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Influence of common juniper berries pretreatment on the essential oil yield, chemical composition and extraction kinetics of classical and microwave-assisted hydrodistillation

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ABSTRACT

The present paper dealt with the influence of the common juniper berries pretreatment on the yield, chemical composition and extraction kinetics of juniper essential oil (JEO) obtained by classical (HD) and microwave-assisted hydrodistillation (MAHD). The highest JEO yield was obtained by HD from one-minute dry-ground juniper berries (2.23 ± 0.00 g/100 g). No statistically significant influence of swelling and distillation technique on JEO yield was observed. Therefore, the optimal pretreatment process involved no swelling and one-minute grinding. However, no significant difference in the chemical composition of the JEOs obtained by the two techniques was observed. A new phenomenological kinetic model was developed on the basis of the mechanism of JEO extraction by both HD MAHD, which assumed three simultaneously-occurring stages: washing, unhindered diffusion and hindered diffusion. The main advantage of developed model was its ability to describe the variations of JEO yield and distillation rates with time. Furthermore, it had the smallest mean relative percentage deviation compared to the well-known kinetics models and the parameters that all were statistically significant, so it was recommended for modeling the kinetics of JEO extraction by HD and especially MAHD.

1. Introduction

The common juniper (*Juniperus communis* L.) is a coniferous evergreen perennial tree or shrub from the Cupressaceae family mostly widespread in the mountains of Europe, Asia and North America (Ložienė and Venskutonis, 2016). Berry-like fruits of common juniper, known as juniper berries (*Juniperi fructus*), are commercially the most essential part due to many medicinal and food-ingredient uses (EMA, 2011; EMEA, 1999; Veljković and Stanković, 2003). Nowadays, the juniper berries and essential oil are pharmaceutical raw materials recognized by the European Pharmacopoeia. Juniper berries are reported to have powerful diuretic, antiseptic, stomachic, antirheumatic, antiviral and anti-inflammatory activities that are primarily associated with the juniper essential oil (JEO) (EMA, 2011). The commonly predominant constituent of JEO is α-pinene, although sabinene, myrcene, limonene, and terpinen-4-ol are also important constituents (Ložienė and Venskutonis, 2016). Therefore, a large number of studies have been dealing with the yield and chemical composition of JEOs obtained by various techniques all over the world (Chatzopoulou and Katsiotis, 1995; Damjanović-Vratnica et al., 2003, 2006; Marongiu et al., 2006; Pavićević et al., 2016; Marković et al., 2017). These studies show that the yield and chemical composition of the JEO are influenced by the soil and climate at which the plants were grown (Butkienë et al., 2004; Tasić et al., 1993), the fruit ripeness (Ložienė and Labokas, 2012), the grinding process (Chatzopoulou and Katsiotis, 1995) and the used extraction techniques (Damjanović-Vratnica et al., 2003, 2006; Pavićević et al., 2016).

The majority of essential oils are commonly obtained by hydrodistillation (HD). During the last decade, typical hydrodistillation have been advanced using microwave radiation for heating the aqueous suspension of the crushed plant material. This technique, known as microwave-assisted hydrodistillation (MAHD), has widely been used to obtain essential oils from various plant materials (Amaresh et al., 2017; Dong et al., 2017; Golmakani and Rezaei, 2008a,b; Kapás et al., 2011; Karakaya et al., 2014; Kusuma and Mahfud, 2017a,b,c; Mohammadhosseini, 2017; Pavićević et al., 2016; Phutdhawong et al.,

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2007; Sourmaghi et al., 2014) due to a number of advantages, such as: higher heating speed, no direct contact of plant material with heat source, easier process control and so on (Nitthiyah et al., 2017). Despite its advantages, MAHD is rarely employed for recovery of the essential oil from juniper berries. So far, only Pavićević et al. (2016) have studied the kinetics of the microwave-assisted separation and chemical composition of the JEO. Besides that, Dahmane et al. (2015) have reported the chemical composition of the essential oil obtained from common juniper needles by MAHD.

The kinetics of essential oil HD from various plant materials has been extensively investigated (Busato et al., 2014; Milojević et al., 2013; Rezazi et al., 2016; Sovova and Aleksovski, 2006) while the MAHD kinetics is less considered (Kusuma and Mahfud, 2017a,b,c; Pavićević et al., 2016). The kinetics of JEO extraction by HD and MAHD are usually described by the two- and three-parameter models (Milojević et al., 2008; Pavićević et al., 2016). Only Pavićević et al. (2016) compared the kinetic models for HD and MAHD of the JEO. These models assume two simultaneous processes: (a) rapid distillation of the essential oil from external surfaces of the plant particles (so called washing) and (b) slow diffusion of the essential oil through the plant particles.

The present paper deals with the effects of the pretreatment of ripen common juniper berries on the yield, chemical composition and extraction kinetics of essential oil obtained by HD and MAHD. The first goal was to estimate the influence of grinding and swelling on JEO yield and to optimize these two pretreatment techniques by the response surface methodology (RSM) in order to get the best JEO yield. Second, a new phenomenological kinetic model was developed, which assumed that JEO distillation by both HD and MAHD occurs via three stages: washing, unhindered diffusion and hindered diffusion appearing simultaneously. The unhindered diffusion involves the JEO mass transfer from ruptured organs without any limitation while the hindered diffusion is the JEO mass transfer through membranes of intact plant organs. So far, these two diffusions occurring within plant particles have been considered as a united mass transfer (diffusion) process. Besides that, the model assumed that the maximum rates of the three extraction mechanisms occurred after certain period of distillation time. This novel kinetic model was compared with the phenomenological model involving simultaneous washing and diffusion (Pavićević et al., 2016; Sovova and Aleksovski, 2006), the model involving instantaneous washing and diffusion (Milojević et al., 2008), the exponential model involving only diffusion (Morin et al., 1985) and the second-order model (Muhammad Hazwan et al., 2012).

2. Material and methods

2.1. Juniper berries

Ripe juniper berries were collected from the southern hillsides of the Kopaonik mountain (1000 m above the sea level, 43°14′6″N, 20°49′18″E), Kosovo and Metohija, Serbia, in September 2016. The juniper berries were dried in the shade and packed in the multilayer paper bags.

2.2. Pretreatment of juniper berries

The juniper berries were ground both dry and wet by a disintegrator (Bosh, 500 W; medium intensity) prior to essential oil distillation. For the dry grinding, juniper berries (100 g) were added into the disintegrator, which was switched on/off each 20 s during 1, 2 or 3 min to avoid overheating of the berries that would cause the loss of a part of JEO. Then, the ground berries (300 g) were suspended into distilled water (1200 mL) and the resulted suspension was subjected to distillation. For the wet grinding, juniper berries (300 g) were first kept in distilled water (1000 mL) for 24, 48 or 72 h for swelling and then separated from the water. One third of the swelled juniper berries and 100 mL of the water collected from the swelling were added to the disintegrator, which was then switched on/off each 20 s during 1, 2 or 3 min. Besides that, for one-minute grinding, 50 mL of the same water was added after 20 and 40 s of grinding (i.e. 100 mL in total). For two-minute grinding, the same water (2 × 50 mL) was added after 40 and 60 s of grinding; for three-minute grinding, the water (2 × 50 mL) was added after 80 and 120 s of grinding. The rest of the swelled berries was wet ground in the same way in the two additional batches. Finally, the three suspensions of the ground swelled berries (300 g in 600 mL of water) were mixed and 600 mL of distilled water was added to the resulted suspension to achieve the juniper berries-to-water mass ratio (hydromodul) of 1:4. The hydromodul is commonly used in the range between 1:3 and 1:10 (Milojević et al., 2008). The former ratio is frequently applied in the industrial production of essential oil from juniper berries (Stanković et al., 1994) while the latter ratio is recommended by official pharmacopoeias (Pharmacopoeia Jugoslavica, 1984). In the present case, the hydromodul of 1:3 was avoided to prevent overheating of the plant material which could occur due to the excessive soaking of water by the ground berries.

2.3. JEO distillation: HD and MAHD

For both HD and MAHD of JEO, the Clevenger apparatus was employed, as in the previous study (Pavićević et al., 2016). For HD, the 2 L distillation round-bottom flask was placed in an electric heater. For MAHD, the Clevenger apparatus with the distillation flask was placed in a laboratory microwave oven (maximum power: 900 W; frequency: 50 Hz). The intensity of heating (700 W) in both HD and MAHD ensured the same aromatic water flow rate (8.5 ± 0.5 mL/min).

The prepared suspension of ground berries was added to the distillation flask and heating was started. The appearance of the first drop of the JEO designated the beginning of the distillation process. From that moment, the time and the volume of the collected JEO were recorded during 4 h of distillation. Occasionally, the JEO collected in the graduated tube was discharged into a 10 mL graduated cylinder having 0.1 mL grading divisions. The JEO collected during the distillation was dried over anhydrous sodium sulfate, stored in glass bottles and held in a refrigerator at 4 °C until its analysis.

2.4. Analytical procedures

The oil was analyzed by analytical GC/FID and GC/MS, using the normalization procedure, based upon the integration of chromatograms obtained by GC/FID.

2.4.1. Gas chromatography (GC)

GC analysis was carried out using a 7890A Agilent gas chromatograph (Agilent Technologies Co. Ltd, Shanghai Branch Company, Shanghai, China) equipped with a split-splitless injector, a flame ionization detector (FID) and a 30 m × 0.25 mm HP-5 (cross-linked Phenyl-Methyl Siloxane) column with 0.25 μm film thickness (Agilent). Hydrogen was used as carrier gas at 210 °C (under constant pressure; 1 mL/min). The temperature of the injector and the detector were 220 °C and 240 °C, respectively. The column was initially at 60 °C, increased linearly to 240 °C at the rate of 3 °C/min and held at 240 °C for 10 min. The solution of juniper essential oil in ethanol (~1%) was injected using ALS (1 μL, split mode, 1:30). Statistics has been covered by FID specification (results with a range of deviation for the level 1%).

2.4.2. Gas chromatography/mass spectrometry (GC/MS)

The same chromatographic analytical conditions as those mentioned for GC/FID were employed for GC/MS analysis, along with capillary column HP-5MS (30 m × 0.25 mm, 0.25 μm film thickness), using HP G 1800C GCD Series II Electron Ionization Detector (EID) system (Hewlett-Packard, Palo Alto, CA, USA). Instead of hydrogen, helium was used as carrier gas. Transfer line was heated at 240 °C. Mass