Industrial Crops and Products 50 (2013) 131–136

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Comparison of matrix-solid phase dispersion and liquid–solid extraction connected with solid-phase extraction in the quantification of selected furanocoumarins from fruits of *Heracleum leskowii* by high performance liquid chromatography

Anna Oniszczuk[a,*], Monika Waksmundzka-Hajnos[a], Krystyna Skalicka-Woźniak[b], Kazimierz Głowniak[b]

[a] Department of Inorganic Chemistry, Medical University in Lublin, 4A Chodzki Street, 20-093 Lublin, Poland
[b] Department of Pharmacognosy with Medicinal Plant Unit, Medical University in Lublin, 1 Chodzki Street, 20-093 Lublin, Poland

ARTICLE INFO

Article history:
Received 5 March 2013
Received in revised form 20 June 2013
Accepted 4 July 2013

Keywords:
Matrix solid-phase dispersion
Liquid–solid extraction
Solid-phase extraction
Heracleum leskowii
Furanocoumarins
High performance liquid chromatography

ABSTRACT

In this study, we compared a novel application of matrix solid-phase dispersion (MSPD) methodology and classical liquid–solid extraction (LSE) connected with solid-phase extraction (SPE) for the determination of furanocoumarins from *Heracleum leskowii* fruits. Fruits of *H. leskowii* contain the following furanocoumarins: umbelliferon, xanthotoxin, angelicin, isopimpinellin, bergapten, imperatorin, isoimperatorin. Several dispersants, eluents and sample to sorbent mass ratio were examined during the optimization of the process in order to obtain the best selectivity and yield. Quantitative analysis was carried out by high performance liquid chromatography with diode array detector (HPLC–DAD). The method was validated. The calibration curves for all standards were linear over the concentration range 10–100 μg/mL. The correlation coefficients of all calibration curves were $R^2 > 0.9990$. LOD and LOQ values ranged from 2.97 μg/mL to 10.82 μg/mL, and from 9.03 μg/mL to 38.32 μg/mL respectively. The recoveries of the LSE–SPE and MSPD method were in the range of 94.04–102.31% and 92.43–96.27%, respectively. The relative standard deviation (RSD%), as a measure of repeatability, was lower than 5.88% for MSPD and 5.09% for LSE–SPE. MSPD extraction method was compared to the classic analytical method combining liquid–solid extraction with solid-phase extraction.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The genus *Heracleum*, belonging to the family Apiaceae, is represented by almost 125 *Heracleum* species in the world (Pimenov and Leonov, 2004). In traditional medicine, some *Heracleum* species are used as antipyretic, analgesic, diaphoretic, antibacterial, anticandidal, carminative and digestive therapeutic agent (Tosun et al., 2008). Various *Heracleum* species were used to treat rheumatic diseases, lumbago, fractures and contusions, epilepsy, paralysis, gastralgia, hypertension, dysentery and diarrhea (Skalicka-Wozniak and Głowniak, 2012). Plants of the genus *Heracleum* are also source of furanocoumarins, thus *Heracleum leskowii* has been used as plant material. In fruits of *H. leskowii* the following furanocoumarins were found: umbelliferon, xanthotoxin, angelicin, isopimpinellin, bergapten, imperatorin, isoimperatorin (Cieśla et al., 2008; Skalicka-Wozniak and Głowniak, 2012).

This group of compounds have important uses in human medicine, are potent phototoxins to both man and domestic animals, are important host resistance mediators in a number of plant species, and exhibit toxicity against a wide range of organisms (Chermenskaya et al., 2010; Tiana et al., 2013). Furanocoumarins exhibit pharmacological activity. They are important drugs in vitiligo and psoriaris therapy (Bhatnagar et al., 2007; Trott et al., 2008) and are also used in therapy erythrodermic variants of cutaneous T-cell lymphoma and chronic graft-versus-host disease (Cieśla et al., 2008; Heinke et al., 2011; Lee et al., 2007).

For this reason it is important to develop rapid, simple and inexpensive method of extraction and purification of furanocoumarins from plant material. Qualitative and quantitative analysis usually includes a sample-preparation procedure, which is still the weakest point and the most time-determining step in the whole analytical method. Due to the complex nature of matrices and the low detection levels required by regulations, efficient sample preparation is an important aspect. Ideally, sample preparation should be fast,

* Corresponding author. Tel.: +48 817564836; fax: +48 815357378.
E-mail address: aoniszczuk@o2.pl (A. Oniszczuk).

0926-6690/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.indcrop.2013.07.015

accurate, precise, and environmentally friendly and use small samples. Various techniques, such as percolation, Soxhlet extraction, ultrasound assisted solvent extraction (USAE), microwave assisted solvent extraction (MASE), accelerated solvent extraction (ASE), supercritical fluid extraction (SFE) have already been used for isolation furanocoumarins from plant samples (Waksmundzka-Hajnos et al., 2004a,b). After the extraction process sample clean-up is required. The most used purification technique is the solid-phase extraction (SPE) (Chen et al., 2008).

An attractive alternative for liquid–solid extraction procedures combined with the method of purification of crude extracts may be matrix solid-phase dispersion (MSPD) (Barker, 2000; Kristenson et al., 2006; Visnevschi-Necrasov et al., 2009). It is an analytical process for the preparation, extraction and fractionation of compounds from solid, semi-solid, liquid and highly viscous biological samples. It can perform homogenization, extraction and clean-up stages simultaneously, and eliminates most of the complications associated with the classical liquid–liquid and solid phase extractions. MSPD has several advantages. Differently from classical extraction methods that require often clean-up steps, large amount of samples, sorbents and organic solvents and thus are expensive and time consuming. This technique is rapid, less manual-intensive, low solvent consumption, and more eco-compatible (Barker, 2007; Capriotti et al., 2010). MSPD chromatographic characteristics show that the elution of a single compound, several classes of compounds or complete fractionation of the sample matrix components can be performed. An additional advantage is the fact that this method may be combined with on-line liquid chromatography, nuclear magnetic resonance spectroscopy and other techniques (Xiao et al., 2004). In the last ten years, several advantages, applications and recent developments of MSPD have been published. This method was applied for the isolation of a wide variety of analyte classes, such as drugs, pesticides, polychlorinated biphenyls, antibiotics and antibacterials, surfactants and naturally occurring compounds, in different matrices (plants, animal originand and environmental samples) (Barker, 2000, 2007; Sergi et al., 2007; Wu et al., 2009).

In the MSPD process, the samples are structurally disrupted by manually blending with a solid-support phase (such as C18 sorbent, C8 sorbent, synthetic polymers, Florisil) to provide a material suitable for extraction. The mixture of sample and solid support is then packed as a column in a tube and analytes are eluted using different solvents (Kristenson et al., 2006). The solvents selected for elution are strictly connected to the nature of solid material. Most commonly organic solvents or their mixtures are employed. The yield of MSPD process can be increased by adding during the blending modifiers such as acids, bases, salts, chelators (Capriotti et al., 2010). The eluent from the column could be analyzed directly by HPLC or LC/MS. MSPD simplifies the process and reduces the time for sample preparation, and has found favor in many applications (Kristenson et al., 2006).

2. Materials and methods

2.1. Materials and chemicals

Fruits of *H. leskowii* were collected in 2009 in Medicinal Plant Garden, Department of Pharmacognosy, Medical University in Lublin, Poland. Fruits were dried at room temperature and powdered to a homogenous size. A voucher specimen was deposited in the Herbarium of Pharmacognosy Department.

Standards of all furanocoumarins were purchased from Sigma Aldrich.

HPLC-grade methanol was purchased from J.T. Baker (Netherlands), water was purified using a Millipore laboratory ultra pure water system (Simplicity^{TM} system, Millipore, Molsheim, France). Other solvents (methanol, dichloromethane, and petroleum ether) used for preparation and purification of the extracts were of analytical grade and obtained from the Polish Reagents (POCH, Gliwice, Poland). The solid phase used for MSPD was Alltech bulk high capacity C18 sorbent, 50 μM (Alltech, Deerfield, IL, USA), end-capped, 17% C. The columns used for SPE were Bakerbond C18 3 mL columns, packed with 500 mg reversed phase, 40 μM (J.T. Baker, Deventer, Netherlands), end-capped, 17.5% C.

2.2. Liquid–solid extraction and solid-phase extraction

Exhaustive extraction was performed under reflux at boiling point of solvent in three 30-minute cycles. A 1 g amount of dried *H. leskowii* fruits powder was extracted with 20 mL of applicable solvent (80% aqueous solution of methanol, dichloromethane, petroleum ether and petroleum ether/methanol 50:50, v/v). Extracts were filtered, combined and evaporated to dryness. The residues were dissolved in 10 mL of 80% aqueous solution of methanol and 2.5 mL of this solution was passed through a Bakerbond C18 SPE column (previously conditioned). The retained furanocoumarins were eluted with 5 mL of 80% aqueous solution of methanol using a SPE vacuum (Zgórka and Głowniak, 1999). Fractions for analysis were transferred into volumetric flask, filled up to their volume with 80% aqueous solution of methanol and injected into the HPLC system. The whole procedure was repeated three times for each solvent.

2.3. Matrix solid-phase dispersion

The dried and powdered *H. leskowii* fruits 0.25 g portion was placed into a glass mortar containing 0.5 g of sorbent (previously conditioned) and homogenized with 1 mL of applicable solvent (80% aqueous solution of methanol, dichloromethane, petroleum ether or petroleum ether/methanol 50:50, v/v). The mixture was then introduced into a 3 mL tube with a polyethylene frit on the bottom and tightly compressed and covered with another polyethylene frit. The coumarins were eluted with 5 mL of 80% aqueous solution of methanol using a SPE set. The collected fractions were evaporated to dryness, dissolved in 80% aqueous solution of methanol in volume flask and analyzed by HPLC. The whole procedure was repeated three times for each solvent.

2.4. Chromatographic analysis

The Agilent 1100 system coupled with diode-array detector (DAD) was employed for HPLC analysis. Separation was performed using the stainless steel column (250 mM × 4.6 mM), packed with 5 μm (Zorbax Eclipse XDB-C18, Agilent Technologies). The sample injection volume was 10 μL. The mobile phase was methanol (A) and water. The A% was changed as follow: 0 min (50%); 5 min (60%); 25 min (80%); 30–40 min (100%). The flow rate was 1 mL min^{-1}, the column temperature was 25 °C (Barker, 2000).

The identification was performed by comparing retention times and UV–DAD spectra with those analyzed under the same conditions for appropriate standards. The qualitative and quantitative determination was performed in following wavelengths: λ = 254, 280 and 320 nM.

2.5. Accuracy, precision, detection limit and quantitation limit

The proposed analytical method for the determination was carefully evaluated in terms of accuracy and precision.

The accuracy of the LSE–SPE and MSPD were evaluated through recovery studies. Pre-analyzed samples (crude extracts in the LSE–SPE and plant material in the mortar in the MSPD) were spiked

Download English Version:

https://daneshyari.com/en/article/6376886

Download Persian Version:

https://daneshyari.com/article/6376886

Daneshyari.com