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Chemical characterization of polyphenols and volatile fraction of coriander (*Coriandrum sativum* L.) extracts obtained by subcritical water extraction

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ABSTRACT

In this work, coriander (*Coriandrum sativum* L.) seeds were extracted by subcritical water extraction (SWE) at different temperature (100–200 °C), pressure (30–90 bar) and extraction time (10–30 min), using Box-Behnken experimental design. Polyphenol compounds in obtained extracts were analyzed by HPLC–MS/MS, and 3,4-dimethoxycinnamic acid was dominant compound with the highest yield (942 mg/100 g DW) obtained at 100 °C, 60 bar and 10 min. Chemical profile of volatile compounds was determined by GC–MS. Linalool, which is a dominant compound in coriander essential oil, was the most abundant volatile compound in all extracts obtained at 100 and 150 °C, however, it almost completely degraded at 200 °C. Total extraction yield (Y), polyphenols content (PC) and total volatile compounds (TVC) were response variables in investigated experimental design. Due to satisfactory statistical parameters, applied models for Y and PC represented good approximation of experimental results. Determined SWE conditions which provided maximized PC (1001 mg/100 g DW) were temperature of 100.5 °C, pressure of 87.6 bar and extraction time of 10 min. Even though, TVC could not be optimized by RSM due to disagreement between observed results and second-order polynomial model, it is concluded that essential oil and polyphenol compounds could be co-extracted with a good yield at optimal conditions for PC, as the highest TVC was obtained at 100 °C, 60 bar and 10 min.

1. Introduction

Coriander (*Coriandrum sativum* L.) is medicinal and aromatic plant belonging to the *Apiaceae* family. It is widely distributed in Mediterranean countries; however it has been cultivated in South America, North Africa and India. Coriander seeds and leaves are increasingly used as condiment in food industry, to add flavour to various commercial foods such as liqueurs, teas, meat products and pickles (Illés et al., 2000). Moreover, they have been recognized for their medicinal properties. In traditional medicine, they have been used for treatment of various ailments such as spasm, neuralgia gastric complaints, dysentery, dyspepsia and giddiness (Chen et al., 2009; Sreelatha et al., 2009). Pharmacological activities of coriander seeds have been ascribed to chemical profile in different preparations of coriander seeds, such as liquid and dry extracts and essential oil. Therefore, antimicrobial (Kubo et al., 2004; Matasyoh et al., 2009), anticarcinogenic (Chithra and Leelamma, 2000), antioxidant (Ramadan et al., 2003; Wangensteen et al., 2004) and antidiabetic (Gallagher et al., 2003) activities have been attributed to various coriander extracts. Pharmacological potential of coriander seeds and leaves and high-value compounds isolated from them, has been reviewed by Sahib et al. (2013).

Chemical profile of coriander seeds essential oil from different geographical regions has been determined. Monoterpenoid linalool was the most abundant compound (>50%) in coriander seeds essential oil, while limonene, camphor and geraniol are present in significant quantity (Bajpai et al., 2005; Zeković et al., 2011), Coriander seeds contain up to 1% (v/w) essential oil, which is able to stay stable and retain its agreeable odour longer than any other oil of its class (Diederichsen, 1996). Standard distillation procedures were used for isolation of pure essential oil, even though, supercritical fluid extraction (SFE) has been successfully employed for extraction

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of essential oil (Grosso et al., 2008; Dima et al., 2016) and other lipid compounds present in coriander seeds such as fatty acids (Mhemdi et al., 2011) and tocopherols (Illés et al., 2000). Subcritical water extraction (SWE) could provide satisfactory yields of essential oil (>60% comparing to hydro distillation) (Eikani et al., 2007), and it could be particularly suitable, as it allows simultaneous extraction of essential oil and polyphenol compounds (Pavlić et al., 2015).

Coriander seeds are also a good source of moderately polar and polar secondary plant metabolites, i.e. polyphenols, particularly phenolic acids and flavonoids (Barros et al., 2012; Msaada et al., 2014), which is interesting since these compounds are playing a significant role in human diet due to various benefits on human health. Dominant phenolic acids were gallic, chlorogenic, ferulic and *p*-coumaric acid, while quercetin, rutin, luteolin, apigenin and kaempferol were the most abundant flavonoid compounds isolated from coriander seeds (Hadjmohammadi and Sharifi, 2009; Barros et al., 2012; Msaada et al., 2014). Chemical characterization of coriander seeds has been performed in extracts prepared by standard solid-liquid extraction procedures. On the other hand, novel extraction techniques are being used nowadays in order to improve yield of polyphenol compounds. Zeković et al. (2014) used SWE for extraction of polyphenols and obtained 2.63 g of total phenols and 0.63 g of total flavonoids per 100 g of coriander seeds. However, detailed chromatographic analysis should be performed in order to precisely determine chemical profile of these extracts.

In order to increase extraction yield of valuable bioactive compounds and overcome common disadvantages of standard solid-liquid extraction, novel extraction techniques have been developed. Increase in mass transfer between solid plant material and solvent could be agitated by use of ultrasonic waves, microwave irradiation or with pulsed electric fields. Other way to improve environmental aspect of extraction is use of pressurized (subcritical and supercritical) solvents, or ionic liquids, which has significant environmental impact since these solvents are usually considered green and eco-friendly. Since it is non-toxic for human health and environment, water has been accepted as the most designated solvent in that manner and SWE is considered as the most prolific novel extraction technique. Moreover, dielectric constant of water which controls solubility of the solute in water is directly connected with temperature which allows modification of water selectivity. However, SWE also has its limitations such as low water solubility of certain compounds and the instability of some analytes towards elevated temperatures (Herrero et al., 2013). SWE demonstrated its ability to selectively extract different classes of compounds, with the more polar organics being extracted at lower temperatures and the less polar organics being extracted at higher temperatures (Kubátová et al., 2001). Since increase of temperature has multiple positive effects on mass transfer during SWE (Wang and Weller, 2006), extractions should be performed at the highest temperature not causing any degradation of target compounds. Therefore, SWE parameters such as temperature, extraction time, solid-to-liquid ratio and pressure must be optimized. SWE has been successfully utilized for extraction of volatile compounds (Kubátová et al., 2001; Ibanez et al., 2003), as well as for phenolic acids and flavonoids (Ko et al., 2011; Alvarez et al., 2014; Ko et al., 2014).

Previous investigations showed that SWE of coriander seeds provides increased yield of total polyphenols (Zeković et al., 2014), while liquid extracts contain certain fraction of essential oil (Pavlić et al., 2015). The aim of this work was to determine chemical profile of polyphenol and volatile compounds, which are simultaneously extracted from coriander seeds. Another aim was to study effects of batch SWE conditions (temperature, pressure and extraction time), and to apply response surface methodology (RSM) approach in order to optimize extraction parameters to obtain the highest yield of target compounds.

2. Materials and methods

2.1. Plant material

Coriander (*Coriandrum sativum* L.) seeds were produced by the Institute of Field and Vegetable Crops, Novi Sad, Serbia (year 2012). Collected plant material was air-dried and stored at room temperature. The dried coriander seeds were milled in blender and mean particle size (0.466 mm) was determined by sieve set (CISA Cedaceria Industrial, Spain).

2.2. Chemicals

Methanol and glacial acetic acid were obtained from Merck (Darmstadt, Germany). Catechin (99% pure), 3,4-dimethoxycinnamic acid (99% pure), coumaric acid (>98% pure), daidzein (98% pure), ferulic acid (99% pure), sinapic acid (98% pure) and *trans*-ferulic acid (99% pure) and a standard mixture of *n*-alkanes C7-C25 were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). 1-Bromo-2-fluorobenzene was purchased from Absolute Standards, Inc. Hamden, CT USA. The ultra-pure water was obtained by a Milli-Q Plus system (EMD Millipore, Billerica, MA). All other reagents used were either analytical or HPLC grade.

2.3. Subcritical water extraction (SWE)

Subcritical water extraction was performed in batch-type high-pressure extractor (Parr Instrument Company, USA) with internal volume of 450 mL and maximum operating pressure of 200 bar and temperature 350 °C, connected with temperature controller (4838, Parr Instrument Company, USA). Extraction procedure and apparatus was described elsewhere (Zeković et al., 2014). In all experimental runs, 10.0 g of coriander seeds sample were mixed with 100 mL of water, and nitrogen was injected in extractor in order to prevent possible oxidation at high temperatures in the presence of oxygen from air. Temperature (100–200 °C), pressure (30–90 bar) and extraction time (10–30 min) were independent variables, while all other factors were held constant. After the extraction, extractor was immediately cooled in ice-bath at 30 °C during approximately 5 min to reach room temperature, and nitrogen was discharged from extractor. Extracts were immediately filtered through filter paper under vacuum, collected into glass flasks and stored at 4 °C until the analysis.

2.4. Total extraction yield (Y)

In order to determine total extraction yield, certain volume of liquid extract (5.0 mL) was added in round flask and solvent evaporated under vacuum at 40 °C, using rotovapor (RV05 basic, IKA, Germany). Flasks were then dried at 103–105 °C until the constant mass. Measurements were performed in three replicates and result was expressed as percentage, i.e. grams of extract per 100 g of dry weight (g/100 g DW; %).

2.5. Liquid chromatography tandem mass spectrometry (LC–MS/MS) analysis

2.5.1. LC–MS/MS system

The chromatographic analyses were performed using an HPLC system consisting of a binary pump (Shimadzu UFLC LC-20AD model), Shimadzu automatic injector (Auto Sampler SIL-20A HT model) and a column oven (CTO-20AC). Analytical separation of compounds was achieved on an X-Terra MS C18 column