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Original Article

Non-destructive profiling of volatile organic compounds using HS-SPME/GC–MS and its application for the geographical discrimination of white rice

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ABSTRACT

The authenticity determination of white rice is crucial to prevent deceptive origin labeling and dishonest trading. However, a non-destructive and comprehensive method for rapidly discriminating the geographical origins of white rice between countries is still lacking. In the current study, we developed a volatile organic compound based geographical discrimination method using headspace solid-phase microextraction coupled to gas chromatography–mass spectrometry (HS-SPME/GC–MS) to discriminate rice samples from Korea and China. A partial least squares discriminant analysis (PLS-DA) model exhibited a good classification of white rice between Korea and China (accuracy = 0.958, goodness of fit = 0.937, goodness of prediction = 0.831, and permutation test *p*-value = 0.043). Combining the PLS-DA based feature selection with the differentially expressed features from the unpaired *t*-test and significance analysis of microarrays, 12 discriminatory biomarkers were found. Among them, hexanal and 1-hexanol have been previously known to be associated with the cultivation environment and storage conditions. Other hydrocarbon biomarkers are novel, and their impact on rice production and storage remains to be elucidated. In conclusion, our findings highlight the ability to rapidly discriminate white rice from Korea and China. The developed method maybe useful for the authenticity and quality control of white rice.

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1. Introduction

Rice (*Oryza sativa* L.), especially white rice, is the staple food of most Asian countries. In the modern era, rice has been cultivated in many countries around the world. This ultimately expands rice diversity in terms of genetics and rice field ecology [1]. Despite the significant divergence in rice quality and composition, it appears impossible to distinguish the geographical origins of white rice through its appearance or routine analyses [2]. Hence, illegal distribution and mislabeling for tax avoidance is a matter of concern for rice consuming countries [3]. To prevent the dishonest trading of white rice, systematic and high-throughput discrimination methods using modern analytical chemistry, which exhibit high sensitivity and precision, are now more crucial than ever.

Among analytical techniques, spectroscopy based techniques have been most commonly employed in rice research and have mainly been used for comparisons of rice constituents and derivatives. For instance, near infrared reflectance (NIR) spectroscopy has been applied in rice quality assessment and authentication because the sampling method is quite simple and the data acquisition time per sample is short [4]. On the other hand, nuclear magnetic resonance spectroscopy (NMR) has also been widely used for rice research [5]. Unlike NIR, NMR distinguishes only the differences of specific functional groups. NMR results consist of spectra in which the constituent elements make the quantitative comparison possible for each component. However, NMR possesses the major drawback that its sensitivity is relatively low [6]. Combinations of a separation technique and a spectroscopic method, such as liquid chromatography (LC) or gas chromatography (GC) coupled with mass spectrometry (MS), are currently the methods of choice for compound characterization in complex samples [7,8]. Especially, MS can profile a large number of components with high sensitivity and selectivity through mass to charge ratios (*m/z*) and fragment patterns of specific components. Nevertheless, one major drawback of MS is the relatively low reproducibility among laboratories. Overall, however, the above mentioned analytical methods have shown excellent performance in observing various biochemical phenotypes and the effects of environmental factors, such as rice cultivation conditions (e.g., temperature) and genetic factors (e.g., varieties) [9].

Although rice constituents have often been analyzed using spectroscopy based techniques, the geographical discrimination of white rice using volatile organic compounds (VOCs) has not been conducted. VOCs constitute the fragrance of rice, which is also an important phenotype [10]. Thus, the composition of VOCs in rice may be applied to differentiate rice samples with different origins. The analysis of volatile materials is mainly performed by integrating various methods for VOC extraction and GC–MS. Among these, headspace solid-phase microextraction (HS-SPME), a non-exhaustive and non-invasive extraction method, has been widely used prior to the analysis of VOCs [11]. The comparative advantages of HS-SPME include simplicity, the ability to reuse the sample, high sensitivity, and reproducibility [12,13].

In this study, HS-SPME coupled with GC–MS was utilized for the comprehensive profiling of various VOCs of white rice originating from different regions without any pre-analytical sample treatment. Our objective was to show that the volatiles can be used for geographical discrimination as well as flavor evaluation. Geographical discrimination is a major topic that include various and complex factors, from morphology to genetics, in which a universal method remains to be elucidated [14]. However, it seems more appropriate to find the discriminatory biomarkers that belong to small molecules whose concentrations vary depending on the environment. In particular, since white rice alters in flavor regarding different cultivation conditions, VOCs that constitute fragrance may be applied not only to the discrimination of cultivars but also to the differentiation of the country. Approaching from this view point, we first selected the optimal fiber and an efficient time for extracting volatile matters from white rice. Next, the aberrant VOCs of white rice originating from Korea and China were subject to advanced multivariate statistical analysis to find the discriminatory biomarkers. Our results suggest that the HS-SPME/GC–MS approach is suitable for the goal of identifying white rice from different geographical origins and evaluating white rice flavor.

2. Materials and methods

2.1. Materials

Twenty four different commercial white rice samples (12 from Korea and 12 from China) cultivated in 2016 were collected from local Korean and Chinese markets during the same period. All samples were stored unopened in a −70 °C frozen cabinet until completely used. The details of the white rice samples are shown in Table 1. In addition, the solid-phase

Table 1 – The origins of the 24 analyzed white rice samples from Korea and China.

Country	No	Origin	Cultivar
Korea	K1	Gunsan	Sindongjin
	K2	Gwangju	Choochung
	K3	Ansung	Choochung
	K4	Cheolwon	Ode
	K5	Jinjoo	Samgwang
	K6	Goheong	Unkwang
	K7	Imsil	Sindongjin
	K8	Yeoncheon	Daean
	K9	Dangjin	Samgwang
	K10	Ganghwa	Choochung
	K11	Boseong	Hopyeong
	K12	Uiseong	Ilpoom
China	C1	Heilongjiang	Daohuaxiang
	C2	Liaoning	Zhenshu
	C3	Jilin	Baijinxiang
	C4	Jilin	Shujing
	C5	Heilongjiang	Wuchang
	C6	Shandong	Zhanglixiang
	C7	Heilongjiang	Zhanglixiang
	C8	Heilongjiang	Zhonghuahe
	C9	Heilongjiang	Daohuaxiang
	C10	Jilin	Daohuaxiang
	C11	Heilongjiang	Zhanglixiang
	C12	Jiangsu	Ruanxiangdao