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Coriander seeds processing: Sequential extraction of non-polar and polar fractions using supercritical carbon dioxide extraction and ultrasound-assisted extraction

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ABSTRACT

In this study, non-polar and polar compounds from coriander (*Coriandrum sativum* L.) seeds (CS) were fractionated using modern extraction techniques. CS were fractionated on non-polar fraction using supercritical fluid extraction (SFE) and influence of mean particle size on yield and chemical profile was investigated. Results were compared with conventional techniques used in essential oil isolation. It has been shown that SFE has certain advantages comparing to traditional techniques in terms of extraction yield and selectivity, since it provided highest linalool content (877.07 mg/100 g CS). Raffinate exhausted by SFE could be suitable for further processing, and it was subjected to ultrasound-assisted extraction (UAE) of moderately polar and polar fraction of polyphenolic compounds. Results showed that ethanolic extracts had higher antioxidant activity than water extracts for all CS mean particle sizes. The highest content of hydroxycinnamic acids was observed in ethanolic extracts obtained from exhausted CS with lowest mean particle size. Therefore, coriander seeds, which have been known for its rich essential oil content, could be used for sequential production of polyphenolic-rich extracts with high antioxidant activity.

1. Introduction

Medicinal and aromatic plants are gaining more and more importance due to their potential application in pharmaceutical, food and fragrance industry. One of them is coriander (*Coriandrum sativum* L.), which is annual plant from *Apiaceae* family, widely distributed in Mediterranean countries (Grosso et al., 2008). Besides being used as condiment in liqueurs, teas, meat products and pickles (Illés et al., 2000), coriander seeds and leaves have been recognized for various pharmacological activities. Even in traditional medicine, they have been used for treatment of indigestion and abdominal distention (Chen et al., 2009). CS have been used in forms of essential oil (Matasyoh et al., 2009) and liquid extracts, both hydrophilic and lipophilic (de Almeida Melo et al., 2005; Guerra and de Almeida Melo, 2005). Essential oil (EO) content in seeds varies from 0.3 to 1%, and monoterpenoid linalool is the main compound (more than 70%), while geraniol, terpinene, limonene, camphor and α-pinene are present in much lower percent (Eikani et al., 2007; Zeković et al., 2011). Volatile compounds of coriander are accumulated in secretory structures, called ducts or vittae, which are present in stems,

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leaves and seeds (Evans, 1996). Besides essential oil, seeds contain significant content of vegetal oil, rich in monounsaturated fatty acids, such as petroselinic acid (Mhemdi et al., 2011). On the other hand, CS are a good source of moderately polar and polar secondary plant metabolites, i.e. polyphenolics (phenolic acids and flavonoids) (Barros et al., 2012; de Almeida Melo et al., 2005; Zeković et al., 2014). They are playing a significant role in human diet due to various, recently reported, benefits on human health. They are found to inhibit human immunodeficiency viral replication (HIV), human simplex virus (HSV), glucosyl transferases of *Streptococcus mutants*, ascorbate auto-oxidation, cytotoxic effects, tumor promotion and xanthine, monoamine oxidases (Havsteen, 2002; Mattila et al., 2000; Middleton et al., 2000). Pharmacological activities of coriander seeds have been connected to chemical profile in different preparations, therefore, essential oil and various extracts expressed antimicrobial (Matasyoh et al., 2009), anticarcinogenic (Chithra and Leelamma, 2000), antioxidant (Wangensteen et al., 2004) and antidiabetic (Gallagher et al., 2003) activities.

Hydrodistillation (HD), solid–liquid extraction with organic solvents (SE) and supercritical fluid extraction (SFE) are used for isolation of volatile, non-polar constituents, i.e. EO, from plant material, where each of these technologies has certain advantages and disadvantages. HD provides isolation of "pure" essential oil, without coextraction of non-volatile compounds. However, increased temperature during HD could induce hydrolysis and other chemical alterations which directly affect quality of obtained essential oil (Anitescu et al., 1997). SE provides satisfactory yields, although extracts are contaminated with cuticular waxes and other lipid compounds. Moreover, possible loss of valuable volatile compounds occurs during vacuum evaporation of solvent and traces of toxic solvent retain in extracts, reducing its quality (Illés et al., 2000). These disadvantages could be overcome by SFE which represents excellent alternative to traditionally used technologies (Brunner, 2005). Carbon dioxide is commonly used in SFE since it is non-toxic, non-explosive, readily available and easy to remove from extracted products (Chen et al., 2009). Moreover, mild critical temperature and pressure of CO_2 prevent from possible thermal degradation during process, and their manipulation leads to change of density which further affects selectivity of supercritical CO_2 (Catchpole et al., 1996). Traditional techniques have certain advantage in term of capital cost, since equipment for high-pressure processes is quite expensive. However, in term of operational cost, SFE is not in disadvantage, because HD demands huge energy consumption for heating on industrial scale. Partially defatted plant material after SFE could be useful for subsequent extraction of moderately polar and polar polyphenolic compounds. Environmental aspect, as well as efficiency, in solid–liquid extraction must be considered since extraction requires at least 50% of the energy of the whole industrial process (Chemat et al., 2012). Therefore, modern extraction techniques, such as ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE) or accelerated solvent extraction (ASE) should be applied. Ultrasonic cavitation provokes production, growth and collapse of the bubbles on the surface of solid plant material, which leads to conversion of energy from kinetic to heating and causes disruption on plant material. Final income of ultrasonic intensification of extraction is increase of mass transfer and accelerated diffusion of solvent to plant cells (Azmir et al., 2013). It has been reported that UAE with ethanol and water mixtures as extraction solvent could be successfully applied for extraction of polyphenolic compounds from various plants (Ghafoor et al., 2009; Ramić et al., 2015; Wang et al., 2008). Moreover, ethanol, together with water, is considered as an environment-friendly solvent and it is non-toxic, unlike majority of common organic solvents.

The aim of this work was to utilize CS for subsequent production of both lipophilic and hydrophilic extracts using modern and environment-friendly processes such as SFE with carbon dioxide and UAE with 70% ethanol and water. Three CS fractions with different mean particle size were used in order to determine its effect on extraction rate and yield. Chemical composition and total extraction yield of lipid extracts obtained by SFE were compared with essential oil obtained by traditional techniques (hydrodistillation and solvent extraction—using Soxhlet apparatus). Partially defatted raffinate after SFE was used for UAE of moderately polar polyphenolics with 70% ethanol, while afterwards, UAE of polar fraction using water as extraction solvent was employed.

2. Materials and methods

2.1. Plant material

Coriander (*C. 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 (CS) separated in three fractions were milled in blender during 10, 20, and 30 s, respectively, and mean particle sizes ($d_1 = 1.368$, $d_2 = 0.775$ and $d_3 = 0.631$ mm, respectively) were determined by sieve set (CISA Cedaceria Industrial, Spain).

2.2. Chemicals

Commercial carbon dioxide (Messer, Novi Sad, Serbia) with >99.98% (w/w) purity was used for laboratory scale SFE. Folin–Ciocalteu reagent, (±)-catechin and 1,1-diphenyl-2-picryl-hydrazyl-hydrate (DPPH) were purchased from Sigma (Sigma-Aldrich GmbH, Steinheim, Germany). Gallic acid was purchased from Sigma (St. Luis, MO, USA). The standard compounds for GC analysis (GC purity) were purchased from Ehrenstorfen, Germany and Carl Roth, Germany. Acetonitrile (HPLC-grade) was purchased from J. T. Baker (Deventer, The Netherlands), and HPLC standards were supplied from Sigma (Sigma-Aldrich GmbH, Steinheim, Germany). All other chemicals used were of analytical reagent grade.

2.3. Extraction techniques

CS fractions with different mean particle size were firstly used for isolation of essential oil/lipid extracts. For that purpose, supercritical fluid extraction (SFE) was applied, while hydrodistillation (HD) and Soxhlet extraction (SE) with methylene chloride were performed in order to compare qualitative and quantitative profile of obtained essential oil/lipid extracts. After SFE, obtained raffinate (RAF-1) was used for ultrasound-assisted extraction (UAE) with 70% ethanol in order to isolate moderately-polar fraction. Furthermore, exhausted raffinate after UAE with 70% ethanol (RAF-2) was dried on room temperature and used for extraction of polar fraction using UAE at same conditions, but with water as solvent (Fig. 1). EOs and lipid extracts were analyzed by GC–MS and GC–FID, while total phenolics content, total flavonoids content, antioxidant