down, and drops back down to the chamber. Whilst the Soxhlet chamber is about full, the chamber automatically gets emptied by a siphon side arm (Ciko *et al.*, 2016), with hexane going back down to the distillation flask. This cycle is allowed to repeat over several hours. In the current work the extraction process was allowed to run 3 hours. During each cycle non-volatile compound dissolve in the hexane. After repeated cycles the desired compounds are concentrated in the distillation flask. The crude extract was taken after the evaporation of the solvent by means of a rotary evaporator and dissolved in hexane.

Vibrational spectroscopic measurements

The oil extracts were analyzed by FTIR spectroscopy. FTIR spectra were obtained by Nicolet 6700 spectrometer, manufactured by Thermo Electron, which allows spectral measurements in NIR (12000 - 4000 cm⁻¹) and MIR (4000 - 400 cm⁻¹) region. This system works in two geometries, the geometry of the transmission and reflectance (Attenuated Total Reflection - ATR). In this study, the

transmission geometry is used in the range mid Infra-Red ($4000 - 400 \text{ cm}^{-1}$). The spectra were analyzed using OMNIC software.

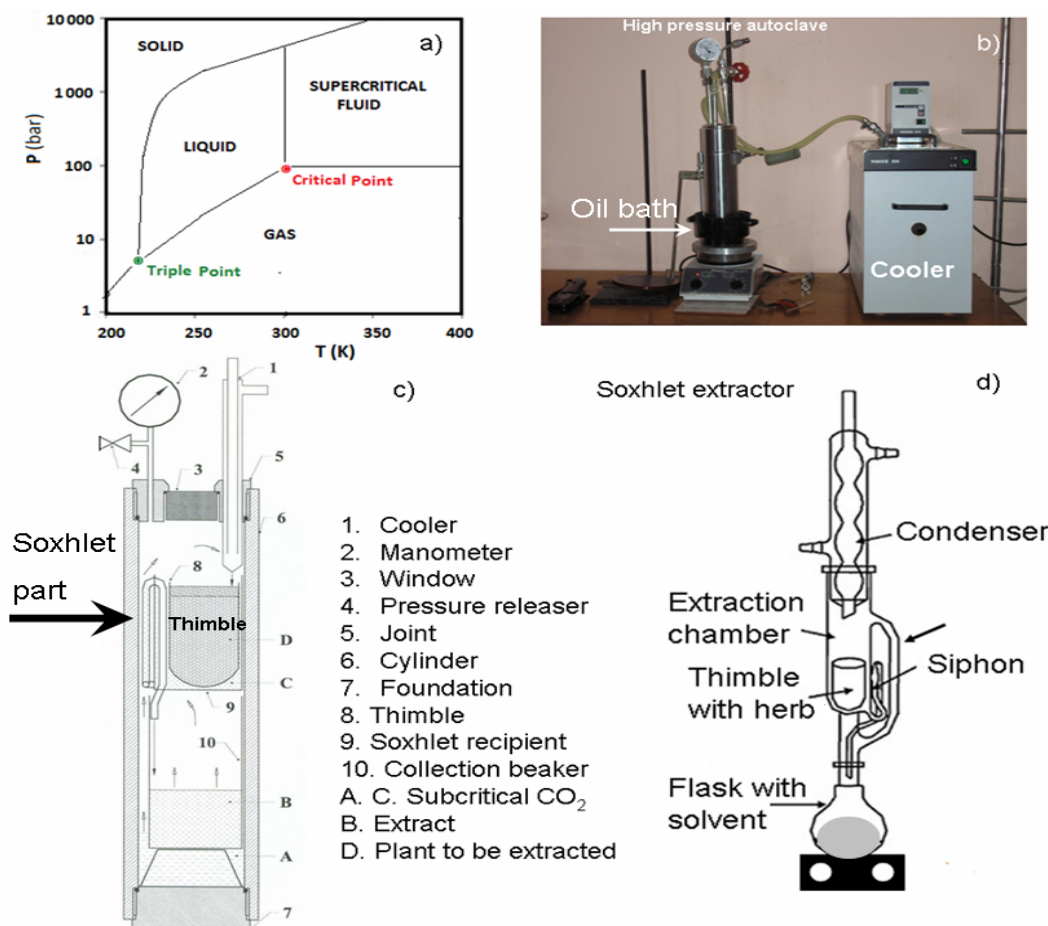


Figure 1. a) Phase diagram of carbon dioxide. b) Photo of autoclave for CO₂ extraction. c) Scheme of the internal part of the autoclave including the Soxhlet extractor d) Scheme of the Soxhlet extractor.

Results and discussion

The yield of the oil extract obtained with liquid CO₂ was 2.37% for 10 g herb, whereas the yield of the oil extract obtained with hexane as solvent extraction was 3.65% for 10 g herb. Table 1 summarizes the results for both extractions. It is obvious from Table 1 that oil extract of *M. recutica* L. obtained with hexane has a higher yield compared to the yield of the oil extract obtained with liquid CO₂.

Table 1. Overall results for the extraction of essential oil of *M. recutica* L.

Extraction method	Amount of <i>M. recutica</i> L.	Extraction solvent	Extraction time	Extraction temperature	Yield of oil extract
Soxhlet (subcritical condition)	10 g	Liquid CO ₂	12 h	40 ⁰ C	2.37%
Soxhlet (distillation)	10 g	Hexane	3 h	80-90 ⁰ C	3.65%

Figure 2 displays FTIR spectrum of the extract obtained with Soxhlet method using hexane as extracting solvent. The band at $\sim 1740 \text{ cm}^{-1}$ present in IR spectrum belongs to C=O stretching vibration and it is attributed to the presence of matricine. Mwazighe (2013) reported a peak appearing between 1770 cm^{-1} and 1720 cm^{-1} in the IR spectra whose intensity ranged from medium to strong and it was characteristic of the chamomile extract. The C=O stretching vibration appears as an intense band between 1800 and 1600 cm^{-1} (Steven, 1999). When the intense band at $\sim 1743 \text{ cm}^{-1}$ is combined with

two bands at $\sim 1240\text{ cm}^{-1}$ (ester C-C-O stretch at 1238 cm^{-1} in Figure 2) and at $\sim 1028\text{ cm}^{-1}$ (at $\sim 1021\text{ cm}^{-1}$ in the spectrum of Figure 2, ester O-C-C stretch), the spectrum follows the rule of three which is a feature of a saturated ester. Therefore, we have assigned the peaks at $\sim 1740\text{ cm}^{-1}$, $\sim 1240\text{ cm}^{-1}$ and at $\sim 1028\text{ cm}^{-1}$ to matricine.

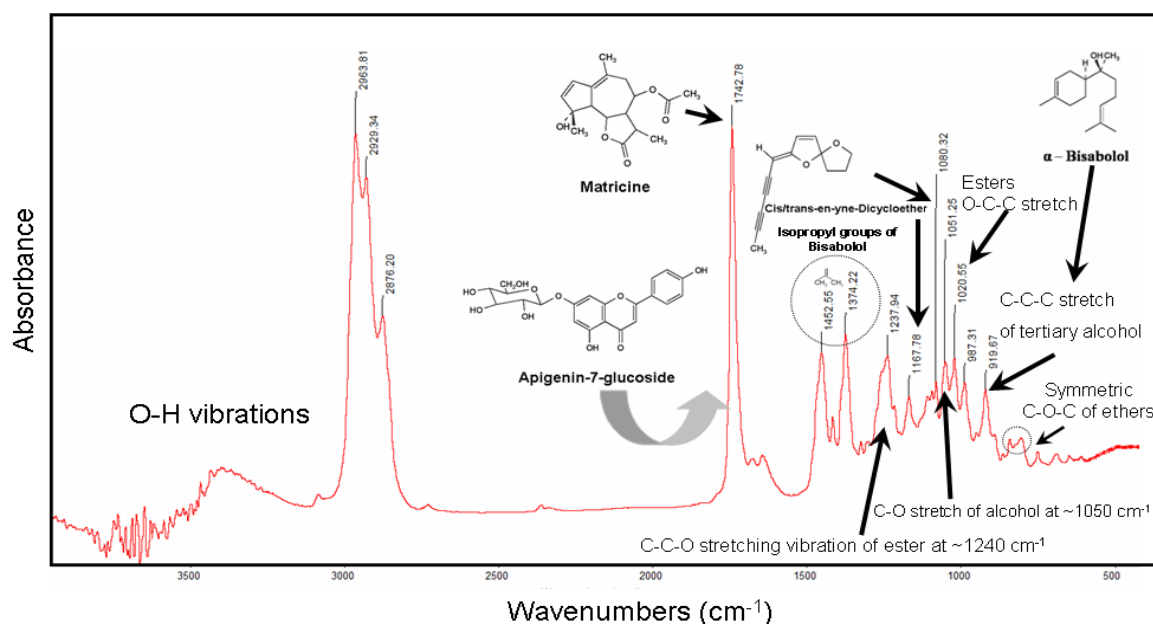


Figure 2. FTIR spectrum of *M. recutica* L. obtained by a Soxhlet extractor using hexane as a solvent. In the insert are indicated the peak assignments of the main components along with their chemical structures as identified in the IR spectrum.

Furthermore, apigenin-7-glucoside features also a C=O functional group in its chemical structure, therefore we cautiously attribute the intense band $\sim 1740\text{ cm}^{-1}$ to apigenin-7-glucoside as well, in addition to matricine. The bands at $\sim 1168\text{ cm}^{-1}$ and at $\sim 1080\text{ cm}^{-1}$ are assigned to dicycloether since ethers give rise two or more bands at $1210\text{-}1070\text{ cm}^{-1}$ (asymmetric C-O-C stretch). The band $\sim 1050\text{ cm}^{-1}$ is attributed to the α -bisabolol, since tertiary alcohols have a diagnostic C-O stretch at $1210\text{-}1100\text{ cm}^{-1}$. In addition, the C-C-C stretch of the tertiary alcohol (α -bisabolol) appears at $\sim 919\text{ cm}^{-1}$ (Steven, 1999).

Lastly, in the FTIR spectrum of *M. recutica* L. oil appears two sharp peaks positioned at $\sim 1452\text{ cm}^{-1}$ and 1374 cm^{-1} . It is known that isopropyl and *gem*-dimethyl groups give rise to a split umbrella mode with two peaks in the IR spectrum positioned at $\sim 1385\text{ to }1365\text{ cm}^{-1}$ (Steven, 1999). The splitting is caused by vibrational interaction between the umbrella modes of the two methyl groups. The split of the umbrella modes is of about equal intensity. Additionally, the band at $\sim 1374\text{ cm}^{-1}$ can also indicate the presence of a CH₃, a CH₂ or both groups; whereas CH₃ symmetric bend (umbrella mode) shows up at $1375\pm 10\text{ cm}^{-1}$ (Steven, 1999). The chemical structure of α -bisabolol consists of an isopropyl group. We tentatively attribute the bands at $\sim 1452\text{ cm}^{-1}$ and 1374 cm^{-1} to the isopropyl group of α -bisabolol. The bands positioned at $\sim 3000\text{-}2800\text{ cm}^{-1}$ correspond to the asymmetric and symmetric C-H stretches (CH₃ and CH₂). The band in the region $3500\text{-}3200\text{ cm}^{-1}$ belongs to the O-H vibration. To this end IR analysis of this work are in good agreement with our previous work on chamomile essential oil extraction by water-distillation method and characterization by FTIR spectroscopy (Andoni *et al.*, 2015).

Table 2. Overall IR analysis for the extraction of essential oil of *M. recutica* L.

Components	Functional group	Wave number (cm ⁻¹)
Matricine	C=O, C-C-O, O-C-C (ester group)	~ 1743 , ~ 1238 , ~ 1021
Apigenin-7-glucoside	C=O (ketone group)	~ 1743
α -Bisabolol	C-O, C-C-C vibration, isopropyl group	~ 1050 , ~ 919 , ~ 1452 and ~ 1374
Dicycloether	C-O-C	~ 1080 and ~ 1167

In addition, oil extract of chamomile obtained with liquid CO₂ was characterized by FTIR spectroscopy as well. The FTIR spectrum (not shown) revealed similar features with the spectrum of oil extract obtained with Soxhlet method using hexane as extracting solvent. The overall IR analyses of peaks assignments are tabulated in Table 2.

Conclusions

Extraction of essential oil from Albanian *M. recutita* L. was carried out by means of a Soxhlet extractor using liquid CO₂ as environmentally friendly solvent and hexane for comparison reasons. The yield of the oil extract obtained with hexane as extracting solvent was higher than the yield of the oil extract obtained with liquid CO₂. IR analysis indicated presence of matricine (ester functional group identified with three bands positioned at ~1743 cm⁻¹, ~1238 cm⁻¹, ~1021 cm⁻¹), possible presence of apigenin-7-glucoside (ketone functional group identified with a band positioned at ~1743 cm⁻¹), α -bisabolol (C-O vibration identified with a band at ~1050 cm⁻¹, C-C-C vibration of tertiary alcohol identified with a band at 919 cm⁻¹ and isopropyl group tentatively identified with two bands at ~1452 cm⁻¹ and ~1374 cm⁻¹) and dicycloether identified by the C-O-C functional group with two bands at ~1080 cm⁻¹ and at ~1167 cm⁻¹.

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