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Determination of triazine herbicides and their metabolites in multiple medicinal parts of traditional Chinese medicines using streamlined pretreatment and UFLC-ESI-MS/MS

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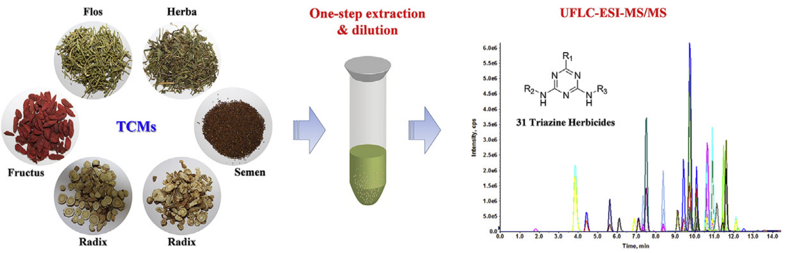
HIGHLIGHTS

- A sensitive and reliable UFLC-ESI-MS/MS method was developed to identify and quantify 31 triazines in a single run.
- Triazine residues were screened for in multiple medicinal parts of TCMs, including radix, flos, herba, fructus, and seed.
- A rapid and streamlined pretreatment using one-step extraction and dilution was proposed.
- Triazine herbicides were found in radix, herba, and seed TCMs, but no residues were detected in either the flos or fructus.

GRAPHICAL ABSTRACT



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ABSTRACT

A rapid, sensitive, and reliable ultra-fast liquid chromatography combined with electrospray ionization tandem mass spectrometry (UFLC-ESI-MS/MS) method was established and applied to simultaneous determination of 31 triazine herbicides and their metabolites in multiple medicinal parts of traditional Chinese medicines (TCMs). A streamlined pretreatment approach using one-step extraction and dilution was proposed, which provided high-throughput processing, excellent recovery, and negligible interference. Afterwards, multiple-reaction monitoring (MRM) and information-dependent acquisition (IDA) triggered enhanced product ion spectra (EPI) was adopted to identify and quantify the targets in a single analysis. The optimized method was then validated according to the guidelines of the European Commission for the following parameters: Matrix effects, specificity, accuracy, precision, linearity, range, and stability. The LOD and LOQ for the 31 triazine herbicides were 0.1–10 μg kg^{-1} and 0.5–25 μg kg^{-1}, respectively. Recoveries at three concentration levels were within 67.9–120.3% with an associated precision RSD <20%. Using the proposed approach, trazines herbicides were determined from 44 commercially available TCMs. The detection rate of triazine herbicides residues was 15.9% of the total samples. Among them, atrazine, simeton, and simetryn were found in the radix, herba, and seed TCMs with values far below the referenced maximum residue limits (MRLs), but no residues were detected in either the flos or fructus. Taken together, this method has the potential to provide a means for triazines

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screening in extensive matrices, thereby laying the foundation for pesticide registration on TCMs. Moreover, it has the potential to guide further triazine residue control in TCMs.

1. Introduction

Triazines are traditional, highly selective, and globally used herbicidal formulations that are highly efficient at weed control. Given these properties, over 70 countries extensively use triazines, particularly atrazine, in both agricultural production and urban utility management (Heri et al., 2008; Zhang et al., 2014b). However, most triazines possess low volatility and long residual activity (Elmore and Lange, 2011). Their widespread and excessive use has led to rapid and serious residue accumulation in soil and water, and then be accumulated in medicinal plants through roots absorption, especially in perennial Traditional Chinese medicines (TCMs). Work investigating the effects of such accumulation on human health has shown that chronic exposure to triazines contributes to interruptions in hormone function, cancers, and birth defects (Wang et al., 2014). Atrazine and simazine have been classified as endocrine-disrupters by the US Environmental Protection Agency (Rodriguez-Gonzalez et al., 2014). Although atrazine has been completely prohibited within the European Union (EU) since 2007, its parent compound and metabolites still exist in water, soil, and a wide variety of local organisms due to their persistency (Pinto and Jardim, 2000; Baranowska et al., 2012; Belzunces et al., 2017). Environmental contamination as well as contamination in foodstuffs and TCMs has dramatically increased human harm potential. Consequently, many countries have crafted strict maximum residue limits (MRLs) regulations for water and a variety of crops (GB/T2763, 2014; European Commission, 2005; Campbell et al., 2016). Critically, the establishment of a rapid, sensitive, and accurate method to evaluate triazine residue is greatly needed.

Previous methods for triazine determination mostly focused on residue found in water (García-Galán et al., 2010), soil (Wu et al., 2010), cereal grains (Mou et al., 2011; Fang et al., 2014), vegetables (Zhang et al., 2014a), and fruits (Sanagi et al., 2012; Pasdar et al., 2016). Despite this large range, little work has been done on residues in traditional Chinese medicines (TCMs). In fact, there have been few regulations for pesticide registration against herbicide abuse in TCMs. Many TCMs originate from perennial plants, and their long growth cycle has increased the risk of herbicide exposure, particularly for systemic triazines (Gonzalez-Barreiro et al., 2006). These systemic herbicides can be absorbed, after which they migrate and are dispersed to other parts of the plant. For example, Astragali radix, Glehniae radix, Lonicerae japonicae flos, Taraxaci herba, Lycii fructus, and Cuscutae semen are extensively used TCMs for medicinal therapy as well as for daily tea-drinking and/or soup-cooking. However, frequent weed control using triazine herbicides has put these TCMs at high risk for residual triazines. Therefore, it is critically important to survey the degree of triazine contamination in these plants, thus guaranteeing the quality and safety of resulting TCMs.

In comparison with soil and water, TCMs with significant difference on medicinal parts and with complicated constituents collectively make the trace detection more difficult. To avoid such interference, extraction and cleanup procedures are often critical steps. Cleanup pretreatment including solid phase extraction cartridge (SPE), molecularly imprinted solid phase extraction (MISPE), and the “quick, easy, cheap, effective, rugged and safe” (QuEChERS) approach have been regularly adopted in past studies (Zhang et al., 2011; Wang et al., 2013; Li et al., 2016b). However, the application of these methods is time-consuming, complicated, and costly, and usually only suitable for a few triazines in one or just a class of matrix. As a result, it cannot be generally applied to multiple TCMs with various medicinal parts.

In recent years, sample preparation has been developing towards more simplified and miniaturized approaches. Previously popular methods for trace analysis in TCMs or food samples have been a one-step extraction pretreatment with sufficient dilution and/or extraction solvent optimization to decrease matrix interference. Subsequently, crude sample extract was injected without additional further cleanup procedures (Abia et al., 2013; Kuang et al., 2013). Given the high selectivity and sensitivity provided by UFLC-MS/MS, a streamlined and effective extraction approach was a solid and highly efficient choice to solve the challenge in analysis of diverse triazine herbicide residues in multiple matrices.

The study presented here sought to establish a fast, simple, sensitive, and high-throughput method for the simultaneous analysis of 31 triazine herbicides, including five dealkylated metabolites in six TCMs with a variety of medicinal parts. This approach was based on a streamlined, one-step extraction and dilution pretreatment followed by UFLC-MS/MS determination. Furthermore, this method was then verified and applied to triazine herbicide target determination in real samples collected from markets. To the best of our knowledge, this is the first report using the UFLC-ESI-MS/MS method for simultaneous analysis of 31 triazine herbicides in six TCMs with five kinds of medicinal parts. This method has the potential to provide solutions for triazine screening in extensive matrices, to lay a foundation for pesticide registration in TCMs, as well as give guidance for triazine residue control in TCMs.

2. Materials and methods

2.1. Chemicals, reagents, and materials

All triazine herbicide standards were supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany). The chemical structures and related information were summarized in Supplementary Material Table S1. Methanol and acetonitrile (HPLC grade) were purchased from Fisher Scientific (Fisher Scientific, Fair Lawn, NJ, USA). Formic acid and ammonium acetate were of analytical grade and supplied by Xilong Chemical (Guangdong, China).

TCM samples included: 11 batches of Astragali radix, 6 batches of Glehniae radix, 7 batches of Lonicerae japonicae flos, 5 batches of Taraxaci herba, 9 batches of Lycii fructus, and 6 batches of Cuscutae semen. All samples were randomly collected from drugstores or medical centers in China, thus ensuring that they were representative of actual consumption in the population. All samples were pulverized and homogenized, sealed in ziplock bags, and stored at room temperature before analysis.

2.2. Preparation of standard solutions

Each individual compound was dissolved in methanol and made to a 1 mg mL^{-1} stock solution, except for DEDIA (atrazine-desethyl-desisopropyl) and simazine prepared in dimethyl formamide at the same concentration. A stock multi-standard solution containing