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INFLUENCE OF EXTRACTION METHODS ON CARAWAY (*Carum carvi* L.) ESSENTIAL OIL YIELD AND CARVONE/LIMONENE RATIO

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Abstract

The caraway (*Carum carvi* L.) samples were collected from little meadows situated in Harghita Mountain (Mădăraş Ciuc, Harghita Băi, Jigodin, Tuşnadu Nou), where a relatively small area was covered by a group of rich populations of wild cumin. The harvested plants are dried by: a) convective laboratory dryer in thick layer, b) static outdoors in sunshine, and (c) static in a warm indoor place in darkness. The hand-picked seeds were separated from debris by sieving and elutriation. The essential oil was obtained with electrically heated Clevenger-type laboratory steam distillation equipment both with and without microwave pretreatment. The variation of the obtained essential oil volume in time was measured and the final yield was determined. For comparison the composition, supercritical fluid extraction of the caraway essential oil with carbon dioxide in a laboratory scale batch supercritical extractor was made. Each sample was analyzed by gas chromatography, following the influence of drying and extraction method on the carvone/limonene ratio. The investigation shows that the essential oil yield is around 7 mL/100 g, less in the case of green plant (6 mL/100 g) and higher in case of the mature plant (10 mL/100 g). The results show that by batch supercritical fluid extraction with CO_2 (at first purge) lowest carvone/limonene ratio was obtained.

Key words: caraway, essential oil, hydrodistillation, supercritical fluid extraction

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1. Introduction

The wild caraway (*Carum carvi* L.) is a well-known spice belonging to Apiaceae family, raw material for food aroma and for pharmaceutical industry (Bernáth, 2000; Csedő, 1980; Sváb, 1992). The caraway is widely used in ethnopharmacology (Johri, 2011), given by effects of their bioactive compounds, namely, the essential oil components.

The health-beneficial properties included carminative (Madisch, 2004), intestinal spasmolytic (Csedő, 1980), antiseptic (i.e. against *Escherichia coli* and *Staphylococcus aureus* (Bonyadian and Karim, 2002; Seidler-Łożykowska et al., 2013)), antimycotic (Grigore et al., 2012) and antiasthmatic effects (Haggag et al., 2003). Recently, pronounced antiulcerogenic gastroprotective effect of the essential oil extracted with supercritical carbon dioxide was demonstrated (Baananou et al., 2013). The caraway extracts (in special their main components) are used in environmental-friendly organic pest control and vegetable product storage. The insect repellent effect is demonstrated, S-carvone is antisprouting and antifungal agent used in potato storage (de Carvalho et al., 2006; Oosterhaven et al., 1995; Toxopeus and Bouwmeester, 1993). The whole

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essential oil is effective against crown gall disease of plants (El-Zemity, 2008), caused by *Rhizobium radiobacter* (formerly known as *Agrobacterium tumefaciens*). The essential oil content of the caraway seed has a wide variability: for annual variety are about 2.5% for biennial variety reach even exceed 7% (Bernáth, 2000; Csedő, 1980), and for wild caraway may reach 6.5-7.5 mL/100 g dry material, even higher, about 9-11 mL/100 g dry material (Bouwmeester, 1998; Csedő, 1980).

The factors involved in the essential oil content and composition are: the characteristics and the tillage of soil, the annual precipitation and fertilization amount, breeding, the maturation, harvesting, drying and the extraction technologies (Kolta and Hornok, 1992), and even the microelement content (heavy metals) of the soil (Abu-Darwis and Ofir, 2014). The main quality criterion for caraway essential oil is the carvone/limonene ratio (Kallio et al., 1994; Sedláková et al., 2003), which is variable during ripening. In green, immature seeds the limonene concentration is higher (Chizolla, 2014). The antimicrobial activity of the essential oil is given by its composition, the higher carvone content results the rising of antimicrobial effect (Seidler-Łożykowska et al., 2013). Having antioxidant and antimycotic activity, the essential oil could be used as natural preservative in bakery products containing fats (Darougheh et al., 2014).

The aim of the research is the study of the effects of pretreatment and extraction methods on wild caraway essential oil yield and composition for plant probes from different geographical locations. As the kinetic of the extraction process is an important factor from tehnological point of view (Ciubota-Roşie et al., 2009) also the kinetic data was represented and a model was fitted.

2. Materials and methods

The wild caraway probes were collected in time period of 2012-2014. The geographical location of the collection point was Mădăraş-Ciuc, Băile Harghita, Jigodin and Tuşnadul Nou (Harghita County). The plant material harvested together with stem was firstly sorted, separating the green and mature shoots, and then it was dried. The seed was picked out and was purified further by sieving and elutriation of the powder-like debris. The such-obtained seeds were stored in a dry place till the extraction of the samples was performed. The seed was ground with Retsch Grindomix GM 200 laboratory scale knife mill, with different milling time, at room temperature. The plant material was dried by three different methods: a) drying in free space; b) drying in closed, cold and dark space; c) convective laboratory drying of the freshly picked seeds. The extraction of the essential oil of the dried (to the equilibrium moisture) caraway seed probes was made by the following, environmentally friendly (so called "green") extraction methods, without solvent residues and artefacts (András et al., 2002; Chemat et al., 2013; Sovová et al., 2006; Sovová and Stateva, 2011).

Hydrodistillation (HD): The laboratory-scale hydrodistillation apparatus, described in European Pharmacopoeia (EDQM, 2014), contains 500 mL volume round-bottom flask connected to a slightly modified Clevenger-head (Kapás et al., 2011), capillary collector tube with 1.5 mL (0.01 mL scaling), electric heating power P=125 W. Each probe was an amount of 10 g solid suspended in 200 mL distilled water. The heating power was P=125 W.

Steam distillation (SD): The steam was generated by electric heating mantle from a 250 mL volume round-bottom flask containing distilled water. The plant material (in 10 g amount) was packed in a glass tube connected to steam generator. The steam leaving the column was condensed in a heat exchanger, and the formed two phases was separated in the Clevenger-head.

Microwave hydrodistillation (MWHD) (Chemat et al., 2013; Kapás et al., 2011): the round-bottom flask containing 200 mL distilled water and 10 g of caraway seed powder in suspension was introduced in a modified domestic microwave oven (Hinari S110) and a Clevenger-head was attached. The hydrodistillation was performed 30 minutes, with heating power of P=125 W.

Hydrodistillation with microwave pretreatment (HDMP) (Navarrete et al., 2011): the round-bottom flask containing 200 mL distilled water and 10 g of caraway seed powder in suspension was introduced in a modified domestic microwave oven (Hinari S110) and a reflux condenser was attached, to recycling the steam containing the released essential oil from the plant matrix.

Supercritical fluid extraction (SFE) (András et al., 2002; Sovová et al., 1994; Sovová and Stateva, 2011): The extraction was made with food-grade (99,99% purity) carbon dioxide (Linde, Romania) using SFT 100 laboratory scale extraction apparatus (Supercritical Fluid Technology, Inc., Newark, USA) represented on Fig. 1.

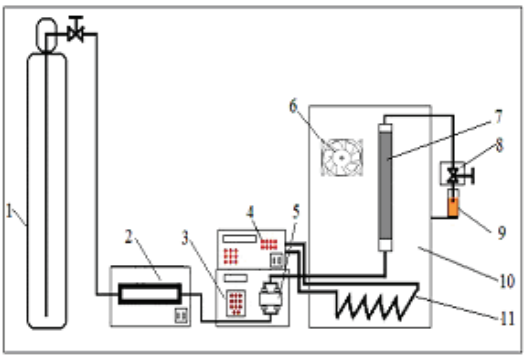

Fig. 1. Schematic representation of the laboratory scale supercritical fluid extraction apparatus (**1.** Tank of liquid CO_2 with a siphon tube**; 2.** Peltier-cooler; **3.** Pump command module;**4.** Command module of the heater; **5.** High pressure piston pump; **6.** Cooler ventilator; **7.** Tubular extraction vessel; **8.** Depressurization/restrictor valve; **9.** Probe collector; **10.** Isothermal oven; **11.** Heater resistor)

The apparatus was equipped with a tubular extraction vessel with an effective volume of 10 mL. The extraction was performed batchwise, using extraction parameters T=40 °C, and pressure over p=100 atm. The condensed essential oil probes were collected from the heated restrictor valve at 42 °C in a glass vial, by purging the extractor content at different moments (purging time was 1 minutes).

3. Qualitative analysis and data processing

The composition (in relative mass percentage) of the essential oil was performed by gas chromatography. For dehydration of the obtained essential oil, anhydrous sodium sulfate was added (Sigma Aldrich) and the probes was stored in sealed glass vials at 2 °C until analysis. In the injected probe (V=1 µl) the essential oil was diluted in amount of 1:15 (V/V) with chromatographic grade n-hexane (Sigma Aldrich).

The measurement was made with a Varian CP-3380 gas chromatograph equipped with flame ionization detector (GC-FID). The setting parameters and chromatographic conditions was the same for the each probes, as follows: quartz-capillary column 100×0.25 mm CP-Sil88 (FAME) film-coated stationary phase; Injector and detector temperature: 270 °C; Carrier gas: H_2 at p=235 kPa. Heat gradient program: heating to 50 °C in 1 minute; heating with 5 °C/minute gradient to 250 °C. For component peaks identification, a reference chromatogram was used (Kubeczka, 2002). The data analysis was made with Excel (Microsoft, Redmond, USA) and Statistica 8 (Statsoft, Inc., Tulsa, USA).

4. Results and discussion

4.1. The effect of pretreatment and extraction methods on essential oil yield

The yield of the hydrodistillation-obtained essential oil from dried and ground caraway seed was represented on two types of diagrams. On first type of diagrams the yield (V, mL oil/100 g dry matter) variation in time (minutes), on the second type, a linearized function, and the natural logarithm of the relative yield variation ($\ln (1-V/V_0)$) vs. distillation time (τ, min) was represented. As can be seen on Fig. 2, the drying method has little effect on the distillation kinetic. The yield was nearly the same for the three drying method. The effect of grinding times on yield can be observed on Fig. 3 (caraway from Mădăraş).

The kinetic of the essential oil hydrodistillation is well described for many plant materials by the simple, one-term, two parameter exponential model (Kapás et al., 2011; Milojević et al., 2008; Milojević et al., 2013), given by the Eq. (1), where: V_0 - final (maximum) yield (mL/100 g dry matter); V - current yield (mL/100 g dry matter); τ - distillation time (minute); A - integration constant; k- kinetic constant ($minute^{-1}$), including the effective diffusion coefficient. The initial distillation rate is given by the Eq. (2).

$$\frac{V_0 - V}{V_0} = A \cdot e^{-k\tau} \quad (1)$$

$$w_0 = \frac{dV}{d\tau}\Big|_{\tau=0} = V_0 \cdot A \cdot k \quad (2)$$

Using nonlinear regression, (Statistica 8, quasi-Newton estimation method), the kinetic curves was fitted on experimental points and the kinetic parameters will be obtained for different grinding time. For every case, the value of integration constant A (with the physical mean of remained relative amount of essential oil at the initial moment) was very close to unity. The highest initial distillation rate (0.803 mL/(100 g.min)) and highest yield (8.3 mL/100 g) was obtained at the grinding time of 15 s.

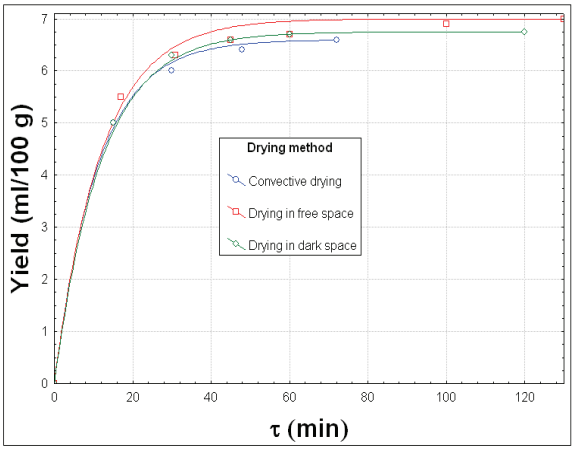

Fig. 2. The effect of drying method on essential oil yield (caraway from Jigodin, ground for 30 s)

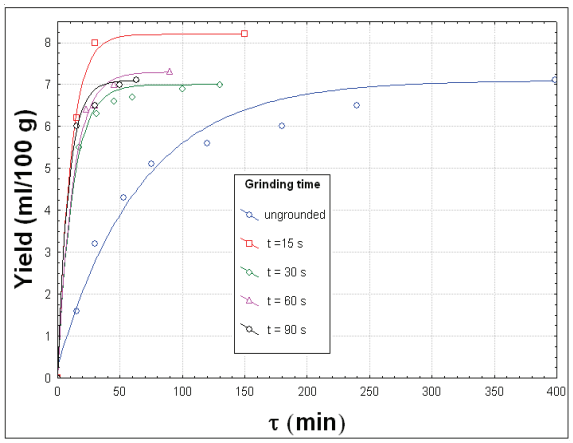

Fig. 3. The effect of grinding time on essential oil yield (ripe caraway dried on free surface, from Mădăraş)

For increased grinding times (30, 60 and 90 s) the initial rate increase (from 0.582 to 0.824 mL/(100 g.min)), but the final yields was close to the value for whole seeds (7.1 mL/100 g). In contrast, the

hydrodistillation of ungrounded seeds was much slower (0.103 mL/(100 g.min)) and the depletion time is more than double and half in comparison with grounded seeds. This behavior is due by two contrary effects. At long grinding time the particle size decrease and the internal diffusion (the velocity determining process) increase, but the increasing temperature cause higher essential oil loss.

By linearization of the Eq. (1) and imposing for A to be equal with unity, the kinetic data vs. distillation time is presented on Fig. 4. The extraction rate was described satisfactory by the two parameter semi-empirical model for HD, MWHD and HDMP of grounded and ungrounded seeds both. Slightly modifying the model, we included the effect of the grinding time. The kinetic constants were further represented in function of grinding time in interval of 30-90 s; a linear regression was made (Fig. 5).

The chosen hydrodistillation model (Eq. 3), with the fitted parameters describes close enough the effect of grinding and distillation time both. To find the optimum grinding time, more experiments are needed.

$$\eta = \frac{V}{V_0} = 1 - e^{-(0.0008 \cdot t + 0.027) \cdot \tau} \qquad (3)$$

where: η- relative yield; V- current yield (mL/100 g dry matter); V_0- final yield (mL/100 g dry matter); t- grinding time (s); τ- distillation time (minute).

The fitted equation reflects well the negative effect of the grinding time on essential oil yield. The obtaining methods have more pronounced influence on the yield in comparison with drying method and grinding time (Fig. 6). The rate of the MWHD was the highest, whilst of the HDMP the lowest. The pretreatment with intermittent microwave heating give lower yield, probable due by imbalance between the momentary high steam production during the heating period, and the moderate capacity of the applied condenser. The high loss of essential oil may produce by this effect.

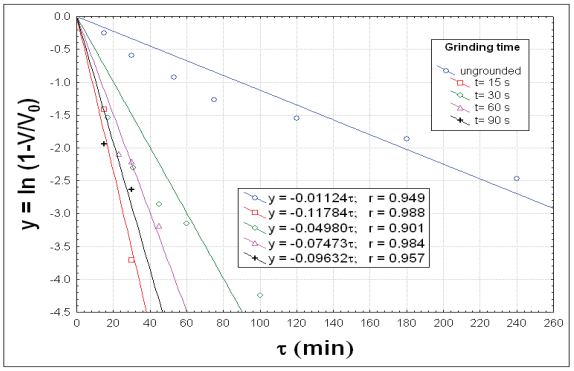

Fig. 4. The validation of the distillation model in function of grinding time ripe caraway from Mădăraş)

Comparing the maximal yields obtained for caraway probes collected from different growing area, harvested years and ripe stage (Fig. 7), it can be seen that the environmental conditions, the maturation status and growing location have an effect on the essential oil contents.

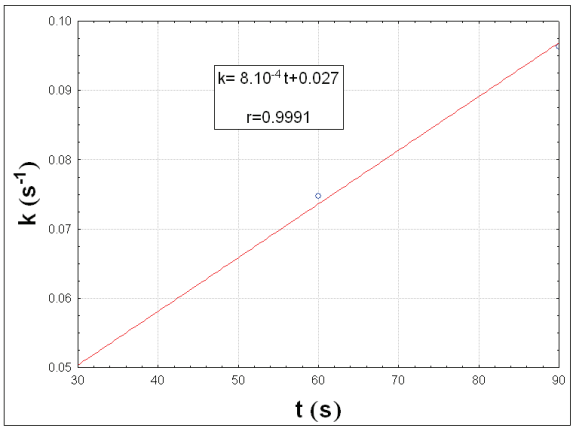

Fig. 5. The correlation between the kinetic constant and grinding time (ripe caraway from Mădăraş)

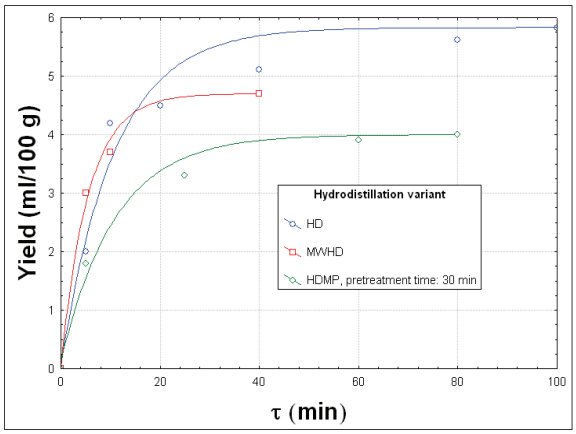

Fig. 6. The effect of distillation method on essential oil yield (caraway collected from Harghita Băi, 2013)

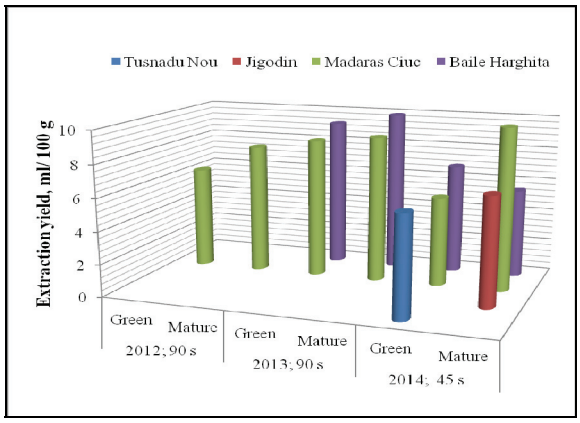

Fig. 7. The maximal hydrodistillation yield in function of growing area and harvesting year

As can be seen from Fig. 7, the meteorological conditions was favorable for caraway in year 2013, for Mădăraş and Harghita Băi growing sites both, since the essential oil yield of the picked seeds approximate the high value of 10 mL/100 g dry matter.

4.2. The effect of pretreatment and extraction methods on the essential oil yield and the ratio of the two main compounds

The pretreatment had the purpose to deteriorate or decompose the plant cellulosic matrix, to enhance the eliberation of the volatile compounds by increase the internal diffusion coefficient. By microwave treatment at moderate pressure and dilute acid condition even the hydrolysis occure (Balcu et al., 2009). At atmospheric pressure only the microexplosion of the water-containing plant structures should be considered. This phenomenon was demonstrated by electron microscopic imaging technique (Chemat et al., 2005).

The main quality criterion for caraway essential oil is the carvone/limonene ratio, we determined the composition of the essential oil and studied the variation of the ratio of the two main components. The carvone/limonene ratio is very similar for laboratory convective dried (51.5/47.9) and for overripe caraway (50.3/47.9) and higher for free space dried caraway seeds (58.4/39.3) as seen on Fig. 8.

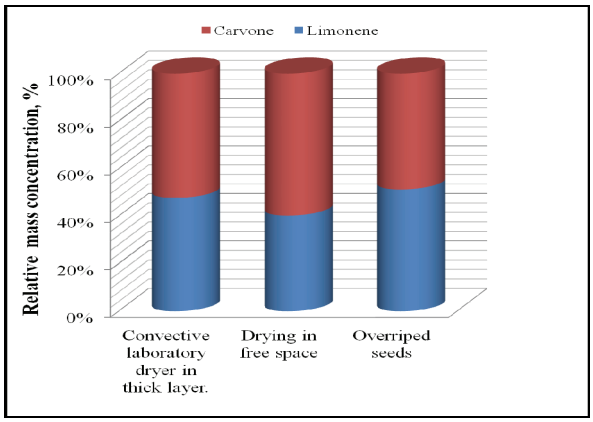

Fig. 8. The effect of pretreatment method on carvone/limonene ratio in the obtained essential oil (caraway from Mădăraş, 2012)

Fig. 9 show that in two cases (HD and MWHD obtained essential oil) the carvone/limonene ratio of was very similar for caraway from Mădăraş location. The microwave pretreatment increase the proportion of the less volatile component (carvone), but, parallel, the total essential oil yield decrease too. This is probable due by the insufficient cooling surface of the condenser. For hydrodistillation variants (HD, SD, HDMP, MWHD) the same trends are observable (Fig. 10). In case of SFE, when high volatile component are extracted, relatively low temperature (40 °C), slightly above the critical value (31.1 °C) and low pressures (in order of 10 MPa) should be used. By this way we assure high selectivity and low solvating power of the supercritical solvent (Marcus, 2006).

This is necessary to avoid the co-extraction of fatty oils and waxes (Kallio et al., 1994; András et al., 2002). With the increasing extraction pressure (up to approx. 207 bar), the limonene amount in the extract increase. This result is in a good agreement with the literature data (András et al., 2002; Baysal and Starmans, 1999; Cabizza et al., 2001; Sovová et al., 1994). The results of SFE experiments showed (Figs. 10 and 11) that independently from the applied pressure, the limonene content of the drained extract decrease with the number of purges.

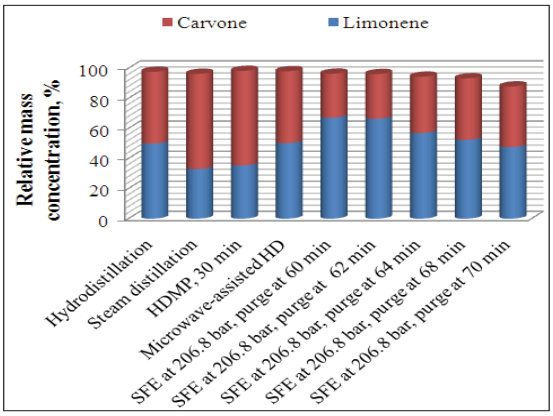

Fig. 9. The effect of obtaining method on carvone/limonene ratio of the essential oil (caraway from Harghita Băi, 2013)

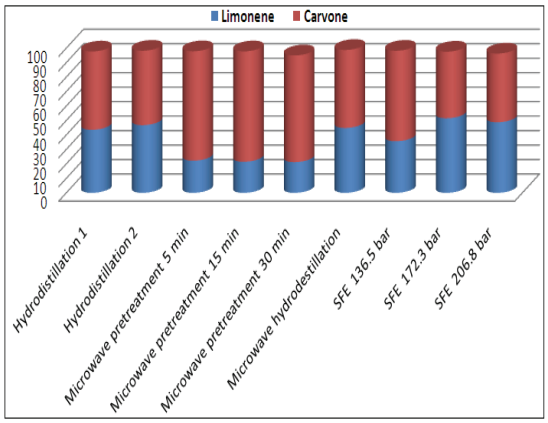

Fig. 10. The effect of extraction method on carvone/limonene ratio (caraway from Mădăraş, 2012)

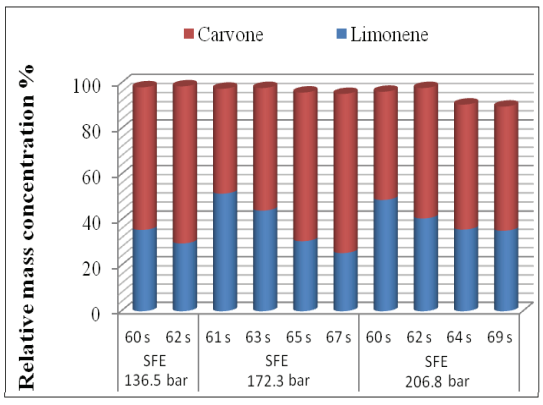

Fig. 11. The effect of pressure and purging time on carvone/limonene ratio in the SFE-obtained essential oil (caraway from Harghita Băi, 2013)

This may be explained with the higher solubility of limonene in supercritical CO_2. The

lower carvone/limonene ratio in case of SFE (first purge) in comparison with SD and MWHD is explained by two facts.

Firstly the solubility of limonene in supercritical CO_2 is higher than the carvone solubility (Sovová et al., 2001) and the easier desorption from the plant matrix of the limonene, comparative to more polar carvone with higher molecular mass. Secondly, despite of the lower boiling point of the limonene comparison with the carvone, given the higher polarity of the carvone, the rate of dissolution in the water is higher. The boiling water penetrate the plant matrix, dissolve some substances, including the essential oil components, too, then the solution diffuse backward through plant matrix in the water pool, this phenomenon is known as hydrodiffusion (Chemat et al., 2006). By this mechanism the amount of the carvone in the formed steam will be higher.

5. Conclusions

The drying methods have the lowest effect on yield comparative with grinding and the extraction modes. The highest yield was obtained with the HD, followed by MWHD and batchwise SFE. The microwave pretreatment decrease the hydrodistillation yield (for the high essential oil containing green and ripe caraway seeds, both), but the carvone/limonene ratio increased.

The quality of the essential oil expressed in the carvone/limonene ratio varies in function of obtaining method. Although the essential oil obtained by SD and MWHD show similar carvone/limonene ratio, this ratio is different for HDMP and SFE function of operation parameters and processing time;

In case of SFE, with pressure increase, the limonene amount increase in the first purge. In the drained extracts obtained by further purges, independently from the extraction pressure, the carvone/limonene ratio increase;

The maximal essential oil yields have high influence the growth location as well as the environmental and meteorological conditions. The highest yield (approx. 10 mL/100 g dry matter) was obtained for the probes harvested in year 2013 (for Mădăraş- and Harghita Băi-harvested caraway). To elucidate the exact correlation between the essential oil content and the meteorological factors, further, more detailed multiannual observation is needed.

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