大豆から味噌および醤油への加工過程におけるカドミウム含有量の変化

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技術報告

Changes in Cadmium Content when Processing Soybean to Miso and Soy Sauce

Kumiko SHINDOH,[§,*] Takashi ABE,[**] and Akemi YASUI[*]

* National Food Research Institute, National Agriculture and Food Research Organization,
2-1-12 Kannondai, Tsukuba, Ibaraki, 305-8642 JAPAN

**Japan Food Research Laboratories, 7-4-41, Saito Asagi, Ibaraki, Osaka, 567-0085 JAPAN

Abstract

This paper investigated changes in cadmium content during processing to final products of miso and soy sauce prepared using two kinds of soybeans, one containing 0.040 μg/g cadmium and the other containing 0.320 μg/g cadmium. In rice miso preparation, 83% of the total cadmium in raw soybeans remained in the final product. However, in *koikuchi* soy sauce preparation, 43 to 53% of the total cadmium in the raw soybeans was calculated to remain in the final product when the yield of nitrogen in the soy sauce versus the total nitrogen contained in the raw materials was 60%. During miso processing, the cadmium content in soybeans decreased mainly during soaking and autoclaving, but in soy sauce processing, the cadmium content changed during several process steps, including soy sauce separation from moromi mash. The amount of cadmium transferred from raw soybean to the final soy sauce product depends more on soybean characteristics than the case of miso processing.

Keywords: Cadmium, Miso (bean paste), Processing, Soybean, Soy sauce

Introduction

Cadmium is a naturally occurring metallic element that is well-known for its potential risks to human health. Cadmium intake has been reported mainly from cereals[1, 2]. According to Ikebe et al.[3], pulses (mainly soybean and its products) contain the same level of cadmium as cereal products. Since soybean is a frequently consumed crop[4], a study of cadmium intake from soybean is crucial.

Prior to utilization, soybean is processed and cooked to eliminate anti-nutritional factors (e.g., trypsin inhibitor) and to improve protein digestibility[5]. Miso (bean paste) and soy sauce are traditional fermented soybean foods and salty seasonings used daily in Japan[6, 7].

Cadmium contents of crops and vegetables and their industrial products have been separately surveyed, but studies on changes in cadmium content during processing and cooking are rare. In fact, there are no reports on changes in cadmium content during the processing of miso and soy sauce. Information on such changes in cadmium content is necessary in order to estimate cadmium intake from agricultural products. In this study, salty rice miso and *koikuchi* soy sauce, which are popular in Japan[6, 7], were prepared to investigate changes in cadmium content during processing.

*Corresponding author: Kumiko SHINDOH (E-mail: shindoh@affrc.go.jp)
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Materials and Methods

Materials for miso and soy sauce making

Two soybean samples, designated as soybean A and soybean B, with different varieties were used to prepare both miso and soy sauce. Soybean B contained a higher level of cadmium than soybean A, of which variety was *Enrei*, while. The following materials were used in this study: rice koji (purchased), roasted and crushed wheat (purchased), tane-koji (mold spore inoculum, Nihon Jozo Kogyo Corp., Tokyo), sodium chloride (guaranteed reagent grade, Kanto Chemical Co., Inc., Tokyo), and ion-ex changed water (Super Q system, Millipore Corp., Bedford MA).

Soybean processing

Soybeans (1 kg) were soaked in 3 L water overnight. After draining, the soaked soybeans were autoclaved under steam pressure of 0.7 kg/cm^2 (112°C) for 30 min.

Preparation of miso

To prepare salty rice miso containing 12% salt and 45% moisture, the autoclaved soybeans (2.20 kg) were mixed with 0.92 kg of rice koji (soybean: rice, 10:8, w/w), 0.44 kg sodium chloride, and water. The amount of water depended on the moisture content of each mixed material. The mixture was minced with a hand-turned meat grinder, then placed into a beaker (3 L capacity) with a weight (0.8 kg) for pressing, and allowed to ferment at 30°C for 40 days.

Preparation of soy sauce

To prepare *koikuchi* soy sauce, autoclaved soybeans (2.20 kg) were mixed with 1.00 kg of roasted and crushed wheat, inoculated with 0.4 g of tane-koji, and incubated at 25 to 30°C under 95% relative humidity for 3 days. The resulting soy sauce koji was mixed with 2.7 L of 23% sodium chloride solution in a beaker (5 L capacity) to make moromi mash, which was then fermented under the following temperature conditions[8) : 15°C for the first 20 days, 25°C for 10 days, 30°C for 30 days, and finally 25 °C for 90 days. During fermentation, the moromi mash was stirred occasionally. After fermentation, the mash was filtered through a small centrifugal filter (SYG-3800-15A, Sanyo Physical & Chemical Appliances Mfg. Co., Ltd., Tokyo) with mesh 15A at 6000 rpm for 10 min.

Moisture content

The moisture content of the raw soybeans was determined after coarsely grinding and drying them at 130°C for 2 hr. The autoclaved soybeans were first made into a paste in a plastic bag, spread thin on aluminum foil, and then measured for moisture content after drying at 130°C for 2 hr. Rice koji, and roasted and crushed wheat were dried to a constant weight at 135°C. The moisture contents of the miso, soy sauce, and soybean cake were determined after drying samples were mixed with silica sand to a constant weight at 70°C under reduced pressure.

Nitrogen content

Nitrogen content was determined by the improved Kjeldahl method[9)]. The yield of nitrogen was calculated based on total nitrogen in the soy sauce versus total nitrogen in the raw materials.

Cadmium content

Cadmium content was determined by the method used in surveys on agricultural products by the Ministry of Agriculture, Forestry and Fisheries of Japan[10)]. Each sample was decomposed with nitric acid and sulfuric acid in a Kjeldahl flask; cadmium was then extracted by ammonium pyrrolidine dithiocarbamate and butyl acetate. The amount of chelated cadmium in the butyl acetate was measured by its absorbance at 228.8 nm using an air-acety lene atomic absorption spectrometer (AA-890, Nippon Jar rell-Ash Co., Ltd., Kyoto). A calibration curve was made with extracted cadmium from standard solutions. Standard stock solutions and reagents used were of the grade for atomic absorption spectrometry[11)].

Results and discussion

Cadmium in soybeans and other crops or vegetables is usually present in trace amounts. Moreover, the miso and soy sauce prepared in this study were high-salt products. Due to the low level of cadmium and the influence of salt on the cadmium measurements, the samples had to be pretreated prior to cadmium determination. Each sample was first decomposed by acid, and cadmium was ex-

Table 1. Changes in cadmium content during rice miso processing using soybean A

Sample	Moisture content %	Cd content* µg/g fw	Weight g	Total Cd* µg	Yield of Cd %
Whole soybeans	15.9	0.040±0.004	1000	40±4	(100)
Autoclaved soybeans	66.7	0.015±0.001	2213	33±2	(83)
Rice koji	26.2	0.081±0.001	916	74±1	–
Rice miso	44.1	0.030±0.002	3549	105±7	(83)**

* Mean ± S.D. (n = 2 or 3).
** Estimated assuming that no cadmium was lost after autoclave.

Table 2. Changes in cadmium content during rice miso processing using soybean B

Sample	Moisture content %	Cd content* µg/g fw	Weight g	Total Cd* µg	Yield of Cd %
Whole soybeans	12.0	0.320±0.006	1000	320± 6	(100)
Autoclaved soybeans	64.4	0.120±0.005	2202	264±11	(83)
Rice koji	26.2	0.081±0.001	916	74± 1	–
Rice miso	42.2	0.106±0.004	3340	352±13	(83)**

* Mean ± S.D. (n = 2 or 3).
** Estimated assuming that no cadmium was lost after autoclave.

tracted from the resulting solution using the solvent extraction method with chelating reagent to concentrate cadmium and remove alkali metals. The amount of extracted cadmium in butyl acetate was measured by atomic absorption spectrometry. The results indicated that soybean A contained 0.040 µg/g cadmium and soybean B contained 0.320 µg/g.

Change in cadmium content of materials during miso processing

Tables 1 and 2 indicate the cadmium content of materials during miso processing. Portions of the materials were sampled and used for cadmium analysis during processing. The values in Tables 1 and 2 were calculated assuming that no sampling was carried out.

After autoclaving, 83% of the total cadmium in raw soybeans A and B remained in the autoclaved samples. These values indicate that a small amount of cadmium was eluted during soaking and autoclaving. Based on the dry matter, for soybean A the cadmium content of the raw soybean was 0.047 µg/g and that of the autoclaved soybean was 0.045 µg/g; for soybean B the cadmium content of the raw soybean was 0.363 µg/g and that of the autoclaved soybean was 0.337 µg/g.

Cadmium contamination from materials other than soybean and rice koji was considered to be negligible, since this study used NaCl and water of high grade and purity, and borosilicate glassware. Additionally, as nothing was released during miso fermentation except for a small amount of volatile compounds and water, all cadmium in the autoclaved soybean was presumed to remain in the final product. Actually, the amount of cadmium detected in rice miso was the sum of cadmium in the autoclaved soybean and the rice koji (Tables 1 and 2).

It was calculated that for the miso prepared using soybean A, which contained 0.040 µg/g cadmium, 31% of the total cadmium in the miso was derived from soybeans and 69% was derived from rice koji. For that prepared using soybean B, which contained 0.320 µg/g cadmium, 78% of the total cadmium was derived from soybeans and 22% was derived from rice koji. The miso contained some cadmium derived from the koji material. Since sweet miso contains more rice koji than salty miso, more attention should be given to the cadmium content of rice used to make koji.

Change in cadmium content of materials during soy sauce processing

Tables 3 and 4 indicate changes in cadmium content during soy sauce processing from the same soybeans A

Table 3. Changes in cadmium content during koikuchi soy sauce processing using soybean A

Sample	Moisture content	Cd content*	Weight	Total Cd*	Yield of Cd
	%	μg/g fw	g	μg	%
Whole soybeans	15.9	0.040±0.004	1000	40±4	(100)
Autoclaved soybeans	66.8	0.015±0.001	2220	33±2	(83)
Roasted and crushed wheat	13.1	0.057±0.001	1000	57±1	—
Raw soy sauce	68.1	0.015±0.002	3257	49±7	(>43)**
Cake	53.6	0.023±0.002	2041	46±4	(<40)**

* Mean ± S.D. (n = 2 or 3).
** Estimated assuming that the ratio of hydrolyzed cadmium in soybeans and wheat of moromi mash was the same.

Table 4. Changes in cadmium content during koikuchi soy sauce processing using soybean B

Sample	Moisture content	Cd content*	Weight	Total Cd*	Yield of Cd
	%	μg/g fw	g	μg	%
Whole soybeans	12.0	0.320±0.006	1000	320± 6	(100)
Autoclaved soybeans	65.4	0.117±0.005	2266	265±11	(83)
Roasted and crushed wheat	13.1	0.057±0.001	1000	57± 1	—
Raw soy sauce	66.8	0.060±0.002	3557	213± 7	(>53)**
Cake	49.0	0.068±0.001	1817	124± 2	(<30)**

* Mean ± S.D. (n = 2 or 3).
** Estimated assuming that the ratio of hydrolyzed cadmium in soybeans and wheat of moromi mash was the same.

and B as those used to make miso described above. The weight of materials and the amount of cadmium in autoclaved soybeans, soybean cake, and the final product were calculated assuming that no sampling was carried out, as with the miso.

After soaking and autoclaving, 83% of the total cadmium in raw soybean A remained in the autoclaved soybeans. It was assumed that cadmium contamination during the soy sauce processing was negligible, as in the miso processing. Therefore, all cadmium in the moromi mash (brine fermentation mixture) was assumed to have come from soybeans and wheat. In the moromi mash from soybean A, 37% of the total cadmium came from soybeans and 63% came from wheat. In the moromi mash using soybean B, 82% of the total cadmium came from soybeans and 18% came from wheat. After moromi mash-making, the amount of cadmium transferred from soybeans to the final soy sauce product could not be estimated accurately because its origin could not be clearly distinguished. After moromi mash fermentation and filtration, 43% of the cadmium in soybean A was estimated to have been carried over to the raw soy sauce and 40% remained in the cake, when the ratio of hydrolyzed cadmium in soybeans and wheat of moromi mash was assumed to be the same. In a similar manner, 17% of the cadmium in raw soybean B had been eluted during soaking and autoclaving, 53% was estimated to have been transferred to soy sauce, and 30% remained in the cake.

The nitrogen content of roasted and crushed wheat was 2.6%, that of raw soybean A was 5.6%, and that of soybean B was 5.5%. The nitrogen content in the raw soy sauce was 1.5% for soybean A and 1.4% for soybean B. The yield of hydrolyzed nitrogen in the soy sauce versus the total nitrogen contained in the raw materials was 60% for soybean A processing and 62% for soybean B processing. In this study, the moisture content of a cake of soybean A was 53.6%, and that of soybean B was 49.0%. These moisture values of cakes are double that in modern soy sauce manufacturing companies[12)]. The high nitrogen yield in modern soy sauce is attributed to good pressing conditions. The yield of nitrogen in the soy sauce versus the total nitrogen contained in the raw materials exceeded 90% in a recently developed soy sauce manufacturing process[7)], which is higher than the nitrogen yield in this study. Because of improved pressing conditions and an increased yield of nitrogen, more cadmium in materials may be transferred to the final soy sauce product in modern factories. However, even if the total amount of cadmium in soy sauce is increased to some extent, its final concentration does not increase because the total volume of the final soy sauce product is also increased.

In miso processing, the cadmium content in soybeans decreased mainly during soaking and autoclaving; in contrast, in soy sauce processing, the change in cadmium content was attributed to several steps in the process, including soy sauce separation from the moromi mash. The yields of soy sauce were 3257g from 2200g of soybean A, and 3557g from 2200g of soybean B. The amount of cadmium transferred from soybean to the final product seemed more dependent on the property of soybeans for soy sauce processing than for miso processing. In this study, the transferred ratio of the amount of cadmium from soybean to the final product was estimated to be 83% in rice miso and 43 to 53% in koikuchi soy sauce when the yield of nitrogen in the soy sauce versus the total nitrogen contained raw materials was 60%. Therefore, controlling the cadmium content in crops and vegetables was considered to be important in these processed food products.

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大豆から味噌および醤油への加工過程におけるカドミウム含有量の変化

進藤久美子*・阿部　孝**・安井明美*

*（独）農業・食品産業技術総合研究機構　食品総合研究所
**　財団法人日本食品分析センター

要　約

0.040μg/g と0.320μg/g のカドミウムを含む異なる品種の大豆を使い，味噌および醤油の加工過程におけるカドミウムの含有量変化を検討した。米味噌への加工過程では，大豆に含まれるカドミウム総量の約83%が最終品の味噌に移行した。一方，こいくち醤油への加工過程では，窒素利用率が約60%の場合に，大豆に含まれるカドミウム総量の43-53%が最終品の醤油へ移行すると推定された。味噌への加工過程では，大豆に含まれるカドミウムが減少する主要なプロセスは大豆の浸漬および蒸煮過程であった。醤油への加工過程では、もろみ圧搾過程を含む複数のプロセスでカドミウムが減少し、その割合は大豆により異なった。このため，最終品へ移行するカドミウム量は，醤油では味噌以上に大豆の持つ加工適性に依存すると考えられた。