The Journal of Supercritical Fluids 128 (2017) 79–88

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Subcritical water extraction of wild garlic (*Allium ursinum* L.) and process optimization by response surface methodology

Alena Tomšik[a,b], Branimir Pavlić[a], Jelena Vladić[a], Marina Cindrić[c], Pavle Jovanov[b], Marijana Sakač[b], Anamarija Mandić[b], Senka Vidović[a,*]

[a] University of Novi Sad, Faculty of Technology, Bulevar Cara Lazara 1, 21 0000 Novi Sad, Serbia
[b] University of Novi Sad, Institute of Food Technology, Bulevar Cara Lazara 1, 21 0000 Novi Sad, Serbia
[c] CEBB d.o.o. Center for Energy, Biomass and Biotechnology, Matka Laginje 1, 47000 Karlovac, Croatia

ARTICLE INFO

Keywords:
Subcritical water extraction
Allium ursinum
Total phenolic compounds
Antioxidant activity
Response surface methodology
HMF

ABSTRACT

Subcritical water extraction (SWE) was employed in order to obtain high valuable extracts from wild garlic (*Allium ursinum*). The influence of temperature (120–200 °C), extraction time (10–30 min) and added acidifier, HCl (0–1.5%) on extraction process was investigated. Analysis of variance was used to determine the fitness of the model and optimal process parameters for SWE, in order to maximize extraction yield, total phenolic compounds and total flavonoids content, and antioxidant activity. The optimal conditions for SWE were determined at temperature of 180.92 °C, extraction time of 10 min, and added acidifier at 1.09%. An insight into the development of Maillard reaction products during SWE was provided through measurement of 5-hydroximethylfurfural(5-HMF) and furfural (F)in all obtained extracts. No influence of 5-HMF and F on antioxidant activity was observed. Using HPLC-DAD, kaempferol derivates were identified as the major phenolic compounds in extract obtained at optimal condition.

1. Introduction

Extracts of herbs, vegetables, fruits and other plant materials are target of interest of pharmaceutical and food industry as they contain a wide variety of compounds that may have beneficial health effects. Application of such extracts thereby may improve the quality and nutritional value of food, and may enable the creation of new functional products and dietetic supplements. Selection of adequate extraction technology and setup of adequate extraction parameters are the key steps in the isolation and recovery of valuable bioactive compounds and in the production of extracts with adequate quality. Nowadays modern production implies implementation of new processes in accordance to the requirements of “green chemistry”. Therefore, beside production of quality final products, these requirements are obligation of modern extracts production. Several extraction technologies are recognized as “green extraction technologies” among subcritical water extraction (SWE) is one of the most promising. According to Xu et al., this extraction technology is one of the best option for the isolation of bioactive compounds from plants and food [1]. SWE exhibits a number of advantages over conventional extraction technologies. Namely, SWE demonstrated the ability to selectively extract different classes of compounds, with the more polar organics being extracted at lower temperatures, and less polar organics being extracted at higher temperatures [2]. Extracts obtained by SWE contain no trace of toxic solvent residues, because water is applied as extraction solvent, therefore no additional separation or purification is needed. In such way obtained extracts can be used directly as semi-products or products for food and pharmaceutical industry. In comparison to classical extraction technologies, extraction time in this extraction technology is much shorter.

In SWE, at elevated process temperatures, the physiochemical properties of water are considerably different from the properties of water at room temperature. Here, according to He et al., over the range of temperatures the density of water decreases, dielectric constant decreases and ionization constant increases [3]. As temperature increases, the physiochemical properties of water being resembled to the properties of organic solvents, which increases a solubility of various organic molecules [4,5]. By this, the main drawback of water (high polarity and low selectivity to the low polar and non-polar constituents) is overcome. Beside, increased extraction of various organic compounds in SWE due to application of high process temperatures, formation of various new compounds can be expected. Thus, according to Zhang et al. [6] the heating in SWE could lead the appearance of non-enzymatic browning reactions, for example the Maillard reaction,

* Corresponding author.
E-mail address: senka.vidovic@tf.uns.ac.rs (S. Vidović).

http://dx.doi.org/10.1016/j.supflu.2017.05.012
Received 4 January 2017; Received in revised form 9 May 2017; Accepted 9 May 2017
Available online 10 May 2017
0896-8446/ © 2017 Elsevier B.V. All rights reserved.

caramelisation and oxidation of phenolic compounds, resulting in a typical dark brown color and formation of some antioxidant compounds. According to Herrero et al. [7], this possibility of new antioxidant formation could further increase the interest of SWE considering that this technique would be capable not only for recovering the naturally present antioxidants, but also for allowing the generation of new antioxidant compounds during the SWE process. However, during SWE process, also through Millard and caramelization reactions, formation of 5-hydroxymethylfurfural (5-HMF) could occur. As 5-HMF has been demonstrated to be cytotoxic in higher concentration, it is of great interest to gain an insight on the formation of this compound during SWE processes from natural matrices.

According to previous statements of advantages of SWE, it can be assumed that SWE can be applied as efficient extraction technology for recovery valuable compounds from plants such as *Alium ursinum*. *A. ursinum*, also known as wild garlic, possess wide range of biological activities such as antioxidant [8,9], antiplatelet [10], cardio protective [11], cytostatic, antimicrobial [12], anti-inflammatory [13] and anti-diabetic [14]. The potential health benefits of *A. ursinum* have been attributed mainly to the sulphur-containing compounds which are one of the most characteristic constituents of *Allium* plants. The antioxidant activity of *Allium* species has been linked to the same compounds and their precursors, but it is also related to other bioactive compounds such as phenolic compounds, flavonoid glycosides [15], dietary fibres and microelements [13]. Moreover, in *A. ursinum* the presence of flavonols such as kaempferol derivatives, which possess protecting properties against heart disease and cancer, and also prevents oxidative damage to cells and DNA, was reported [16–18]. The short harvesting period *A. ursinum* is the main obstacles in the wider use and application of this plant. Therefore, one of the best ways to utilize *A. ursinum*, as well as its bioactive compounds, could be through application of appropriate extraction technology and production of extracts with much higher concentration of bioactive compounds compared to the raw material.

Therefore, in this study, possibility for application of SWE as environmentally friendly extraction technology, for extraction of bioactive compounds, especially antioxidants, from *A. ursinum* was investigated. Response surface methodology (RSM) and Box-Behnken (BBD) experimental design were employed to investigate the effect of three process parameters (temperature, time and amount of added acidifier) on the extraction of targeted compounds. Beside, effect of same parameters on formation of Millard's reaction products was observed.

2. Materials and methods

2.1. Plant material

Dried *A. ursinum* was donated by a local tea factory (Fructus doo, Bačka Palanka, Serbia). Before extraction material was ground in a blender, and the granulation of the obtained material was determined (0.325 mm) using sieve sets (Erweka, Germany). The fraction of the same particle size was used in all extraction runs. Moisture content (6.12%) was determined prior to extraction.

2.2. Chemicals

1, 1-Diphenyl-2-picryl-hydrazyl-hydrate (DPPH), Folin-Ciocalteu reagent, (±)-catechin and 2, 2′-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) and standard substances including gallic acid and kaempferol were purchased from Sigma (Sigma-Aldrich GmbH, Sternheim, Germany). Trolox (6-hydroxy-2, 5, 7, 8-tetramethylchroman-2-carboxylic acid) (Sigma Aldrich GmbH, Sternheim, Germany) was used as an antioxidant standard. Potassium persulfate (99%, p.a.) was obtained from Acros Organics (Acros Organics, Geel, Belgium). All other chemicals and reagents were of analytical and HPLC reagent grade.

2.3. SWE procedure

SWE was performed in a batch-type high-pressure extractor (Parr Instrument Company, Moline, USA) with an internal volume of 450 mL and maximum operating pressure of 200 bar and temperature 350 °C, connected with a temperature controller (4838, Parr Instrument Company, Miline, USA), previously described elsewhere [19]. The extraction vessel jacket was heated electrically and stirring of the media was performed by a magnetic stirrer (750 rpm). All extractions were maintained under isobaric condition at 36 bar, using sample-to solvent ratio 1:10 (w/v). Temperature (120–200 °C), time (10–30 min) and percent of acidifier, HCl (0–1.5%) were independent variables. During extraction period, temperature was held constant depending on experimental run. Prior to each experiment, an extraction cell heat-up was carried out for a given time, which changed according to extraction temperature. Time needed to reach desired temperature of extraction (120, 160 and 200 °C) was approximately 20, 25, and 30 min, respectively. Cooling phase in ice bath was the same for all experimental runs, approximately 11 min. After cooling, extracts were immediately filtered thought filter paper Extracts were immediately filtered through filter paper (4–12 μm pore size, Schleicher and Schuell, Germany) under vacuum (V-700, Büchi, Switzerland) and stored at 4 °C until further analysis.

2.4. Determination of total phenolic content

In the obtained *A. ursinum* extracts content of total phenolic compounds (TP) was determined using the Folin–Ciocalteu reagent [20]. Absorbance was measured at 750 nm using Janway 6300 spectrophotometar (Bibby Sciencific, France). Content of phenolic compounds was expressed as gallic acid equivalents (GAE) on dry weigh of *A. ursinum* (g GAE/100 g DB). All experiments were performed in three replicates.

2.5. Determination of total flavonoids content

In the obtained *A. ursinum* extracts content of total flavonoids (TF) was estimated using the aluminum chloride colorimetric assay [21]. Results were expressed as catechin equivalents (CE) on dry weight of *A. ursinum* (g CE/100 g DB). All experiments were performed in three replicates.

2.6. Determination of phenolic compounds by HPLC

For analysis dry extract of *A. ursinum* was dissolved in solvent mixture of methanol and 1% formic acid in water (50:50, v/v) and ultrasonicated for 10 min. Solutions were filtered through 0.45 μm regenerated cellulose membrane filters (Agilent, Paolo Alto, CA, USA) before injection into the HPLC system.

HPLC analysis of phenolic compounds in extract obtained at optimal SWE conditions was performed by a liquid chromatography (Agilent 1200 series, Paolo Alto, CA, USA) on an Agilent, Eclipse XDB-C18, 1.8 μm, 4.6 × 50 mm column using a diode array detector (DAD), according to the method of Mišan et al. [22]. The following solvent linear gradient program with solvent A (methanol) to solvent B (1% formic acid in water) was used as follows: initial 85% B; 0–6.2 min, 85% B; 6.2–8 min, 85–75% B; 8–13 min, 75–61% B; 13–15 min, 61% B; 15–20 min, 61–40% B; 20–25 min, 40–0% B.A flow rate of 1.000 mL/min was set. The run time and post-run time were 25 and 10 min, respectively. The column was operated at 30 °C. Into the system, 5 μL of samples were injected, using an auto sampler. The spectra were acquired in the range 190–400 nm and chromatograms plotted at 280, 330 and 350 nm. Phenolic compounds in samples were identified by matching the retention time and their spectral characteristics against

Download English Version:

https://daneshyari.com/en/article/4909691

Download Persian Version:

https://daneshyari.com/article/4909691

Daneshyari.com