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Research article

Qualitative and quantitative analysis of furosine in fresh and processed ginsengs

Yali Li [1], Xiaoxu Liu [2], Lulu Meng [3,**], Yingping Wang [1,*]

[1] Institute of Special Wild Economic Animals and Plants, Chinese Academy of Agriculture Sciences, Changchun, China
[2] Flight Training Base, Air Force Aviation University, Changchun, China
[3] Jilin Province Science and Technology Department, Changchun, China

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ABSTRACT

Background: Furosine (ε-N-2-furoylmethyl-L-lysine, FML) is an amino acid derivative, which is considered to be an important indicator of the extent of damage (deteriorating the quality of amino acid and proteins due to a blockage of lysine and a decrease in the digestibility of proteins) during the early stages of the Maillard reaction. In addition, FML has been proven to be harmful because it is closely related to a variety of diseases such as diabetes. The qualitative analysis of FML in fresh and processed ginsengs was confirmed using HPLC-MS.

Methods: An ion-pair reversed-phase LC method was used for the quantitative analysis of FML in various ginseng samples.

Results: The contents of FML in the ginseng samples were 3.35–42.28 g/kg protein. The lowest value was observed in the freshly collected ginseng samples, and the highest value was found in the black ginseng concentrate. Heat treatment and honey addition significantly increased the FML content from 3.35 g/kg protein to 42.28 g/kg protein.

Conclusion: These results indicate that FML is a promising indicator to estimate the heat treatment degree and honey addition level during the manufacture of ginseng products. The FML content is also an important parameter to identity the quality of ginseng products. In addition, the generation and regulation of potentially harmful Maillard reaction products-FML in ginseng processing was also investigated, providing a solid theoretical foundation and valuable reference for safe ginseng processing.

1. Introduction

Ginseng has been consumed as a dietary supplement and herbal medicine for thousands of years in China, Korea, and Western countries [1,2]. The processing of ginseng is known to have an influence on its bioactive components and pharmacological activities; therefore, its processing is crucial for ginseng's dietary and medical functions [3,4]. During the storage (time, humidity, and temperature) and processing (steaming, drying, and excipients addition) of ginseng, reactions between the amino and carbonyl groups often develop randomly. These reactions are called as the Maillard reactions (MRs), amino-carbonyl reactions, or nonenzymatic model glycation reactions [5,6]. Because abundant carbonyl and amino compounds (reducing sugars or ginsenosides with amino acids or proteins) are contained in ginseng, various MRs may occur [7]. MRs in ginseng processing not only produce a large number of functional components but also generate a small amount of harmful substances which cannot be ignored [8]. In 2012, planted ginseng was advocated to be "homology of medicine and food" in China within 5 yr, stimulating higher standards with respect to the quality and safety of ginsengs [9].

Furosine (ε-*N*-2-furoylmethyl-L-lysine, FML) is an amino acid derivative, generally binding with proteins to generate Amadori products (*N*-substituted 1-amino-1-deoxy-2-ketose) such as fructose-lysine, lactulose-lysine, and maltuloselysine [10]. FML is one of the MR products (MRPs) from MRs of lysine with glucose and other reducing sugars or ginsenosides. The scheme for the formation of FML from the Amadori product of glucose is shown in Fig. 1. In addition, FML is also considered to be an important indicator of the extent of damage (reducing the quality of amino acid and

* Corresponding author. Institute of Special Wild Economic Animals and Plants, Chinese Academy of Agriculture Sciences, Changchun, Jilin 132122, China.
** Corresponding author.
E-mail addresses: Yalilee@126.com, Yingpingw@126.com (Y. Wang).

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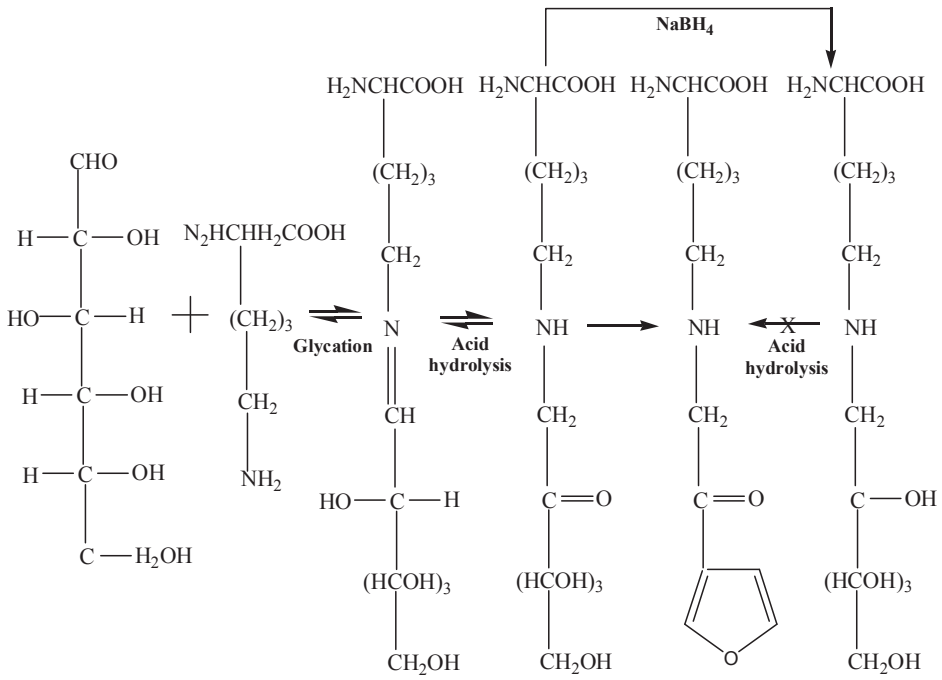

Fig. 1. Scheme for the formation of furosine from the Amadori product of glucose.

proteins due to a blockage of lysine and a decrease in the digestibility of proteins) during the early stages of MR. Harris et al [11] reported that FML could degrade slowly to form many different advanced glycation end products (AGEs). Partial AGEs have been proven to be closely related to a variety of diseases, such as diabetes, and a high amount of AGEs in human bodies is considered harmful [11]. AGEs in human bodies are mainly derived from two pathways, *in vivo* transformation and *in vitro* intake, but the *in vitro* intake from foods and medicines is the main source. A number of previous researches have reported on the FML for identifying the quality or processing and storage effects in foods, such as liquid nutritional products [12], milk-cereal-based baby foods [13], dietary products [8], meat products [14], honey [15], pasta products [16], milk [17], as well as cookies, crackers, and breakfast cereals [16]. However, the presence of FML in ginseng products and suggestion to consider FML as an evaluating indicator of quality for ginseng has not been reported.

In the present study, qualitative and quantitative analysis of FML in fresh and processed ginsengs was confirmed using HPLC-MS, and it was found that the FML content in various ginsengs was variable. The presence of FML in the acid hydrolysates of five kinds of ginseng samples was confirmed by comparing its retention time and mass fractions with that of an FML standard using HPLC-MS. The FML content in various ginseng products was analyzed using an ion-pair reversed-phase LC method and comparing its retention time and peak area with the standard. At the same time, the generation and regulation of potentially harmful MRPs-FML in ginseng processing was also analyzed, providing a solid theoretical foundation and valuable reference for safe ginseng processing and also providing a basis for the development of recommended ginseng dosage.

2. Experimentals

2.1. Materials and methods

Five kinds of different ginseng samples were purchased from local markets in Ji'an, China and Cheong Kwan Jang, South Korea. Three of the five were solid samples (fresh, dried raw, and red ginseng), and the other two were liquors (red ginseng liquor and black ginseng concentrate). FML standard was purchased from NeoMPS (Strasbourg, France). Trifluoroacetic acid (TFA) was purchased from Sigma (San Francisco, USA). HPLC-grade acetonitrile was purchased from Fisher-Scientific (USA). Hydrochloric acid and other chemicals were of reagent grade.

2.2. Sample preparation

The preparation of the samples follows the traditionally-adopted procedures [18,19]. Briefly, five kinds of ginseng samples (3.0 g each) were hydrolyzed with 6M HCl at 110°C for about 22 h in a screw-capped Pyrex vial with PTFE-faced septa. The hydrolysates were filtered with a medium-grade filter paper, and then a 2 mL portion of the filtrate was applied to a Millipore Sep-Pak C18 cartridge (Massachusetts, USA) pre-wetted with 5 mL methanol and subsequently with 10 mL water. The FML portion was eluted with 3 mL of 3M HCl, and the resulting solutions were collected for HPLC-MS or HPLC analysis.

2.3. Protein content analysis

The protein content in fresh and processed ginseng was measured on a Dumas Nitrogen Analyzer (Velp NDA 701-Monza, Brianza-Italy), according to a previous method with minor modification [20]. The total nitrogen level was converted to protein content using a conversion factor of 6.25. The working conditions of NDA were as follows: O_2 gas at 400 mL/min, He gas at 195 mL/min, combustion reactor at 1030°C, reduction reactor at 650°C, and pressure at 881.0 mbar.

2.4. Qualitative analysis of FML

To identify the presence of FML in fresh and processed ginseng samples, HPLC-MS analysis was performed. Qualitative analysis of FML was performed at 25°C using HPLC (Agilent1200, USA) coupled

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