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Keywords: Essential oils; microwave extraction; GC-MS; TG; TG-FTIR; oxygenated monoterpenes.

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Abstract: Lavender, sage, rosemary, fennel seed and clove bud essential oils (EOs) were isolated using a microwave-assisted Clevenger-type device, where the microwaves are applied by means of a coaxial antenna and by conventional hydrodistillation (HD). The yield and chemical composition of EOs were analyzed as a function of the microwave (MW) extraction time. A complete chemical characterization was performed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) analysis. The analysis of the thermal behavior and stability of the EO were performed by thermogravimetry (TG) and thermogravimetry coupled to infrared spectrometry (TG-FTIR). Thermal analysis showed that the EO thermal behavior is described by the evaporation of its main compounds. The most volatile EO was the rosemary, while clove EO was the most thermally stable. The coaxial MWHD extraction leads to a high concentration of oxygenated monoterpenes, different product selectivity, energy savings, and reductions in heating time compared to the EO obtained by conventional HD. The coaxial antenna method allows the scale-up to industrial level without any limit of power and size.

Title:

Coaxial Microwave assisted hydrodistillation of essential oils from five different herbs (lavender, rosemary, sage, fennel seeds and clove buds): *chemical composition and thermal analysis*

Authors:

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Dear Editor,

I would like to thank you for the opportunity to re-submit the manuscript.
We accepted all the reviewers' suggestions: we have added a photo of the device (Fig. 1), a basic scheme for the industrialization of the method and we have added a paragraph (3.4) with scale-up and green chemistry considerations of the coaxial antenna method. Finally, we have added some items in the bibliography.
I hope that the material added to the manuscript is sufficient to meet reviewers wishes and to make the manuscript more interesting.

Yours Sincerely,

Carlo Ferrari

Detailed Responses to Reviewers

Reviewers' comments:

Reviewer #1: The article deals with an innovative and highly possible application of microwave extraction at industrial scale.

Referee has some remarks which will enhance the readability of the article

1. Authors have to add a figure and photo of the system, it is important for readers for the comprehension of the system which is different from the microwave reactors in monomodes (CEM) or multimodes (Milestone) used in laboratories

R.: We added a photo of the system (Fig. S1)

2. This technique will enhance the extraction by reducing time, energy... It is important that authors add a paragraph explaining what is the added value of their article regarding Green extraction and green chemistry in term of energy, solvents, by products, process…

R.: We added a paragraph (3.4) explaining the added value.

N. Rombaut et al.

Green extraction processes of natural products as tools for biorefinery

Biofuels, Bioprod. Bioref. 8:530-544 (2014)

R.: We added the reference.

2. Referee suggests to add a paragraph about possible industrialisation of their system, and compare with the MW reactors used for extraction of natural products

R.: We added a paragraph (3.4) and a scheme dealing about industrialization.

A. Filly et al.

Solvent-free microwave extraction of essential oil from aromatic herbs:

From laboratory to pilot and industrial scale.

Food Chemistry, 2014,150, 193-198.

L. Petigny et al.

Simultaneous Microwave Extraction and Separation of Volatile and Non-Volatile

Organic Compounds of Boldo Leaves. From Lab to Industrial Scale

Int. J. Mol. Sci. 2014, 15, 7183-7198

R.: We added the last references.

Industrial relevance

In literature there are many articles that show the effectiveness and usefulness of the microwave in the chemical and food processing. This technology offers the possibility of faster and more uniform heating, and gives rise to processes that are not completely identical to the methods of conventional heating. However, the application of microwave technology in industry is very limited. This is due to the difficulty in industrial scale-up of microwave ovens. In fact, the use of microwave ovens or resonant cavities involves drawbacks that limit their use. In particular, they have irregular distributions of electromagnetic fields, forming hot-spot, non-uniformity of irradiance, difficulty using common sensors. In addition, the depth of irradiation is limited to a few centimeters.

In this article we presents an application of an innovative method to irradiate microwave, which uses coaxial antennas. The use of such antennas removes many of the constraints of microwave ovens. For example, it is possible to use glass reactors, use several antennas, immerse the antennas in depth in a liquid overcoming the limits of the depth of penetration and thus treat high volumes.

We believe that this technology is mature for the industrial application.

Highlights

- Lavender, sage, rosemary, fennel and clove EOs isolated by two methodologies;
- Coaxial MWHD yields EOs with high concentrations of oxygenated monoterpenes;
- Thermal behavior and stability study of EOs by TG and TG-FTIR techniques;
- Energy and time saving as a result of the coaxial MWHD approach to EO isolation;
- Easy industrial scale-up.

Coaxial Microwave assisted hydrodistillation of essential oils from five different herbs (lavender, rosemary, sage, fennel seeds and clove buds): *chemical composition and thermal analysis*

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ABSTRACT

Lavender, sage, rosemary, fennel seed and clove bud essential oils (EOs) were isolated using a microwave-assisted Clevenger-type device, where the microwaves are applied by means of a coaxial antenna and by conventional hydrodistillation (HD). The yield and chemical composition of EOs were analyzed as a function of the microwave (MW) extraction time. A complete chemical characterization was performed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) analysis. The analysis of the thermal behavior and stability of the EO were performed by thermogravimetry (TG) and thermogravimetry coupled to infrared spectrometry (TG-FTIR). Thermal analysis showed that the EO thermal behavior is described by the evaporation of its main compounds. The most volatile EO was the rosemary, while clove EO was the most thermally stable. The coaxial MWHD extraction leads to a high concentration of oxygenated monoterpenes, different product selectivity, energy savings, and reductions in heating time compared to the EO obtained by conventional HD. The coaxial antenna method allows the scale-up to industrial level without any limit of power and size.

Key words: Essential oils; microwave extraction; GC-MS; TG; TG-FTIR; oxygenated monoterpenes.

Chemical compounds studied in this article

1,8-Cineole (PubChem CID: 2758); Camphor (PubChem CID: 2537); α-bisabolool (PubChem CID: 10586); α-Pinene (PubChem CID: 6654); verbenone (PubChem CID: 29025); borneol (PubChem CID: 64685); (E)-anethole (PubChem CID: 637563); fenchone (PubChem CID: 14525); Eugenol (PubChem CID: 3314); Eugenol acetate (PubChem CID: 7136).

1. INTRODUCTION

Essential oils (EOs) are renewable products that can be isolated from aromatic herbs, namely lavender, rosemary, thyme, cloves, sage, etc. These complex mixtures of volatile organic compounds have been used for many years as flavors and aromatic components in the formulation of personal care products and food preservation (Schimdt, 2010), and more recently as therapeutic agents in biomedical applications (Bilia et al., 2014).

Three main steps are involved EO isolation: i) selection of the raw material, ii) the extraction process and chemical characterization, and iii) the final applications and safe manipulation.

The raw materials to obtain EOs are available worldwide and can be taken directly from nature or by the cultivation of EO bearing plants. The final use (restricted by the chemical composition) and its local availability (wild or cultivated product) must be considered in the selection of the raw material . The yield and quality of the essential oils are influenced by the particular part of the plant used to perform its extraction.

During the EO isolation of lavender, for example, the yield is favored by the use of flowers, producing an approximately 4 to 5 times larger (percent yield) quantity of EO than the yield obtained using leaves exclusively (Nadjalin et al., 2014). Lavender EO from flower extraction is more desirable for cosmetics and personal care formulations, since linalyl acetate, which is found in the flower extract, is responsible for its characteristic odor (Lim, 2012). On the other hand, the leaves and stems produce an EO that is more suitable for medicinal and insecticidal use because of its higher content in 1,8 cineolel and camphor (Lim, 2012). These compounds are also present in other plants such as sage and rosemary, where leaves and stems are used for EO isolation.

The yield, extraction time and chemical composition are influenced not only by parameters such as the growing environmental conditions, genetic variety and organ of the plant sample, but they also depend on the extraction approach used in their isolation. Steam extraction (STE) and hydrodistillation (HD) using a clevenger condenser are traditionally employed for its production (Schimdt, 2010). However, novel extraction techniques have been developed in order to maximize the percent yield, while reducing the time processing and energy demands (Li, Fabiano-Tixier, & Chemat, 2014).

The success of green extraction approaches, such as microwave assisted extraction (MWAE) (Chemat et al., 2006; Chen, S.S. and Spiro, 1994; Flamini et al., 2007), supercritical fluid extraction (SFE) (Guan, Li, Yan, Tang, & Quan, 2007) and ultrasound assisted extraction (Roldán-Gutiérrez, Ruiz-Jiménez, & Luque de Castro, 2008), is based on the capacity of producing EOs with the same quality and sensorial properties as those obtained by conventional techniques, but more rapidly and at a lower cost. Microwave (MW) technology is thus a suitable methodology for obtaining essential oils from several herbs (Li et al., 2014).

Several configurations using MW irradiation for classical hydrodistillation have been developed, involving microwave-assisted hydrodistillation (MWHD) (Golmakani & Rezaei, 2008), microwave steam distillation (MWSD) (Chemat et al., 2006), and microwave assisted hydrodiffusion and gravity (MWHG) (Vian, Fernandez, Visinoni, & Chemat, 2008).

However, most of these approaches make use of MW oven-type devices, which are expensive and difficult to scale up. In a previous work, we used a coaxial dipole antenna to apply the electromagnetic energy inside the aqueous extraction medium using in-situ MW assisted hydrodistillation of *Laurus nobilis L.* essential oil (Flamini et al., 2007). The coaxial MW hydrodistillation extraction (coaxial MWHD) was achieved with high savings in heating time (400%)

and energy demands (30%) compared to the conventional hydrodistillation technique (conventional HD). In addition, the coaxial MWHD extraction device presents a cheap, safe and easy scale-up configuration as an alternative to the conventional closed-device MW oven configurations.

In this work, the versatility of the coaxial MWHD approach is explored in the extraction of essential oils from five different herbs: i) fresh aerial parts (leaves and stems) of lavender (*Lavandula angustifolia*), sage (*Salvia Officinalis* L.) and rosemary (*Rosmarinus Officinalis*), and ii) dry seeds of fennel (*Foeniculum vulgare*) and clove buds (*Syzygium aromaticum L*.). For comparative purposes, traditional hydrodistillation using conventional heating was also performed for all the herbs investigated. The EOs obtained by the two different procedures were fully characterized by GC, and GC-MS techniques. The thermal stability of the EOs obtained by MWHD was also investigated by a TG-FTIR approach.

Sage, rosemary and lavender are of the *Lamiaceae* family and are native to the Mediterranean, while fennel and cloves belong to the *Apiaceae* and *Myrtaceae* families, respectively. The corresponding EOs are attractive materials which are well known for their antibacterial, antioxidant properties (Bouajaj et al., 2013) and anti-inflammatory (Tosun et al., 2014) or antifungal activities (Da Silva Bomfim et al., 2015). EOs have been successfully applied in green chemistry. Rosemary EO has been used as a new reducing agent to synthesize silver nanoparticles (work on progress), and clove EO has been used as a green monomer to produce polymers (Deng, Yang, Chen, & Liang, 2015).

Several works concerning EO extraction using different approaches can be found in the literature. Table S1 (supporting information) summarizes the key factors involved in the EO isolation obtained by the MW or HD, such as the type of raw material, the yield and the extraction time, for lavender, sage, rosemary, fennel seeds and clove buds EOs. For each EO, the yield is strongly dependent on the raw material however and is also slightly dependent on the type of extraction process. On the other hand, the extraction time is much higher in the conventional extraction process than the MW approaches.

Knowledge of the volatility behavior of EOs is useful for a safe and proper handling of EOs during product formulation. In this work, the thermoanalytical characterization of the five EOs using thermogravimetry and TG-FTIR was also performed. Thermal analysis techniques have been successfully used to investigate the thermal stability of oils, in particular their drying, polymerisation and oxidative degradation (Bonaduce et al., 2012a; Bonaduce et al., 2012b; Duce et al., 2014). However few reports have explored the thermal behaviour and stability of EOs, (Hazra, Alexander, Dollimore, & Riga, 2004; Chiu et al., 2009 and 2010; Martins, Sbaite, Benites, & Maciel, 2011), and to the best of our knowledge there are no works on the use of TG-FTIR for EO characterization nor on the thermal characterization of fennel and sage EOs.

In summary, this work covers the following: i) the extraction of the essential oils of lavender, rosemary, sage, fennel and cloves through coaxial MWHD and conventional HD, ii) a comparison of the EOs extracted (yield and chemical composition) by coaxial MWHD and by conventional HD for the five different herbs investigated, iii) the study of the yield and product distribution as a function of the MW extraction time for the lavender EO, iv) the thermoanalytical characterization by thermogravimetry (TG) of the EOs isolated by the coaxial MWHD approach and the FTIR analysis of the evolved gases, and v) study of the effect of using coaxial MWHD in terms of energy and time savings and EO quality.

2. MATERIALS AND METHODS

2.1 Raw materials

The leaves and stems of fresh lavender, sage and rosemary plants were collected in October 2014 in Pisa (Tuscany, Italy). These raw plant materials were harvested daily during the experimental period and used as a substrate to obtain their EO. Dry fennel seeds (India) and clove buds (Madagascar) were purchased from a local market. Deionized water obtained with a Milli-Q system (Millipore, Bedford, MA, USA) was used as a solvent for the EO extraction.

2.2 EO extraction by coaxial MWHD

A modified Clevenger-type scheme, where the MW irradiation was applied by a coaxial antenna, was used to obtain the EO (see Fig. 1). The apparatus was built and tested in our laboratory as part of the project PRIN 2010-2011 (n.2010C4R8M8). The experimental setup is described elsewhere (Flamini et al., 2007), but the MW power and the experimental procedure has been optimized. In particular, 100 g of fresh lavender, sage or rosemary (leaves and stems) were cut into small pieces and loaded with 500 mL of deionized water in the MW assisted device. The water:substrate ratio (W/S) was fixed to 5:1 (w/w). In the dry samples, fennel seeds were used without any physical pretreatment, while clove buds were ground to a fine powder using a laboratory blender. The aqueous substrate dispersion was loaded into a 1000 mL MW assisted flask vessel. The vessel was wrapped by a metallic grid to prevent the loss of MW irradiation out of the reaction medium and to ensure safe operating conditions. A magnetic stirrer was placed on the base of the MW-assisted extractor device. MW energy was applied by means of a coaxial dipole antenna immersed into the extraction medium, protected by a glass tube. The MW source was a magnetron oscillator that supplies up to 1200 W of continuous MW irradiation power at a frequency of 2450 MHz. The substrate dispersion was heated using 500 W of MW power for 9 min and stirred at 250 rpm. Once the hydrodistillation had started, the power was reduced to 300 W and kept at steady state conditions for different times, in order to study the kinetic of the process.

The yield and chemical composition were first investigated for the lavender as a function of the coaxial-MWHD extraction time at 5, 15, 30 and 60 min. Each experiment was performed as a batch extraction process. For the other EOs, the yield and chemical composition were explored at a fixed extraction time. The extraction time for rosemary and sage, was 30 min, whereas for the dry seeds (fennel and clove buds) it was 120 min. These conditions were chosen on the basis of the results obtained for lavender (the first herb investigated) and the literature reports (see Table S1, column 5). After completion of the extraction process, the EO was collected, decanted, weighed and stored at 4 °C in dark containers for further characterization.

2.3 EO extraction by conventional HD

Hydrodistillation using conventional heating was performed for the five herbs. The extraction conditions were chosen on the basis of the literature data (see Table S1, column 8) as follows: the extraction time was 180 min for lavender, sage and rosemary essential oils, and 360 min for fennel and clove buds. The conventional HD was performed at a W/S ratio of 5:1. The extraction was thermally activated using a standard electric mantle operating at 250 W. After completing the extraction, a similar treatment to the EO was performed as described previously for the EO obtained using the coaxial MWHD.

2.4 GC and GC-MS Analysis

The essential oils were analyzed by gas chromatography (GC-FID) and gas chromatography-mass spectrometry (GC-MS) techniques. GC-MS analysis was carried out using a gas chromatograph (Agilent, Model 6890N, Palo Alto CA, USA) equipped with a split-splitless injector, an Agilent model

7683 autosampler and an Agilent HP5-MS fused silica column (5% phenyl-methylpolysiloxane, 30 m × 0.25 mm i.d., film thickness 0.25 μm). The column temperature was programmed to be heated from 60 °C to 246 °C at a rate of 3 °C/min, and kept under isothermal conditions for 20 min. The injector was maintained at 250 °C. Helium was used as carrier gas at a flowing rate of 1.0 mL/min through the column. Samples were diluted in hexane with a ratio of 1:100 and (1 μL) were injected in the split mode (1:20). The GC was fitted with a quadrupole mass spectrometer with an Agilent model 5973 detector.

The MS conditions were as follows: ionization energy, 70 eV; electronic impact ion source temperature, 200 °C; quadrupole temperature, 150 °C; scan rate, 3.2 scan/s; mass range, 30-480 u. Agilent MSD ChemStation E.01.00.237 was used to analyse the mass spectra and chromatograms . The linear retention indices (RIs) for all of the compounds were determined by injection of a hexane solution containing the C8-C26 series of n-alkanes (Van den Dool & Dec. Kratz, 1963) and were compared with authenticated samples from our database. The constituents of the EOs were identified by comparing their retention indices and their mass spectra with a home-made library or with the literature data and the mass spectra databases, including HPCH2205 (R. P. Adams, 2007) and W8N05ST (Wiley ver. 8.0 & NIST, ver. 5.0).

Analytical GC was carried out in a gas chromatograph (Agilent, Model 7890A, Palo Alto, CA), equipped with a flame ionization detector (FID), an auto-sampler (Agilent, Model 7683B), an Agilent HP5 fused silica column (5% phenyl-methylpolysiloxane), 30 m × 0.25 mm i.d., film thickness 0.25 μm, using the Agilent ChemStation software system. The oven temperature was programmed from 60 °C to 250 °C (3 °C/min), the injector temperature was set at 250 °C and the carrier selected gas was helium flowing at 1.0 mL/min. The splitting ratio was 1:10, and the temperature of the detectors was 300 °C. Percentages of individual components were calculated based on GC peak areas, without FID response factor corrections.

2.5 TG and TG-FTIR analysis

The TG experiments were performed using a TA Instruments Thermobalance model Q5000IR equipped with an FTIR Agilent Technologies spectrophotometer model Cary 640 for Evolved Gas Analysis (EGA). TG and TG-FTIR measurements were performed using Pt crucibles at a rate of 10 ◦C/min, from 30 ˚C to 350 ˚C under nitrogen flow (80 ml/min). The amount of sample in each measurement varied between 10 and 11 mg. Mass calibration was performed using certified mass standards, in the 0-100 mg range, supplied by TA Instruments. The temperature calibration was based on the Curie Point of paramagnetic metals. A multipoint calibration with five Curie Point reference materials (Alumel, Ni, Ni83%Co17%, Ni63%Co37%, Ni37%Co63%) was performed. TG-FTIR measurements were performed in the range 600-3000 cm^{-1} with a 4 cm^{-1} width slit. To reduce the strong background absorption from water and carbon dioxide in the atmosphere in the TG-FTIR spectra, the optical bench was usually purged with nitrogen. In addition, a background spectrum was taken before the beginning of each analysis in order to zero the signal in the gas cell and to eliminate any contribution from ambient water and carbon dioxide.

3. RESULTS AND DISCUSSION

3.1 Yield and chemical composition

The percent yield of lavender EO was obtained at four different times (5, 15, 30 and 60 min) using the coaxial MWHD extraction approach, and at 180 min using conventional HD. Figure 2(a) shows the kinetics of lavender EO extraction using the coaxial MWHD approach. The percent yield (w/w) showed a strong dependence on the extraction time. After the first 5 min of MW extraction time, the yield was 0.53%, and the maximum yield (0.75%) was achieved at 30 min, after which no more essential oil was hydrodistillated, although the extraction time was prolonged for 60min.

The extraction process can be described by three main steps of the simultaneous washing and diffusion model reported by (Milojevic, Radosavljevic, Pavicevic, Pejanovic, & Veljkovic, 2013). Briefly, lavender EO isolation can be described as follows: i) an initial step, occurring in the first five minutes (see Fig. 2(a)), when the EO extracted is obtained after the release of the volatile compounds from exogenous secreting glands (washing effect). Once the temperature has increased, an increase in pressure follows within the exogenous glands (due to the expansion of the volatile compounds), leading to cellular wall breakage and the release of the essential oil, ii) the second step occurs in the time interval from 5 to 30 minutes, where the remaining essential oil is progressively extracted due to its diffusion out of the endogenous sites, and iii) the final step, indicated by a flat area from 30 to 60 min, where no more EO is obtained, which represents the end of the extraction process.

The percent yield obtained at the fixed time of 180 min with conventional HD was 0.74 % in agreement with the maximum yield with the MWHD approach (0.75% after 30 min).

The extraction of lavender EO has been previously reported using several approaches (see Table S1). However, such approaches focus on the lavender EO isolation from flowers, making it difficult to compare with our percent yield obtained from fresh leaves and stems.

GC and GC-MS analysis of the lavender EO led to the identification of 27 volatile compounds, which represent more than 98% of the total essential oil. Table 1 shows the main chemical composition of lavender EO obtained by coaxial MWHD at 30 min, and by conventional HD at 180 min. Table S2 (supporting information) shows the full chemical characterization obtained by GC-

MS. Figure 2(b) shows the main compounds of lavender EO obtained at different coaxial MWHD extraction times (from 5 to 60 min) and by conventional HD at 180 min.

The EO isolated by both approaches has a similar qualitative composition, however some differences were highlighted in the quantitative analysis of the main compounds. A lavender EO with three main compounds (1,8-cineole, camphor and α-bisabolool), representing more than 70% of the composition, was obtained (see Table 1).

The product distribution of the EO also depends on the MW extraction time (see Fig. 2(b) and (c)). Figure 2(b) shows the percentage lavender EO composition for compounds higher than 2% analyzed at different extraction times. The main compound, 1,8-cineole, constituted 52% of the total composition of the EO extracted at 5 min, while the composition in the EO obtained at 15 min was 45.2% due to the extraction of other compounds over time. Only slight differences were observed (less than 1% variation) for the samples analyzed at 30 and 60 min, compared with the sample isolated at 15 min.

Consequently, lavender EO with a high 1,8-cineole content can be obtained in the first 5 minutes of the coaxial MWHD extraction. In the case of conventional HD, despite the longer extraction time (180 min), the percentage of 1,8-cineole in the EO (around 33%) was lower than the percentage obtained by the MW approach.

The second most abundant compound was camphor (Fig. 2(b)), which was obtained with a similar percentage among the different microwave extraction times (around 25%) and was slightly lower (by about 2%) in the lavender EO obtained by conventional HD. As expected, the chemical composition of lavender EO obtained from the leaves and stem used in this work is different from the lavender EO obtained by other authors using flowers, where linalool, coumarin, borneol and linalool acetate are the predominant compounds (see Table S4). Our methodology, particularly with 5 min of coaxial MWHD, obtains a higher quality lavender EO (regarding the 1,8-cineole and camphor content) for medicinal and insecticidal applications.

The content of α-bisabolool increased from 2.3% to 7.8 % with the microwave extraction time, and with approximately twice as much lavender EO than obtained by conventional heating (14.1%). The content of linalool decreased from 2.5 % (5 min) to 1.5% (60 min) with the MW extraction time, and its content in the EO obtained by conventional HD was 2.2%. Linalyl acetate was not detected in any of the samples analyzed. The low or null concentration of linalool and linalyl acetate is due to the use of leaves and stems instead of lavender flowers, as mentioned above.

Figure 2(c) shows other differences in both quantitative and qualitative compositions with compounds with a composition lower than 2%. Fenchone and (Z)-ocimene were extracted in higher amounts (yield of 1.5%) using conventional HD (180 min), compared with the yield obtained by MWHD at different extraction times (varying from 1.1% to 1.0 % and, from 0.6% to 0.4%, respectively). Other compounds such as camphene and sabinene were extracted in similar amounts (around 1 %) by the two different methodologies.

Some compounds were only detected in particular extraction conditions (data not shown in Fig. 2). For example b-phellandrene (1.8%) was only found in the lavender EO obtained by conventional HD, while γ-terpinene (0.2%) and cryptone (0.4%) were only detected in the EO obtained after 60 min of MW extraction time. Trans-pinocamphone (0.3-0.5%) and cis-sabinene hydrate (0.5-0.7%) were only found in the EO oil obtained by the coaxial MWHD.

The sage and rosemary EO isolation by the coaxial MWHD was carried out by 30 min of MW irradiation and at the W/S ratio equal to 5:1. These conditions were selected on the basis of the results obtained for the lavender EO, which showed the maximum yield for the extraction process at 30 min. Yields of 0.18% and 0.40% were achieved for sage and rosemary EO, respectively. The yield of sage oil increased with conventional HD leading to a value of 0.30% (at 180 min of extraction time), whereas the extraction of rosemary EO was unchanged, i.e. 0.4 %. These yields are lower than the yields described in the literature (see Table S1) ranging from 0.80% to 1.27% for sage EO (Panda, 2003; Bouajaj et al., 2013; Veličković, Ristić, Karabegović, Stojičević, & Lazić, 2012), and from 0.33% to 2.28% for rosemary EO (Bousbia et al., 2009; Da Silva Bomfim et al., 2015; Karakaya et al., 2014). This is related to the use of fresh leaves and stems in our work instead of dry material, as described in Table S1.

Table 1 shows the main chemical compounds extracted from the sage and rosemary EO obtained by coaxial MWHD at 30 min, and conventional HD at 180 min. The GC-MS analysis of EO identified 44 volatile compounds for sage and 29 for rosemary, which represent 99.6% and 98.0%, respectively (see Table S2). In the sage EO obtained by the coaxial MWHD approach, the main compounds identified were camphor (37.3%), 1,8-cineole (17.9%), cis-thujone (5.7%), (E)-caryophyllene (5.4%) and α-humulene (4.4%). These five compounds represent about 71% of the oil extracted. Most of the other chemical compounds identified were present in trace amounts. In conventional HD the composition is similar to MW extraction and, in both approaches, the predominant components are camphor, 1,8-cineole and cis-thujone. The percentages of compounds isolated by conventional HD are different, since in HD smaller quantities of the main compounds are obtained, but with larger amounts of the minor components. The main compounds were camphor (23.8%), 1,8-cineole (13.7%), cis-thujone (5.9%), camphene (5.2%) and (E)-caryophyllene (4.7%) (see Table 1 and Table S2). Table S4 shows that the sage EO obtained by other authors using aerial parts of sage differ from each other and from our oil in terms of composition. Only the EO obtained by (Bouajaj et al., 2013) with HD extraction has camphor as one of its main compounds, although in a lower amount (9.14%) than our oil (37.3% and 23.8%

with MW and HD extraction, respectively). On the other hand, most of the literature data show a higher content of trans or cis-thujone (ranging from 14.10 to 29.84 %) than in our oil (about 6 %). The content of 1,8-cineol reported in the literature is strongly dependent on the extraction process (ranging from 5.10 to 19.59%), see Table S4.

The rosemary EO isolated by the coaxial MWHD approach was mainly composed of six compounds: α-Pinene (21.9%), verbenone (12.7%), camphor (9.9%), 1,8-cineole (9.4%), borneol (9.1%) and camphene (5.1%). A similar composition was observed for the rosemary EO obtained by conventional HD (see Table 1). Rosemary EO with a comparable composition has been reported by other authors (see Table S4) although there are some differences regarding the quantity of the individual compounds.

The EO extraction from dried fennel seeds was performed using whole seed. A yield of 0.83% and 1.10% was obtained by coaxial MWHD extraction at 120 min and conventional HD extraction at 360 min, respectively. These data are comparable with the data reported in the literature with both MWHD (Koşar, Özek, Kürkçüoglu, & Başer, 2007) and HD (Diao, Hu, Zhang, & Xu, 2014; Zoubiri, Baaliouamer, Seba, & Chamouni, 2014). The former found yields ranging from 1.20% to 1.90 % using a time extraction from 60 to 480 min (see Table S1).

The EOs from clove buds were extracted using ground clove buds. The yields obtained by MWHD extraction at 120 min and HD extraction at 360 min were 5.9% and 9.7%, respectively.

Clove EO is particularly interesting regarding its high yield as already reported in the literature (see Table S1). However, to the best of our knowledge there are no works on the extraction of EOs from clove buds by MWHD. The typical extraction approach is maceration using a mixture of ethanol-water followed by solvent evaporation. In addition several reports exploit supercritical fluid extraction because of the yield enhancement to 19.5% (Guan et al., 2007). Traditional HD yields are around 11% in extraction times from 4 to 6 h (Guan et al., 2007), which are in good agreement with our results.

For both fennel and clove EO, the conventional HD approach leads to a substantially higher yield than the coaxial MWHD approach. The differences between the two approaches may be related to the fact that the coaxial MWHD has not been experimentally optimized. However a detailed investigation of the best extraction conditions for each herb is beyond the aim of this work.

The analysis of the chemical composition of fennel and clove EO by GC and GC-MS analysis led to the complete characterization of the EOs, which contain 17 and 13 volatile compounds, respectively (see Table S3). Table 1 shows the main chemical composition of fennel EO and clove EO obtained by both coaxial MWHD and conventional HD.

The main compounds in the fennel EO extracted by MWHD were: (E)-anethole (79.0%) followed by fenchone (10.9%), estragole (4.2%) and limonene (3.2%). These four compounds represent more than 97% of the total essential oil. A similar trend was observed for the EO obtained by conventional HD: (E)-anethole (81.6%), fenchone (8.7%), estragole (4.0%), and limonene (3.5%). The amount of fenchone was higher in the essential oil obtained by MWHD. Fenchone is used in flavors and fragrances and a composition of fennel EO richest in fenchone increases the value of the essential oil for particular applications such as cosmetics and foods (Schimdt, 2010).

Clove bud EO obtained by coaxial MWHD was mainly composed of eugenol (66.9%), (E)-caryophyllene (24.8%), α-humulene (3.1%) eugenol acetate (2.7%), while for the clove bud EO obtained by conventional HD, the composition was: eugenol (87.1%), eugenol acetate(6.4%) and (E)-caryophyllene (5.1%). Therefore, a clove EO with high antioxidant properties associated with its high content of eugenol acetate and eugenol (Lee & Shibamoto, 2001) can be obtained by coaxial

MWHD. A clove EO, on the other hand, with anti-inflammatory properties due to the high content of (E)-caryophyllene can be isolated by conventional HD .

The EO extracted from fennel and clove buds showed a similar composition reported by several authors (see Table S4) yielding (E)-anethole and eugenol as the main compounds, respectively.

3.2 Thermogravimetric and TG-FTIR analysis

Figure 3 compares the thermogravimetric curves and the corresponding derivatives, recorded under nitrogen flow for the five EOs extracted by the coaxial MWHD procedure. We analyzed the samples extracted at 30 min for lavender, sage and rosemary EO, and at 120 min for fennel and clove.

Essential oils are typically multi-component systems consisting of various volatile compounds. Thus, according to the literature (Chiu, Chiang, Lo, Chen, & Chiang, 2009; Hazra et al., 2004; Martins et al., 2011), weight losses during the heating process are due to the evaporation of the volatile components rather than their thermal degradation.

The thermogravimetric curves of all the oils investigated in this work, showed a loss of the entire mass below 175 °C. This indicates the complete evaporation of the oil, as was to be expected given its composition (see Tables S1, S2 and S3). Under air flow, we obtained the same TG profiles as under nitrogen, suggesting that EOs evaporate completely before being oxidized.

The thermogravimetric profiles of the EOs of lavender, rosemary and sage show similar behaviours (Fig. 3(a)) with the main DTG peak in the range 78-100 °C, the oils of fennel and clove volatize at a higher temperature, with the main DTG peak at 135 °C and 165 °C, respectively (Fig. 3(b)). The DTG maxima of the first mass loss are in the order: $T_{clove} > T_{fennel} > T_{sage} > T_{lavender} > T_{rosemary}$, in agreement with the normal boiling points (T_B) of the main components of the oil (see Table 1): eugenol, T_B = 254°C; (E)-anethole, T_B = 234°C; camphor, T_B = 209°C; 1,8-cineole, T_B = 176°C; α-pinene, T_B = 155°C (P.J. Linstrom & W.G. Mallard). The discrepancies between the temperatures of the DTG peaks and values of the boiling points are due to the interactions between the components in the mixture. The value of a DTG peak also depends on the rate and amount of sample employed in the TG analysis.

With the exception of clove EO, which has a single evaporation step, the profiles of other oils exhibit two peaks according to their composition and the T_B of their components. The lavender EO shows a first massive mass loss (88%) starting at about room temperature up to 125 °C (DTG peak at 95°C), and a second step which leads to total evaporation (mass loss 12% DTG peak at 153°C). The second step could be related to the evaporation of α-bisabolool (T_B = 153°C), β-pinene (T_B = 155°C) and α-pinene (T_B = 155°C), which represent the 12% of the mass weight (Table 1).

Rosemary oil evaporates completely at the lowest temperature. The evaporation starts from room temperature and ends up at 125°C in a two-step process, as indicated by the thermal profile, which shows two overlapping peaks at 78°C and 104°C. This behaviour could be explained by the observation that the main components of rosemary oil (Table 1) can be clustered into two groups according to their $T_{B.}$ The first group, with T_B below 200 °C, is formed by α-pinene and 1,8-cineole, while the second, with T_B above 200 °C, by verbenone (T_B = 227°C), camphor, and borneol (T_B = 213°C) and each group represents about 31% of the total mass.

Sage and fennel EOs show a main mass loss at 99°C (90%) and 135 °C (97%) respectively, and minor mass losses at higher temperatures, as highlighted by the shoulders in the thermal profile. Clove EO shows a higher stability and is completely evaporated at around 170°C.

Figure 4 reports the FTIR spectra of the gases produced by thermal evaporation under nitrogen of the five EOs prepared by coaxial MWHD. In lavender, sage, rosemary and clove EO, the FTIR spectra of the evolved gas did not show significant differences in the temperature range corresponding to the total evaporation process. Therefore, the FTIR spectra were recorded at the maximum of the main DTG peak (see Fig. 3(b)), where the FTIR analysis showed the best resolved spectra. In contrast fennel EO showed two different spectra at 135°C and 157°C (see Fig. 4(d)), which correspond to the different evaporation rates of its main compounds.

All the FTIR spectra displayed several peaks that can be associated with the principal components of the essential oils. Signals associated with the vibration modes of 1,8-cineole were detected in the spectrum of lavender, sage and rosemary (Figs. 4 (a), (b), (c)) since these EOs contain a high concentration of 1,8-cineole (44.4, 17.9 and 9.4% for lavender, sage and rosemary, respectively); i.e. the peaks related to the bending of the C–O at 1379 cm^{-1}, the asymmetric (at 1217 cm^{-1}) and symmetric (at 1080 cm^{-1}) stretching of C–O–C, and CH_2 wagging at 984 cm^{-1}. The peak at 1761 cm^{-1}, which corresponds to the stretching vibration of the carbonyl group (C=O), can be associated with camphor, whose concentration was 25.1% in the lavender EO, 37.2% in the sage EO, and 9.9% in the rosemary EO. The peak at 3089 cm^{-1} is associated with the C═C stretching of the different alkenes contained in the oils, while the peaks at 1013, 916, 881, 690 cm^{-1} are due to C–H deformations. The strongest peaks of the spectra are due to the stretching of methyl (2933 and 2889 cm^{-1}) and methylene groups (2976 cm^{-1}).

Both the FTIR spectra of the gases evolved by fennel EO recorded at 135 °C and 157 °C (Fig. 4(d)) showed peaks associated with the principal components of the oil, namely (E)-anethole (79%), fenchone (10.9%) and estragole (4.2%). According to the literature, since (E)-anethole and estragole have a similar structure, they can be distinguished only by the signals resulting from the non-aromatic C=C double bond (Gudi, Krähmer, Krüger, Hennig, & Schulz, 2014). These authors mentioned that, due to the resonance effect, in trans-anethole, the C=C stretching vibration and the CH deformation shift to higher wavenumbers (1656 cm^{-1} and 962 cm^{-1} respectively), compared to estragole (1638 cm^{-1} and 912 cm^{-1}). These four peaks were detected at 1606 and 948 cm^{-1} in the fennel EO spectrum recorded at 157°C, and with a much lower intensity at 1602 and 948 cm^{-1} in the spectrum recorded at 135°C (Fig. 4(d)). In agreement with the shift reported in the literature and with the boiling temperature of (E)-anethole (T_B = 234°C) and estragole (T_B = 216°C) and, taking into account that (E)-anethole is the predominant compound, we could suppose that (E)-anethole is detected in the spectrum at 157°C, whereas estragole is detected in the spectrum at 135°C. The FTIR spectrum recorded at 135°C also showed a strong band at 1753 cm^{-1} due to the stretching vibration of the carbonyl group (C=O) in a ketone group, which can be assigned to the fenchone compound. Thus fenchone (T_B = 193.5°C) evaporates before anethole, and is detected together with estragole.

The TG-FTIR spectrum of clove EO showed the characteristic peaks of eugenol: O–H stretching at 3591 cm^{-1}, C–O bending at 1238 cm^{-1}, and C–C stretching vibrations in the phenyl ring at 1609 cm^{-1}, 1512 cm^{-1} and 1433 cm^{-1}. No significant differences were observed in the FTIR spectra of the cloves EO obtained by the conventional HD approach.

Table 2 summarizes the characteristic IR absorptions of the EOs investigated with the corresponding references.

3.3 Advantages of the Coaxial MWHD approach: qualitative oxygenated compound isolation, including energy and time savings

In the lavender, sage, rosemary, fennel and clove EOs obtained by conventional HD, around 40 min were needed to start the hydrodistillation when the extracted mixture (70 g of plant substrate

+ 350 g of water) was heated with a standard electric mantle operating at 250 W. On the other hand, by applying 500 W of MW power to the same extracted mixture ratio but using 100 g of plant substrate and 500 g of water, the first distillated drop appeared after around 9 min. The electric energy needed to start the hydrodistillation from room to boil temperature was 1.43 KJ/g using conventional heating, while 0.63 KJ/g were needed by the in situ irradiation of MW energy (considering an efficiency η= 60% of the magnetron oscillator, at 1.2 kW, 2.45 GHz). The energy and time savings using the coaxial MWHD approach were similar to those previously described for *Laurus Nobilis L* (Flamini et al., 2007).

Figure 5 shows the difference in the chemical composition (in terms of the percentage content of the oxygenated and hydrocarbon monoterpenes) of the five essential oils isolated by coaxial MWHD and conventional HD. For all the EOs investigated, the coaxial MWHD approach yields a composition richer in oxygenated monoterpenes. Microwaves obtained oxygenated monoterpenes ranging from 30.6% (5 min) to 17.8% (60 min) in the case of lavender EO, 23.5% (30 min), 31.6% (30 min) and 21.7% (120 min) of the total composition for sage, rosemary and fennel EO, respectively. On the other hand, the essential oils obtained using conventional heating resulted in a higher amount of hydrocarbon monoterpenes, and were about 37.2% larger at 5 min and 26.4% at 60 min for lavender, 43.7% and 20.5% at 30 min for sage and rosemary (see Fig. 5). In the case of fennel seeds, the hydrocarbon monoterpenes were 4% of the total composition for both methodologies.

These results are in agreement with previous results obtained for the extraction of *Laurus Nobilis* (Flamini et al., 2007), lavender (Chemat et al., 2006), sage (Veličković et al., 2012), rosemary (Bousbia et al., 2009) and fennel (Koşar, Özek, Kürkçüoglu, & Başer, 2007). The selectivity of the MWHD approach regarding the isolation of oxygenated monoterpenes is related to a specific MW interaction and to the water solubility (S_w) of some essential oil compounds. The interaction between the microwaves and a heterogeneous material, such as a body made up of cells and connective tissue (leaves and seeds), is not predictable and may give rise to strong temperature gradients in the material, both at macroscopic and microscopic levels. Local overheating could destroy some structures (for example the cell membrane) or increase the mobility of some chemical species rather than others.

The energy transfer to the material takes place through several mechanisms: i) dipolar heating, depending on the permanent or induced dipole moment of the chemical species involved; ii) surface effects at the boundary between different materials (Maxwell-Wagner effect); iii) Joule effect, due to the electrical conduction of the material (Tombari, Ferrari, Salvetti, & Johari, 1999). In addition, the energy transfer depends on the amount of coordinated water of the molecules, since water shows strong absorbance of microwave radiation at 2.45 GHz. Thus, different compounds of the EO can be selectively heated regarding their dipole moment value, electric impedance and coordinated water (Tombari et al., 1999). The oxygenated compounds, such as 1,8-cineole and camphor, which have a high complex permittivity, can be extracted more easily due to their strong MW interaction. In contrast the hydrocarbon monoterpenes, such as α-pinene and limonene, which show less MW interaction lead to a different release of the volatile compounds from exogenous secreting glands (washing and diffusion effects) (Milojevic et al., 2013). This possible mechanism is favored since a high substrate/water ratio (1:5) was involved in both extraction approaches (coaxial MWHD and conventional HD).

3.4 Scale-up and green chemistry considerations towards the industrial applications of a microwave-assisted extraction

Unlike the methods conventionally used for applying the microwaves, such as microwave ovens and waveguide, the use of coaxial applicators allows the ease industrial scale-up. Conventional methods have inherent limitations related to the low penetration depth of microwaves at 2.45 GHz, a few centimeters in a medium with high absorption like water, and the non-uniform distribution of the electromagnetic fields. The coaxial antennas made possible to radiate large volumes, simply by inserting the antennas in the reactor, at various depths. In fact, it is possible to set up any desired number of applicators in an arbitrarily large volume. Antennas placed orthogonally do not affect each other significantly, and each antenna (diameter 13.5 mm) can be fed from a magnetron of 1.5 kW. This configuration can also be used in continuous reactors, where the applicators can protrude inside a pipe and the applied power can be controlled in a feedback loop by means of a sensor placed at the end of the pipe. The protrusion may be made so as to withstand the high temperatures and pressures, not limiting in any way the possible applications of the method.

The absence of a resonant cavity implies that the electromagnetic field does not reach high values and is more uniform with respect to the microwave ovens. In particular, there is no formation of hot-spots which has several implications: i) the treated material is irradiated with greater uniformity and there are minor temperature gradients, thus obtaining a more uniform and higher quality thermal treatment; ii) the industrial scale-up is more simple, since there aren’t dimensional constraints and a wide range of materials is elegible (Teflon, quartz, glass, plastic, etc.); iii) No additional industrial requirements are needed, since the low cost sensors (e.g. thermocouple temperature sensors and manometers) typically used in the industry can be kept.

Therefore, towards the successful industrialisation of the coaxial MWHD extraction process here depicted, the following facts can be pointed out as intrinsic and benefic advantages:

- While it is clear that the use of the coaxial MW antenna helps to overcome the typical drawbacks shown by the oven-type MW assisted extraction processes, the design of new MW assisted extractors or the modification of the current commercial industrial extractors is likely permissible using the coaxial technology.

- Essential oils obtained by the coaxial MWHD are valuable products with very high purity and competitive price market. Additionally, the hydrodistillation produces condensed water and solid residues are obtained as by-products. The condensed water (also named as herbal water) contains non-volatile organic compounds (NVOC), which are bio-compounds such as proteins/enzymes, aminoacids, polysaccharides, alkaloids, alcoholic compounds and vitamins, and they posse strong antioxidant properties (Petigny et al., 2014). Herbal water has also market value like the lavender aromatic water. Moreover, a high amount of solid residues is produced after the EO and NVOC extraction process. These solid residues are mainly biopolymers like polyphenols or insoluble cellulosic materials (Santana-Méridas et al., 2014) which can be used as biomass precursors to obtain energy or bio-compounds derivatives (biorefinery) (Rombaut, Tixier, Bily, & Chemat, 2014). Therefore, the industrialisation of new processes for essential oil extraction will result in a large scale production of NVOC and solid residues as by-products, opening new opportunities to re-valorise these resources, increasing the shareholder value and maximising the profit of the herbs used as raw materials. This fact ensures a promising market introduction of new competitive processes.

- Regarding the environmental point of view, the coaxial MWHD extraction process makes use of water as the only solvent involved in the production and once the by-products are treated as sources to obtain value-added products, this approach can offer a clean and green chemical processing.

The development of the proposed green extraction process with time and energy savings by means of the coaxial MW technology and the minimization of waste by its own valorisation in new derivative bioproducts are illustrated in scheme 1.

4. CONCLUSIONS

The coaxial MW Clevenger-type extractor produced essential oils from five different herbs with a high concentration of oxygenated monoterpenes and different product selectivity regarding the microwave extraction time. The versatility of the different kinds of substrates used and the advantages regarding energy and time savings compared to the conventional HD, makes the coaxial MWHD extraction a desirable technology with promising scale-up in the development of solid-liquid green extraction.

EOs with different qualities in terms of composition can be obtained using different approaches. Camphor and 1,8-cineole were isolated in high concentrations and short extraction times from sage, rosemary and lavender using the coaxial MWHD approach. These EOs have a high value as renewable products especially for medicinal and insecticidal applications. On the other hand, the high amount of fenchone isolated from fennel seeds using the coaxial MWHD increases the value of the essential oil for cosmetics and food applications, while the high content of (E)-caryophyllene in the clove bud EO isolated by the conventional HD increases its anti-inflammatory properties .

The TG of the EO and the TG-FTIR analyses of the evolved gas, for the five herbs investigated, showed that the EO thermal behavior is described by the volatilization of its main components and that thermal degradation does not occur. The most volatile EO was rosemary, while clove EO showed the highest thermal stability. The volatility behavior of the EO analyzed is in agreement with the boiling point and the concentration of its main compound.

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Figure captions

Figure 1. Laboratory coaxial microwave assisted extraction system.

Figure 2. Lavender essential oil: (a) kinetic investigation of the percent yield of lavender essential oil obtained by coaxial MWHD extraction; (b) main compounds (higher than 2%) of essential oil obtained at different extraction times of MWHD (from 5 to 60 min) and at 180 min of HD* extraction; and (c) chemical composition of the compounds lower than 2%.

Figure 3. TG curves (a) and DTG curves (b) under nitrogen flow for the EO isolated by the coaxial MWHD at 30 min.

Figure 4. FTIR spectra of the gas evolved during the TG experiments under nitrogen flow (a) Lavender EO, (b) sage EO, (c) rosemary EO, (d) fennel seeds EO and (e) cloves EO obtained by the coaxial MWHD at 30 min.

Figure 5. Total composition of the oxygenated and hydrocarbon monoterpenes in the essential oils isolated from the five herbs. Extraction time: Lavender (MWHD = 30 min, HD = 180 min), Sage (MWHD = 30 min, HD = 180 min), Rosemary (MWHD = 30 min, HD = 180 min) and fennels seeds (MWHD = 120 min, HD = 360 min).

Scheme 1. Towards the green extraction processes using a continuous operation systems assisted by coaxial MW technology.

Table 1

Table 1

Chemical composition of the main compounds of EO extracted from lavender, sage, rosemary, fennel and clove buds by the two methodologies explored in this work.

Essential Oil	**Raw material**	**Main compounds isolated**	
		Coaxial-MWHD*	**Conventional HD****
Lavender **(Lavandula angustifolia Mill.)**	Fresh leaves and stems	1. 1,8-cineole (44.4%) 2. Camphor (25.1%) 3. α-bisabolool (6.5%) 4. β-pinene (3.4%) 5. α-pinene (2.5%)	1. 1,8-cineole (33.0%) 2. Camphor (23.1%) 3. α-bisabolool (14.1%) 4. β-pinene (4.1%) 5. α-pinene (3.4%)
Sage **(*Salvia Officinalis* L)**	Fresh aerial parts	1. Camphor (37.3%) 2. 1,8-cineole (17.9%) 3. cis-thujone (5.7%) 4. (E)-caryophyllene (5.4%) 5. α-humulene (4.4%)	1. Camphor (23.8%) 2. 1,8-cineole (13.7%) 3. cis-thujone (5.9% 4. Camphene (5.2%) 5. (E)-caryophyllene (4.7%)
Rosemary **(Rosmarinus Officinalis L.)**	Fresh leaves and stems	1. α-Pinene (21.9%) 2. verbenone (12.7%) 3. camphor (9.9%) 4. 1,8-cineole (9.4%) 5. borneol (9.1%)	1. α-Pinene (28.2%) 2. verbenone (11.6%) 3. camphor (7.9%) 4. 1,8-cineole (7.4%) 5. borneol (6.5%)
Fennel **(*Foeniculum vulgare*)**	Dry seeds	1. (E)-anethole (79.0%) 2. fenchone (10.9%) 3. estragole (4.2%) 4. Limonene (3.2%)	1. (E)-anethole (81.6%) 2. fenchone (8.7%) 3. estragole (4.0%) 4. Limonene (3.5%)
Clove **(*Syzygium aromaticum L.*)**	Dry buds	1. Eugenol (66.9%) 2. (E)-Caryophyllene (24.8%) 3. α-humulene (3.1%) 4. Eugenol acetate (2.7%)	1. Eugenol (87.1%) 2. Eugenol acetate (6.4%) 3. (E)-Caryophyllene (5.1%) 4. α-humulene (0.6%)

*extraction time 30 min

**extraction time 180 min

Table 2

Table 2

The characteristic FTIR absorption frequencies of the main compounds in the EOs investigated.

Compounds	Frequency (cm^{-1})	Assignment	Essential oil (composition)
1,8-cineole	1379	δ_s ($CH_3(CO)$)	Lavender (44.4%)
(Schulz, Özkan, Baranska,	1217	ν_{as} (C–O–C)	Sage (17.9%)
Krüger, & Özcan, 2005)	1080	ν_s (C–O–C)	Rosemary (9.4%)
	984	ω (CH2)	
	844		
Camphor	1761	ν (C=O)	Lavender (25.1%)
(Schulz et al., 2005)			Sage (37.3%)
			Rosemary (9.9%)
(E)-anethole	1606	ν (C=C)	Fennel (79%)
(Gudi et al., 2014)	948		
Fenchone	1753	ν (C=O)	Fennel (10.9%)
(Gudi et al., 2014)			
Estragole	1602	ν (C=C)	Fennel (4.2%)
(Gudi et al., 2014)	948		
Eugenol	3591	ν (O–H)	Clove (66.9%)
(Wu, Sun, Zhou, Tao, & Noda,	1609	ν (ph)	
2008)	1512		
	1433		
	1269	ν_{as}(=C–C–O)	
	918	γ(C–H)	
	791	ν_{as} (C–H)	

ν=*stretching vibration*

δ=*in-plane deformation*

γ= *out-of-plane deformation*

ω= wagging vibration

s= symmetrical

as= asymmetrical

ph= phenyl ring

Figure 1

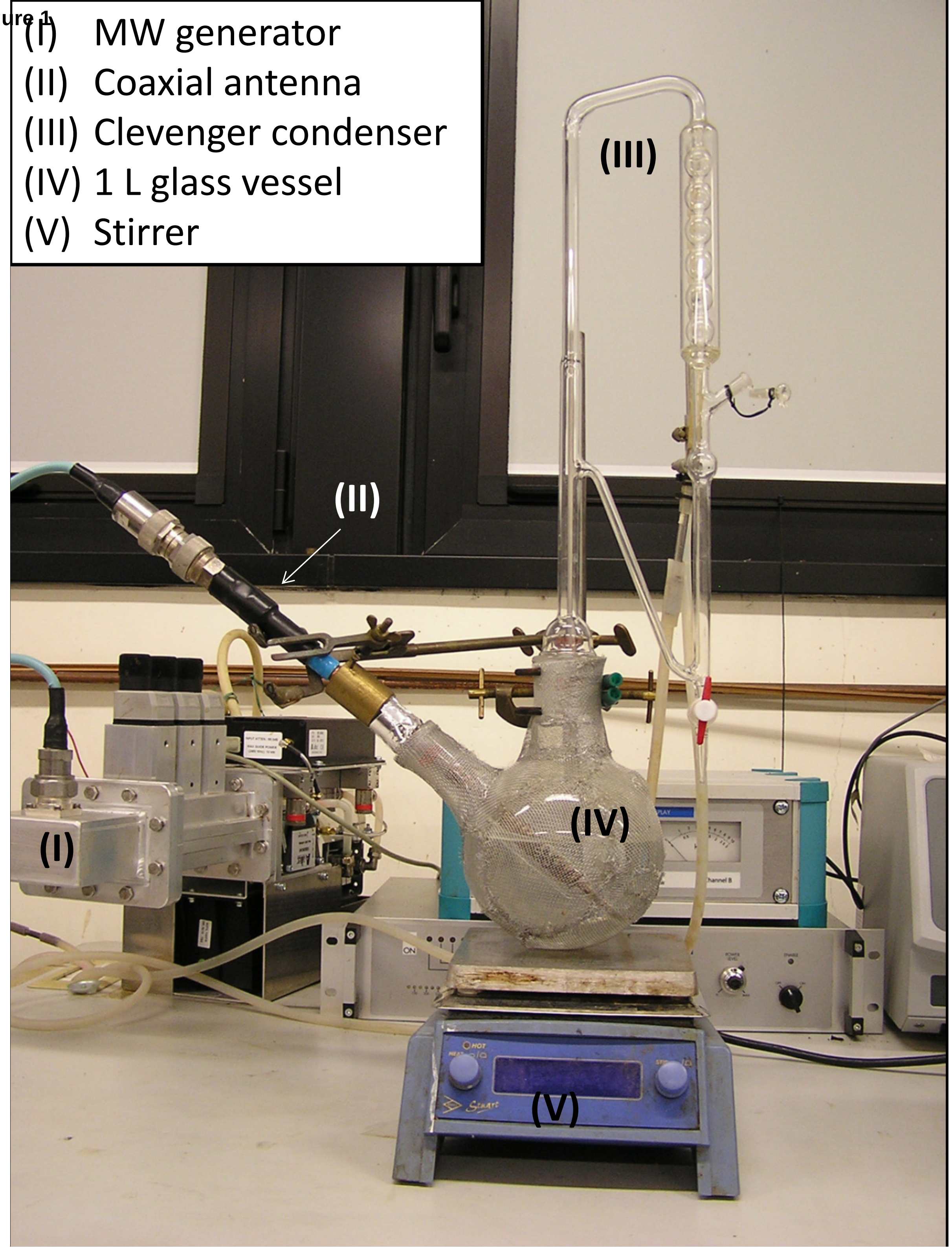

(I) MW generator
(II) Coaxial antenna
(III) Clevenger condenser
(IV) 1 L glass vessel
(V) Stirrer
(III)
(II)
(IV)
(I)
(V)
Stuart

Figure 2

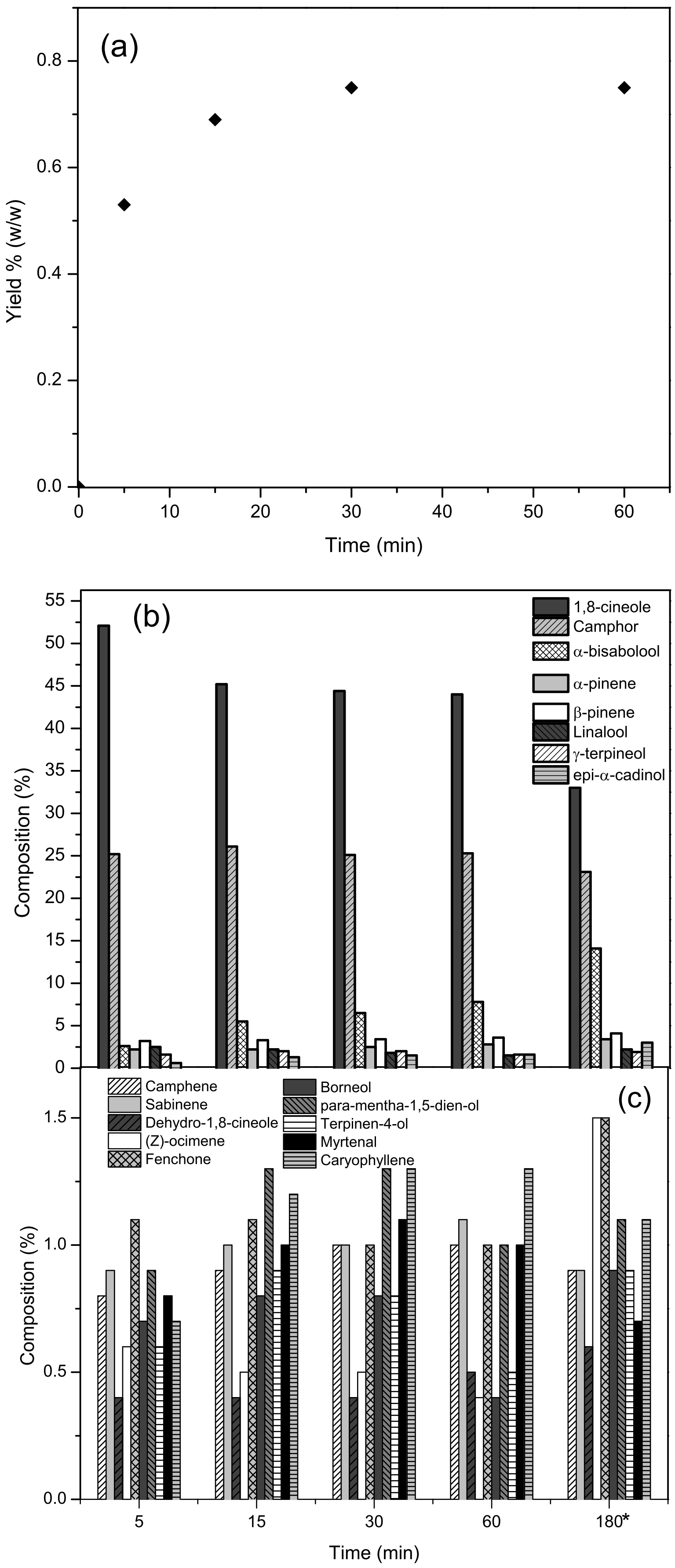
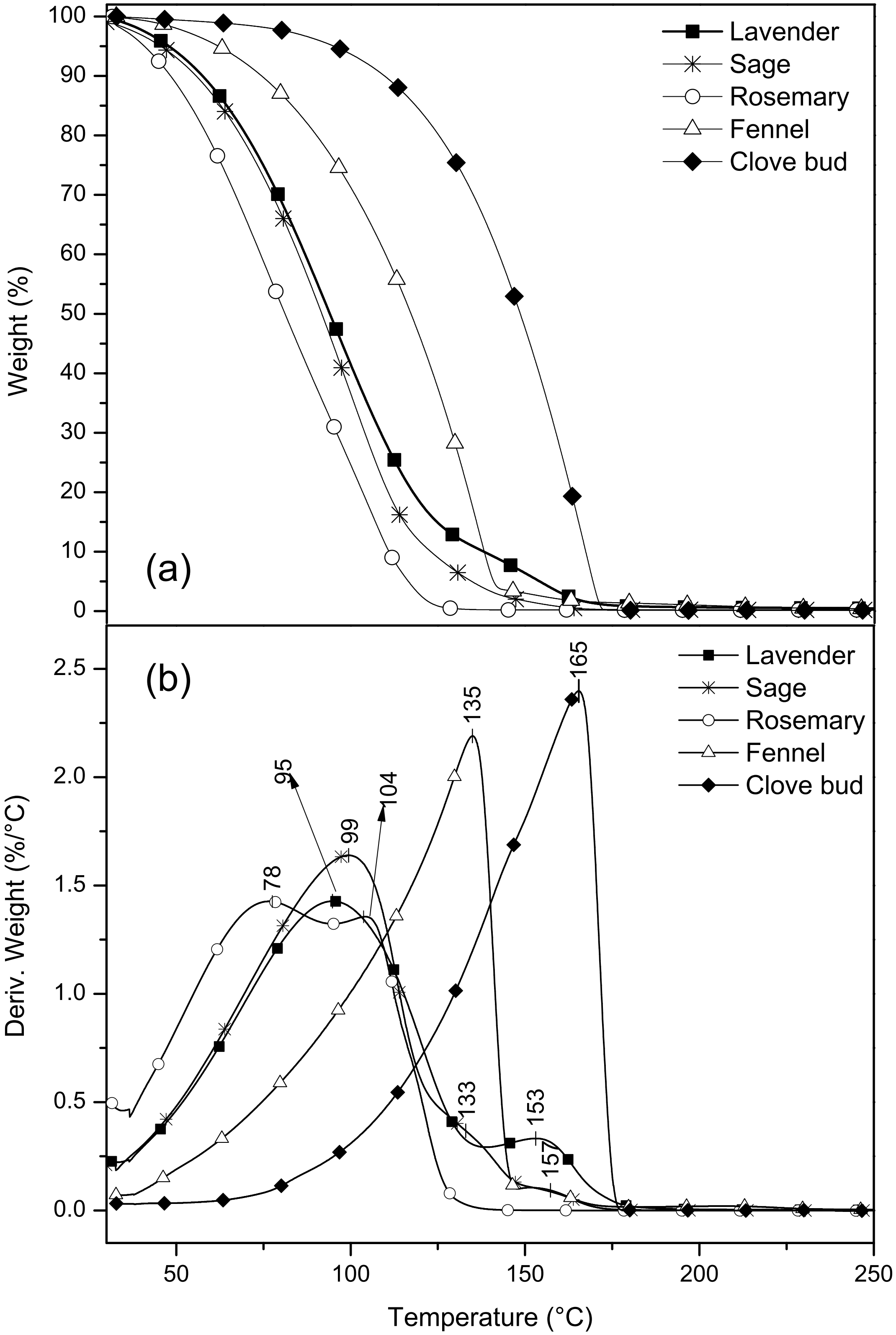

(a)
Yield % (w/w)
0.0
0.2
0.4
0.6
0.8
0
10
20
30
40
50
60
Time (min)
(b)
Composition (%)
0
5
10
15
20
25
30
35
40
45
50
55
1,8-cineole
Camphor
α-bisabolool
α-pinene
β-pinene
Linalool
γ-terpineol
epi-α-cadinol
(c)
Composition (%)
0.0
0.5
1.0
1.5
Camphene
Sabinene
Dehydro-1,8-cineole
(Z)-ocimene
Fenchone
Borneol
para-mentha-1,5-dien-ol
Terpinen-4-ol
Myrtenal
Caryophyllene
5
15
30
60
180*
Time (min)

Figure 3



(a)
Weight (%)
100
90
80
70
60
50
40
30
20
10
0
Lavender
Sage
Rosemary
Fennel
Clove bud
(b)
Deriv. Weight (%/°C)
2.5
2.0
1.5
1.0
0.5
0.0
95
104
78
99
135
165
133
153
157
Temperature (°C)
50
100
150
200
250

Figure 4

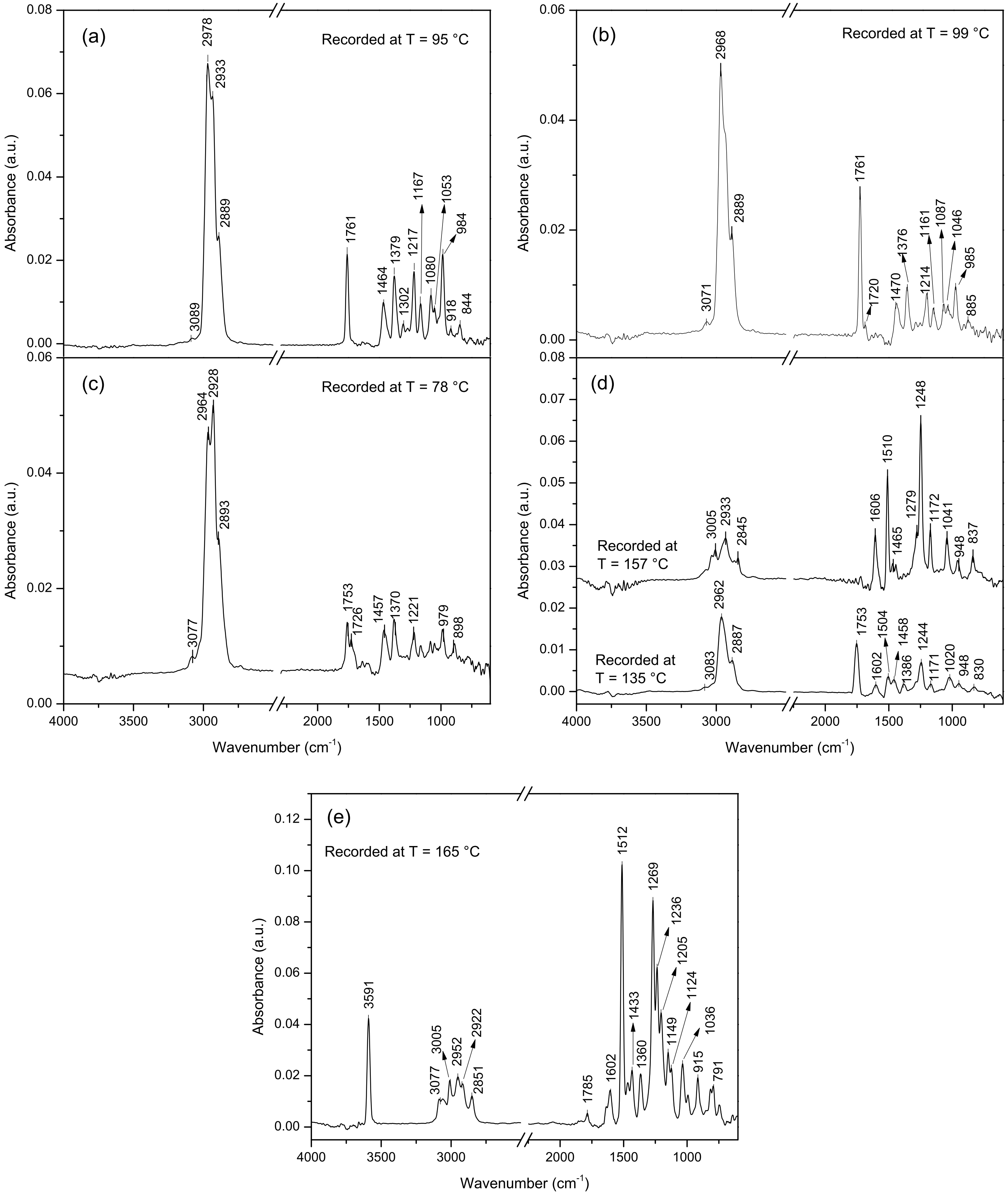
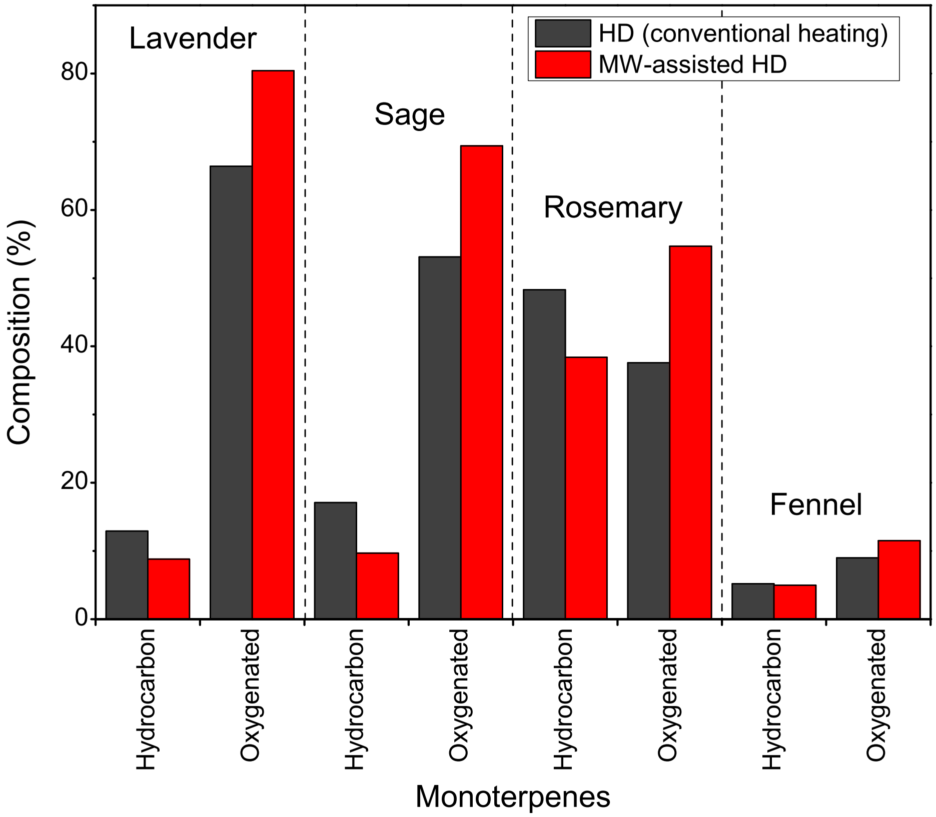
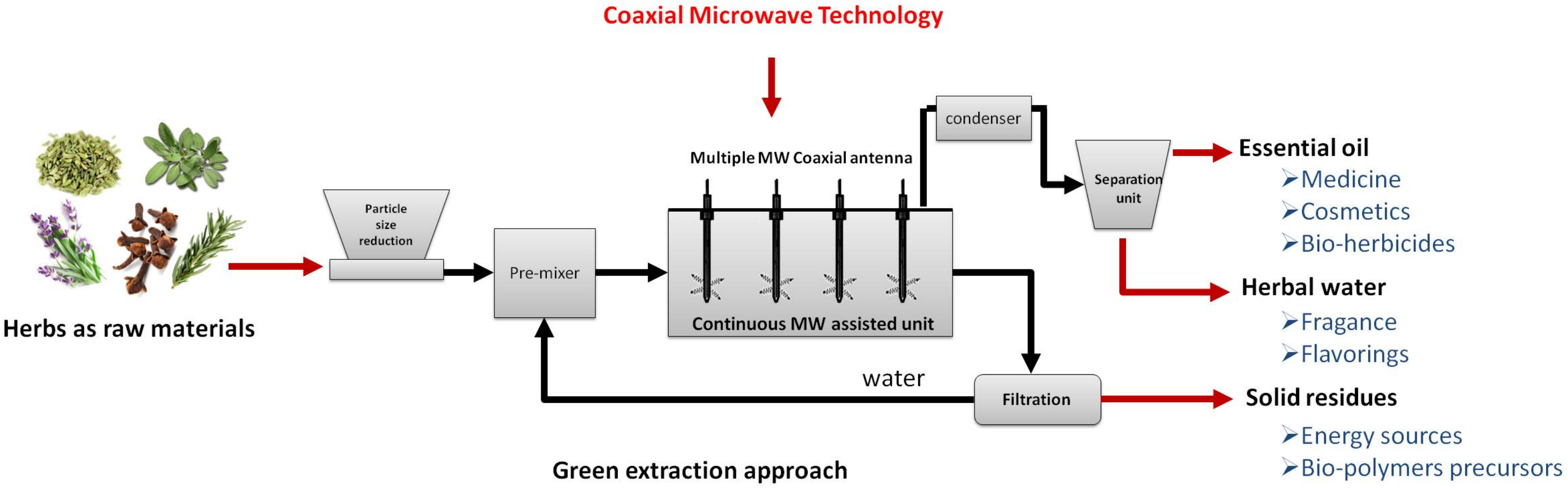

(a)
Recorded at T = 95 °C
2978
2933
2889
3089
1761
1464
1379
1302
1217
1167
1080
1053
984
918
844
(b)
Recorded at T = 99 °C
2968
2889
3071
1761
1720
1470
1376
1214
1161
1087
1046
985
885
(c)
Recorded at T = 78 °C
2964
2928
2893
3077
1753
1726
1457
1370
1221
979
898
(d)
Recorded at T = 157 °C
3005
2933
2845
1606
1510
1465
1279
1248
1172
1041
948
837
Recorded at T = 135 °C
2962
3083
2887
1753
1602
1504
1458
1386
1244
1171
1020
948
830
(e)
Recorded at T = 165 °C
3591
3077
3005
2952
2922
2851
1785
1602
1512
1433
1360
1269
1236
1205
1149
1124
1036
915
791
Absorbance (a.u.)
Wavenumber (cm^{-1})
0.00
0.02
0.04
0.06
0.08
0.01
0.03
0.05
0.07
0.10
0.12
4000
3500
3000
2000
1500
1000

Figure 5


Lavender
Sage
Rosemary
Fennel
HD (conventional heating)
MW-assisted HD
Composition (%)
0
20
40
60
80
Hydrocarbon
Oxygenated
Hydrocarbon
Oxygenated
Hydrocarbon
Oxygenated
Hydrocarbon
Oxygenated
Monoterpenes

Scheme 1


Coaxial Microwave Technology
Multiple MW Coaxial antenna
condenser
Separation unit
Essential oil
➢Medicine
➢Cosmetics
➢Bio-herbicides
Particle size reduction
Pre-mixer
Continuous MW assisted unit
Herbal water
➢Fragance
➢Flavorings
Herbs as raw materials
water
Filtration
Solid residues
➢Energy sources
➢Bio-polymers precursors
Green extraction approach