

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.jfda-online.com

Original Article

Simultaneous analysis of 23 illegal adulterated aphrodisiac chemical ingredients in health foods and Chinese traditional patent medicines by ultrahigh performance liquid chromatography coupled with quadrupole time-of-flight mass spectrometry

Xiao-Bing Wang^a, Jing Zheng^a, Jun-Jie Li^a, Hai-Ying Yu^a, Qi-Yan Li^{a,*},
Li-Hua Xu^{a,**}, Ming-Jie Liu^a, Rui-Qing Xian^a, Yang-En Sun^b,
Bing-Jie Liu^c

^a Shandong Institute for Food and Drug Control, Jinan, China

^b Dong-E E-jiao Co., Ltd, National Engineering Technology Research Center of Gelatin Medicine, Shandong Province Key Laboratory of R&D of the Gelatin Medicine, Liaocheng, China

^c Shanghai AB Sciex Analytical Instrument Trading Co., Ltd, Shanghai, China

ARTICLE INFO

Article history:

Received 21 September 2017

Received in revised form

31 January 2018

Accepted 12 February 2018

Available online xxx

Keywords:

Q-TOF MS

Illegal adulteration

Aphrodisiac chemical ingredients

Qualitation

Quantitation

ABSTRACT

This paper presents an application of ultra high-performance liquid-chromatography-quadrupole-TOF high resolution mass spectrometry (UHPLC-Q-TOF HRMS) for simultaneous analysis of 23 illegal adulterated aphrodisiac type chemical ingredients in health foods and Chinese Traditional Patent Medicines (CTPMs). The mass spectrometer was operated in Information Dependent Acquisition (IDA) mode, which provides crucial information for the elemental composition analysis, structure elucidation and quantitative analysis simultaneously. Quantitative analysis was performed using the peak areas of the precursor ions in the XICs. The method validation included assessment of selectivity, sensitivity, calibration curve, accuracy, precision, recovery, matrix effect and stability. The results show good linear relationship with the concentrations of the analytes over wide concentration ranges (e.g., 0.05–10 µg/g for sildenafil) as all the fitting coefficients of determination r^2 are >0.9984. The detection limits (LODs) were in the range of 0.002–0.1 µg/g. The recoveries were able to reach 82.5–103.6%, while the matrix effects ranged from 87.7 to 109.3%. The intra- and inter-day accuracies were in the range of 82.3–113.8%, while the intra- and inter-day precision ranged from 0.4 to 13.6%. Among 40 batches of health foods and 32 batches of CTPMs (including 28 capsules, 32 tablets, 10 liquid and 2 pills) samples, 28 batches of health foods were positive. The detected chemical ingredients involved sildenafil, tadalafil, aildenafil and sulfoildenafil. This method can be used for the screening,

* Corresponding author. Fax: +86 531 81216558.

** Corresponding author. Fax: +86 531 81216598.

E-mail addresses: 15253118118@163.com (Q.-Y. Li), xlh6404@163.com (L.-H. Xu).

<https://doi.org/10.1016/j.jfda.2018.02.003>

1021-9498/Copyright © 2018, Food and Drug Administration, Taiwan. Published by Elsevier Taiwan LLC. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

identification and quantification of illegal adulterated aphrodisiac chemical ingredients in health foods and CTPMs. Moreover, the LC-Q-TOF MS is very useful to structural elucidation of unknown compound.

Copyright © 2018, Food and Drug Administration, Taiwan. Published by Elsevier Taiwan LLC. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

In recent years, health foods and Chinese Traditional Patent Medicines (CTPMs) have been booming because of being believed as safer and healthier than synthetic drugs and free of side effects [1]. However, for some unscrupulous manufacturers, the deliberate addition of chemical ingredients into health foods and CTPMs is a profit-driven practice aiming to intensify the claimed natural health benefits of the products [2]. Over the past few years, many types of illegal adulterants are being detected in various forms of health foods and CTPMs without labeling, which can lead to potentially serious public health consequences [3–11].

Erectile dysfunction (ED) is a highly prevalent inability to achieve and maintain adequate erection and sexual performance. Synthetic phosphodiesterase type 5 enzyme (PDE-5) inhibitors (e.g. sildenafil, tadalafil, vardenafil) are a class of drugs clinically used for the treatment of ED. In addition, other drugs which mechanism of action is different from PDE-5 can also be used in clinic. These drugs include yohimbine (α -2 receptor antagonist), apomorphine (dopamine receptor agonist), phentolamine (α adrenergic receptor blocker), dapoxetine (selective serotonin reuptake inhibitor), testosterone (androgen), etc. However, clinically adverse side effects, such as headaches, gastrointestinal distress, tachycardia, facial flushing, hypertension, nasal congestion, visual disorders, muscle aches, dizziness, and possibility of blindness and hearing loss have been reported [12–17]. Moreover, PDE-5 inhibitors may also cause potentially serious drug–drug interactions [18]. The patients taking nitrate medications should not use PDE-5 inhibitor, as this combination may result in severe hypotension and syncope [18,19]. Fatal cases caused by adulterated dietary supplements have been reported [20,21].

Therefore, it is dangerous for unknowing patients to be taking such health foods or CTPMs adulterated with PDE-5 inhibitors and other aphrodisiac chemical ingredients. Over the past few years, the approved PDE-5 inhibitors and their unapproved synthetic analogs have been routinely identified in “all-natural” health foods and CTPMs which claim to enhance sexual performance [22–31].

To escape regulatory detection and quality checking, the manufacturers of such illicit and adulterated sexual performance enhancement products are now using new analogs and other aphrodisiac drugs which are difficult to be detected by routine screening and inspection methods. A number of analytical methods have been developed for screening and confirmation of PDE-5 inhibitors in illicit sexual performance enhancer products, such as immunoassay [32], ion mobility spectrometry [33], thin-layer chromatography [34], high

performance liquid chromatography (HPLC) with ultraviolet or fluorescence detection [35–38], gas chromatography–mass spectrometry (GC–MS) [39–42], liquid chromatography–mass spectrometry (LC–MS) [43–49]. Several literature have reported the detection of chemical substances in food or dietary supplements using high-resolution mass spectrometry (HRMS) with quadrupole-Orbitrap (Q-Orbitrap), atmospheric solids analysis probe (ASAP) or Fourier transform ion cyclotron resonance (FTICR) mass analyzers [8,50–54].

Time-of-flight (TOF) is one of the importance remembers of high resolution mass spectrometers analyzer. The development of TOF technology in high resolution mass spectrometers has enabled mass spectrometers to provide accurate mass up to 4–6 decimal places. This is importance for us to deduce elemental composition and the molecular formula of a compound [7,55]. In the previous reports, the methods based HRMS analyzers with TOF (such as LC-MS/TOF, LC-IT/TOF, LC-Q/TOF) have been adopted for screening, identification of PDE-5 inhibitors and deducing its fragmentation pathways [22,56–59].

However, these methods focus on PDE-5 inhibitors and its analogs. Since profit purpose and lack of test method, the possibility of other types of impotence drugs as adulterant in health foods and CTPMs is greatly increasing. The aim of the present study was to develop a rapid and effective multi-analyte method coupling ultrahigh-performance liquid chromatography (UHPLC) to Q-TOF HRMS for the detection of 23 illegal adulterated aphrodisiac chemical ingredients. This method was successfully applied to the screening, identification and quantification of 23 illegal adulterated aphrodisiac chemical ingredients. To the best of our knowledge, this is the first time to report the application of UPLC-Q-TOF/MS in screening of various types illegal adulterated synthetic chemicals in health foods and CTPMs.

2. Materials and methods

2.1. Chemicals and reagents

Noracetildenafil (99.8%), acetildenafil (99.7%), vardenafil hydrochloride (99.2%), hydroxyhomosildenafil (99.8%), sildenafil (99.6%), homosildenafil (99.2%), aminotadalafil (99.9%), tadalafil (99.5%), pseudovardenafil (99.5%) and norneosildenafil (99.9%) were purchased from TLC Pharmaceutical Standards Ltd. (Aurora, Canada). Sulfoildenafil (98.0%), apomorphine hydrochloride hemihydrates (98.0%), yohimbine hydrochloride (98.0%), aildenafil (98.5%), avanafil (99.0%), N-desmethyldildenafil (98.5%), udenafil (96.1%), propoxyphenylthiohydroxyhomosildenafil (96.0%), dapoxetine hydrochloride (98.0%) and phentolamine methanesulfonate salt (98.3%)

Download English Version:

<https://daneshyari.com/en/article/8520852>

Download Persian Version:

<https://daneshyari.com/article/8520852>

[Daneshyari.com](https://daneshyari.com)