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Simultaneous determination of 23 amino acids and 7 biogenic amines in fermented food samples by liquid chromatography/quadrupole time-of-flight mass spectrometry

Shaodong Jia [a], Yun Pyo Kang [a], Jeong Hill Park [a], Jeongmi Lee [b,*], Sung Won Kwon [a,*]

[a] College of Pharmacy and Research Institute of Pharmaceutical Sciences, Seoul National University, Seoul 151-742, Republic of Korea
[b] School of Pharmacy, Sungkyunkwan University, Suwon 440-746, Republic of Korea

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ABSTRACT

A novel liquid chromatography coupled with quadrupole time-of-flight mass spectrometry (LC–Q-TOFMS) method was developed for the simultaneous determination of 23 amino acids and 7 biogenic amines in food samples. These analytes were pre-column derivatized with dansyl chloride and then separated in an Acquity™ column (1.7 μm; 2.1 mm × 100 mm). The separation of 31 compounds including an internal standard was achieved within 25 min at a flow rate of 0.2 mL/min. The method linearity for each amino acid and biogenic amine had a relatively wide range with $r^2 > 0.99$. The intra- and inter-day precision, expressed as relative standard deviation (RSD), ranged from 1.1 to 4.6% and from 2.0 to 11.2%, respectively. The limit of detection was between 0.005 and 0.4 μg/mL. With a simple dilution, recoveries of around 80–120% were obtained for most of the compounds. No significant matrix effect was observed, and the developed method was successfully applied to the analysis of amino acids and biogenic amines in beer, cheese and sausage samples.

1. Introduction

Amino acids and biogenic amines (Fig. 1) are naturally occurring compounds that exist in a variety of food products, such as fish, alcoholic beverages, cheese and meat products. They play an important role in human metabolism as the building blocks of proteins, as growth factors or as stabilizers of DNA and RNA [1]. Biogenic amines are usually formed from the decarboxylation of amino acids in foods, and undesirable toxicological and organoleptic effects to human health are observed when large amounts are ingested. In food chemistry, the food treatment processes or storage conditions, including smoking [2], fermentation [3], ripening [4] or storage temperature [5], can cause structural changes in both the amino acids and biogenic amines. These changes can be used to evaluate the ripening times [6] or as indicators to reflect the degree of freshness or spoilage of food products. Consequently, sensitive methods for the simultaneous detection of amino acids and biogenic amines in food matrices are required for both food quality and food safety, and efficient analytical methods that can cover a wide range of amino acids and biogenic amines are especially desirable because foods are natural sources for a variety of amine compounds.

The simultaneous analysis of amino acids and biogenic amines is difficult due to their structure diversity, high polarity and the absence of specific chromophores. In the literature, liquid chromatography (LC) [7–11] and capillary electrophoresis (CE) [12,13] are mostly used for separation tasks for food or biological samples. CE methods have advantages of short analysis time, high sensitivity and less consumption of solvents, but the numbers of separated amino acids and biogenic amines are usually much smaller than those provided by LC methods. However, for LC methods, since most amino acids and biogenic amines are highly polar, the conventional reverse phase LC is rarely used for separations. Hence, pre-column derivatization combined with reverse phase LC separation has been widely accepted in recent years. The reagents used for the simultaneous derivatization include o-phthaldialdehyde (OPA) [8], diethylethoxymethylenemalonate (DEEMM) [14], dabsyl chloride [11], N-(9-fluorenylmethoxycarbonyloxy)succinimide (Fmoc-OSU) [10], 9-fluorenylmethyloxycarbonyl chloride (Fmoc-Cl) [15] and o-phthalaldehyde-ethanethiol-9-fluorenylmethyl chloroformate (OPA-ET-FMOC) [9]. In the studies mentioned above, the number of separated amino acids and biogenic amines varied, but the separations usually took more than an hour when a large number of compounds (~30) were analyzed.

Recently the use of columns with sub-2 μm particles under the liquid chromatography system has become popular because it provides better resolution, narrower peaks and shorter retention time. It was successfully applied for the separation of derivatized

* Corresponding author. Tel.: +82 2 880 7844/31 290 7784; fax: +82 2 886 7844.
E-mail addresses: jlee0610@skku.edu (J. Lee), swkwon@snu.ac.kr (S.W. Kwon).

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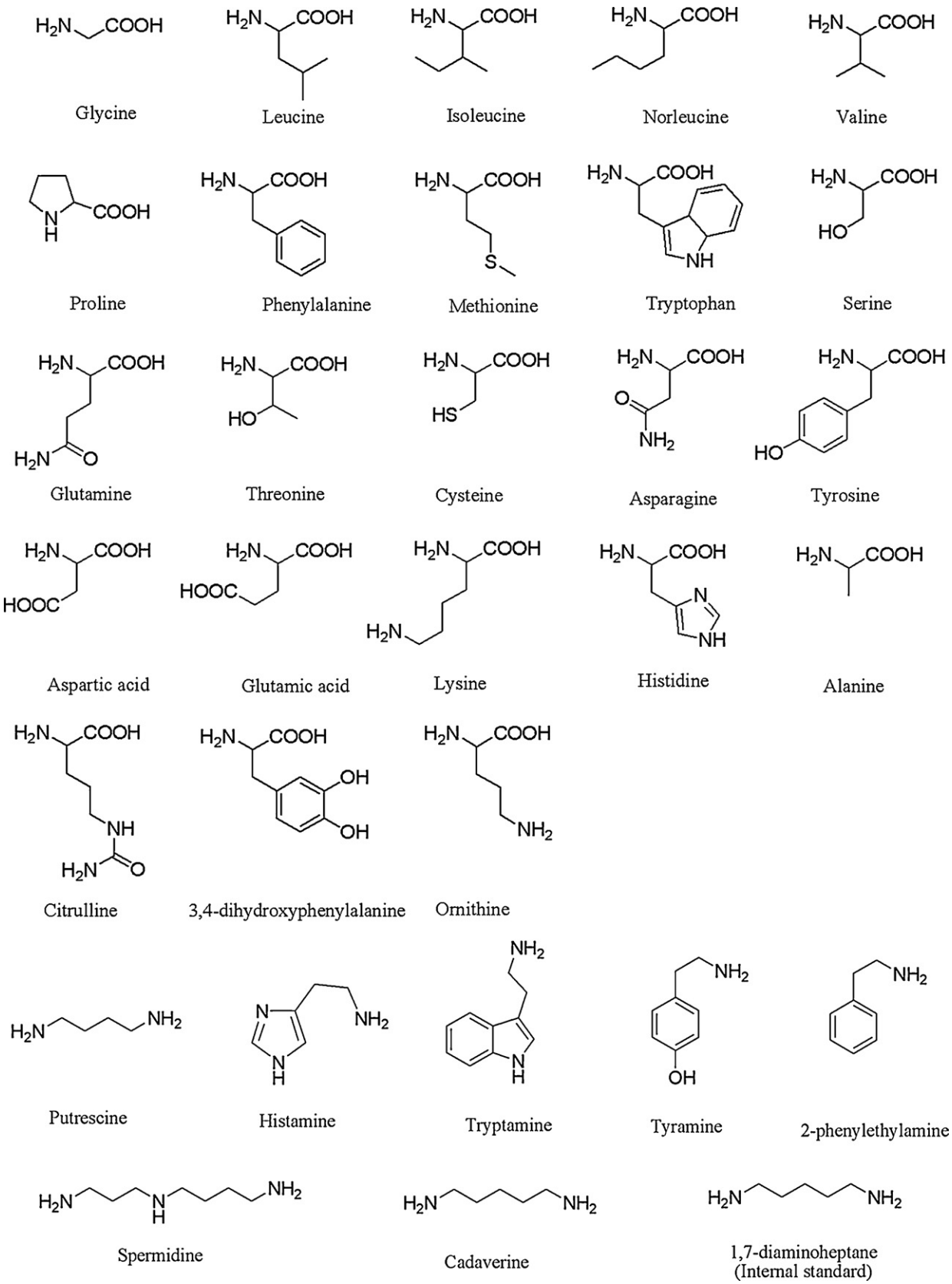

Fig. 1. Structures of amino acids, internal standard and biogenic amines.