

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.jfda-online.com

Original Article

The integration of multi-platform MS-based metabolomics and multivariate analysis for the geographical origin discrimination of *Oryza sativa* L.

Dong Kyu Lim^a, Changyeun Mo^b, Jeong Hee Lee^a, Nguyen Phuoc Long^a, Ziyuan Dong^a, Jing Li^a, Jongguk Lim^b, Sung Won Kwon^{a,c,*}

^a Research Institute of Pharmaceutical Sciences and College of Pharmacy, Seoul National University, Seoul 08826, Republic of Korea

^b National Institute of Agricultural Sciences, Rural Development Administration, Jeonju 54875, Republic of Korea

^c Plant Genomics and Breeding Institute, Seoul National University, Seoul 08826, Republic of Korea

ARTICLE INFO

Article history:

Received 15 July 2017

Received in revised form

14 September 2017

Accepted 28 September 2017

Available online xxx

Keywords:

White rice (*Oryza sativa* L.)

Metabolomics

Discrimination marker

Phospholipid

Multivariate analysis

ABSTRACT

For the authentication of white rice from different geographical origins, the selection of outstanding discrimination markers is essential. In this study, 80 commercial white rice samples were collected from local markets of Korea and China and discriminated by mass spectrometry-based untargeted metabolomics approaches. Additionally, the potential markers that belong to sugars & sugar alcohols, fatty acids, and phospholipids were examined using several multivariate analyses to measure their discrimination efficiencies. Unsupervised analyses, including principal component analysis and k-means clustering demonstrated the potential of the geographical classification of white rice between Korea and China by fatty acids and phospholipids. In addition, the accuracy, goodness-of-fit (R^2), goodness-of-prediction (Q^2), and permutation test p -value derived from phospholipid-based partial least squares-discriminant analysis were 1.000, 0.902, 0.870, and 0.001, respectively. Random Forests further consolidated the discrimination ability of phospholipids. Furthermore, an independent validation set containing 20 white rice samples also confirmed that phospholipids were the excellent discrimination markers for white rice between two countries. In conclusion, the proposed approach successfully highlighted phospholipids as the better discrimination markers than sugars & sugar alcohols and fatty acids in differentiating white rice between Korea and China.

Copyright © 2017, 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/>).

* Corresponding author. Research Institute of Pharmaceutical Sciences and College of Pharmacy, Seoul National University, Seoul 08826, Republic of Korea.

E-mail address: swkwon@snu.ac.kr (S.W. Kwon).

<https://doi.org/10.1016/j.jfda.2017.09.004>

1021-9498/Copyright © 2017, 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/>).

Please cite this article in press as: Lim DK, et al., The integration of multi-platform MS-based metabolomics and multivariate analysis for the geographical origin discrimination of *Oryza sativa* L., Journal of Food and Drug Analysis (2017), <https://doi.org/10.1016/j.jfda.2017.09.004>

1. Introduction

As a principal food source of the world, rice (*Oryza sativa* L.) is one of the most important cereal crops. Rice provides approximately more than 20% of the calorific needs for the world population. In particular, in East Asia, it comprises over 70% of the calorific intake [1]. *O. sativa* L., which is considered to be the “Asian rice”, consists of two subspecies: *indica* and *japonica* [2]. *Japonica* rice is the most common cultivar in East Asia, particularly in three major markets: Korea, China, and Japan [3].

The less milled brown rice does not appeal to most consumers because of its appearance and taste. Consequently, rice in the markets is usually milled to become white rice, where its brown sea coat, germ, and bran are removed. Different types of highly milled white rice look considerably similar, and mislabeling of the white rice origin occurs frequently, especially in East Asia. To find effective discriminating factors, except genetic markers, for plant materials from different locations, we usually consider variables those significantly affect the cellular processes in the plant, such as the annual temperature, drought, cultivate techniques, and biological hazards [4]. Among these variables, temperature is known for its significant effect on the starch and oligosaccharide metabolism [5]. The alterations of this mechanism caused by different annual temperatures induce the aberrant of the associated metabolites. In other words, the temperature of the growth fields alters the metabolic regulations and metabolite composition of rice plants. Moreover, this change directly affects the metabolite composition of rice seeds [6]. As a result, the difference of cultivation temperature between Korea and China is predicted to induce the divergence in the metabolomes of white rice.

Untargeted metabolomics is a comprehensive approach to investigate the metabolic responses of plants to environmental factors [7–9]. It can also reveal the relationship among metabolic networks because of its unbiased and exhaustive analysis of metabolites [10]. Common technologies such as gas chromatography–mass spectrometry (GC–MS) and liquid chromatography–mass spectrometry (LC–MS) have been well established. GC–MS is suitable for the separation and detection of primary metabolites (amino acids, sugars & sugar alcohols) with high reproducibility of the retention index. In addition, this approach is strengthened by invaluable reference databases in which the National Institute of Standards and Technology (NIST) library is an excellent example. LC–MS, on the other hand, detects a wide range of analytes yet it is more appropriate to analyze secondary metabolites such as lipids, alkaloids, flavonoids, and glucosinolates, which represent the quality of plants regarding their nutritional values [7]. Above all else, compare with other spectroscopy techniques, such as near-infrared spectroscopy (NIR), mass spectrometry-based untargeted metabolomics has great advantages regarding the discrimination analysis and novel markers discovery with outstanding sensitivity and accuracy [8].

Although untargeted metabolomics for plant origin discrimination has been well established and thoroughly studied in previous studies [11–14], rice metabolomics,

particularly the metabolite-based discrimination of white rice from different origins has received less attention. This fact comes from several reasons. First, white rice from the local markets is not rigidly controlled. Uncontrollable variables, such as pesticide, temperature, storage time, and storage conditions may affect the metabolite composition of white rice [15]. These uncontrolled variables may result in misleading conclusions of a particular analysis. However, if these uncontrollable variables are not included in the discrimination, the analytical method is not practical and cannot be applied to actual adulteration problems. Second, there is a serious metabolite loss because most nutrients are removed during the milling procedures [16]. It is of importance to mention that the amount of the metabolites is the most important element in untargeted metabolomics [17]. However, nutrients such as sugar, several amino acids, and lipids still remain in white rice [16], some of which are closely related to the starch and oligosaccharide metabolism [5]. Therefore, an evaluation of these compounds in search for potential markers, which surmount the constraints of white rice from different origins, should be meaningful.

In this study, novel markers for the discrimination of non-waxy type of white rice from Korea and China were established and compared. Thereafter, we estimated the discrimination efficiency of markers using several multivariate analyses. Using GC–MS and LC–MS, we identified both primary and secondary metabolites with the full-scan mode. Partial least squares-discriminant analysis (PLS-DA) analysis was conducted to develop discriminatory models and the variable importance in projection (VIP) score was employed to seek for the potential markers. The potential markers and classification efficiencies were also evaluated by using Random Forests (RF), a state-of-the-art supervised learning method. This study, therefore, suggests and evaluates the most potential markers that are responsible for the geographical differences, in which temperature is putatively considered as the main factor.

2. Materials and methods

2.1. Materials and chemicals

HPLC-grade acetonitrile, methanol, isopropanol, water, and chloroform were purchased from JT Baker (Phillipsburg, NJ, USA). Formic acid, derivatizing reagent N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA), trimethylchlorosilane (TMCS), methoxyamine hydrochloride, and pyridine were purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.2. Information and preparation of white rice samples

White rice samples cultivated in 2014, 2015, and 2016 were purchased from the local markets of each country. Detailed information on all collected samples, which include the number of samples and cultivated places, is shown in Tables S1, S2 and S4. The collected samples were directly freeze-dried in the dark within two days after collecting and stored at -70°C to avoid metabolite changes.

Download English Version:

<https://daneshyari.com/en/article/8520925>

Download Persian Version:

<https://daneshyari.com/article/8520925>

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