A Sruvey of Mycotoxins In Commerical Foods and Fate of Mycotoxins During Food Processing

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ABSTRACT—The natural ocurrence of mycotoxins in food and foodstuffs and the fate of mycotoxins during food processing were investigated. Aflatoxins and/or Fusarium mycotoxins (nivalenol, deoxynivalenol and zearalenone) were detected in commercial samples of various foods and foodstuffs collected at Tokyo markets. It was found that the mycotoxins were decomposed at high temperature, but some remained after heating at usual temperatures for an ordinary period for domestic cooking (boiling, deep-frying or grilling). Industrial food manufacturing processes were relatively effective for removing mycotoxins.

Agricultural products which are used as foods are always exposed to the danger of fungal contamination during their cultivation, harvest, transport and storage. When the foodstuff, temperature and humidity are suitable for the growth of certain fungi, there is always the danger of mycotoxin production.

Among such fungi, some species of the genus *Aspergillus*, well-known aflatoxin producers, are frequently found. Natural infection by *Fusarium* is observed as often as, or more often than, that of *Aspergillus*. Among *Fusarium* species, *F. graminearum* has been reported from many countries to cause the contamination of cereals and various other foods with nivalenol, deoxynivalenol and zearalenone.

Aflatoxins and *Fusarium* mycotoxins have been detected in wheat, barley and their products, and also in nuts and seeds, beans, species, oils and dairy products. Therefore, aflatoxins and *Fusarium* mycotoxins represent a potential food hygienical problem. In order to learn whether there might be a risk to human health from the intake of mycotoxins contaminating agricultural products, the stabilities of mycotoxins under various cooking conditions employed in daily life and the possibility of removal of mycotoxins during manufacturing processes were investigated.

OCCURRENCE OF MYCOTOXIN IN COMMERCIAL FOODS

Among products from Tokyo markets, mycotoxins have been detected in various foods. The results of a survey of aflatoxins and *Fusarium* mycotoxins in 1123 samples of foods and foodstuffs are shown in Table 1 and 2. Various points should be borne in mind.

1) Aflatoxins

For example, nutmeg is mostly imported from Indonesia, and various grades are available. Nutmeg of high grade is used as pharmaceutical, while nutmeg of poor grade is used as food and spice after being pulverized. Nutmeg of poor grade, used for food, was examined. Among 56 samples of nutmeg, 25 samples were positive for aflatoxin B_1. The content of aflatoxins in 4 samples exceeded the Japanese regulation value (B_1 10 ppb). The highest content of aflatoxins was 60.3 ppb, which was aflatoxin B_1. The average level of aflatoxin B_1 was 4.8 ppb.

Coix seed and others were imported from southeast Asia. Coix seed has long been used as folk medicine to treat warts and rough skin, but the demand had been so small that it could be supplied domestically. However, with the recent boom in health foods, the demand for Coix seed exceed-

Table 1. Analytical results of aflatoxins in foodstuffs

Sample	No. of sample	No. of positive	Aflatoxin (ppb)				
			B_1	B_2	G_1	G_2	M_1
Cereals							
Buckwheat	123	23	0.1-4.2	0.1-0.9	0.2-0.8	Tr-0.1	ND
Coix seed	144	34	0.1-14.9	Tr-1.8	0.3-0.7	ND-Tr	ND
Spices							
Nutmeg	56	25	0.2-60.3	0.1-6.5	0.4-15.8	0.3	ND
Pepper	24	7	0.6-2.3	0.1-0.2	0.2-1.4	ND-Tr	ND
Dairy products							
Cheese	158	40	ND	ND	ND	ND	0.1-1.2

Tr; below 0.1 ppb ND; not detected

Table 2. Analytical results of *Fusarium* mycotoxins in wheat products

Sample	No. of sample	No. of positive	*Fusarium* mycotoxins (ppb)			
			Trichothecenes			ZEN[d]
			DON[a]	NIV[b]	Others[c]	
Flour	65	19				
		8[e]	3-210	ND	ND	ND
		2	ND	4, 12	ND	ND
		7	4-24	5-18	ND	ND
		2	11, 16	ND	ND	22, 41
Germ	16	3	ND	ND	ND	63-360
Bran	3	1	28	ND	ND	ND
Spaghetti	6	2	9, 14	ND	ND	ND
Macaroni	4	1	19	ND	ND	ND
Noodle	10	0				
Biscuit	7	1	27	ND	ND	ND

[a]DON; deoxynivalenol
[b]NIV; nivalenol
[c]Others; fusarenone-x, dicetoxyscirpenol, neosolaniol HT-2 toxin and T-2 toxin
[d]ZEN; zearalenone
[e]Table of items

ed the domestic supply, and imports from Thailand and other southeast Asian countries began. Among 144 samples of Coix seed, 34 samples were contaminated with aflatoxins. The content of aflatoxin B_1 in one sample exceeded the regulation value of 10 ppb. The highest concentration and average level of aflatoxin B_1 were 14.9 ppb and 1.8 ppb, respectively.

In the case of buckwheat, 23 samples out of 123 tested samples were found to contain aflatoxins. In natural cheese, aflatoxin M_1 was detected in 40 samples of 158 tested. The level of aflatoxin M_1 was between 0.1 and 1.2 ppb. In future the import of foodstuffs is expected to increase so that danger of exposure to food contaminated with aflatoxins will increase accordingly.

2) *Fusarium* mycotoxins

Natural infection by *Fusarium* spp. is observed as often as, or more often than, that by *Aspergillus*. Agricultural products and foods contaminat-

Table 3. Behavior of *Fusarium* mycotoxins in the cooking process

Material	Process	Mycotoxin	*Fusarium* mycotoxins (ppb)			
			Before cooking		After cooking	
Spaghetti	Boiling	DON[a]	14	8,	tr[d],	ND[e]
Coix seed	Boiling	ZEN[b]	840	620,	770,	830
Pressed barley	Boiling	DON	264	210,	245,	250
		NIV[c]	282	195,	224,	247
		ZEN	53	38,	40,	49
Popcorn	Popping	DON	196, 233, 344	145,	184,	220

[a]DON; deoxynivalenol
[b]ZEN; zearalenone
[c]NIV; nivalenol
[d]tr; below 2 ppb
[e]ND; not detected

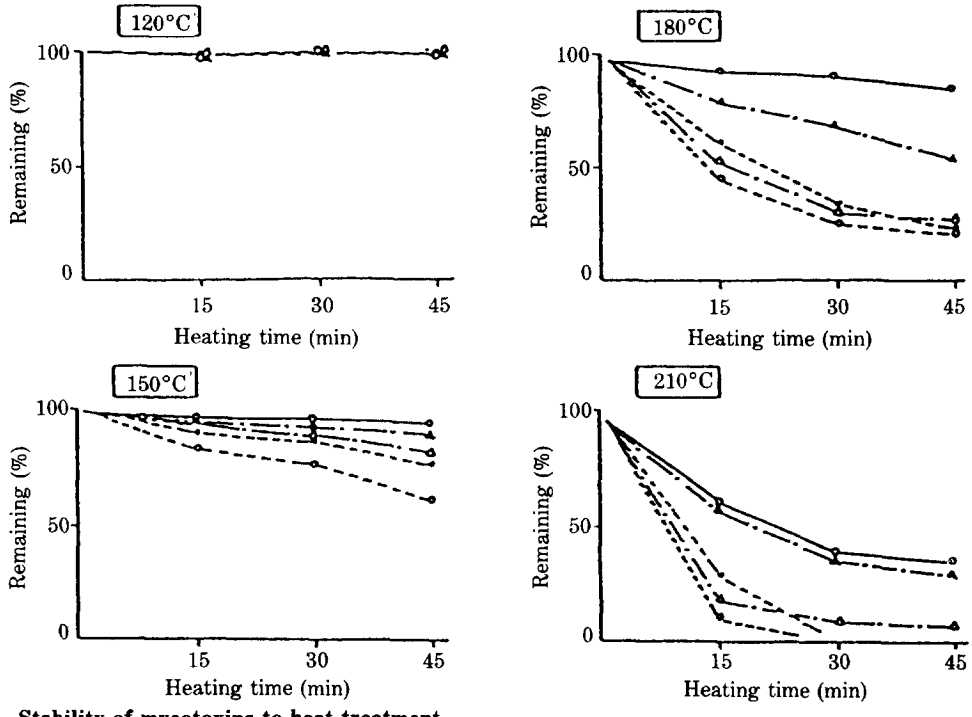

Fig. 1. Stability of mycotoxins to heat treatment
-○-○-: Zearalenone --○-○--: Nivalenol type -●-●-: T2 type
--△-△-- Aflatoxin B_1 and G_1 --▲-▲-- Aflatoxin B_2 and G_2

ed with *Fusarium* mycotoxins are mostly cereals, including, wheat and its processed products such as wheat flour, barley and its processed products such as pressed barley, coix seed and its processed products and maize. Analytical results for cereals and these processed products are shown in Table 2. *Fusarium* mycotoxins were detected in 19 samples of wheat flour among 65 tested samples and concentrations of deoxynivalenol were in the range from 3 to 210 ppb. Zearalenone was found in 3 samples of wheat germ among 16 at concentrations ranging from 63 to 360 ppb. Deoxynivalenol was

Table 4. Behavior of mycotoxins in the neutralization process

Mycotoxins	Residual amount (%)			
	Centrifugation		Washing	
	Oil	Fats	Oil	Water
AF-B_1[a]	Tr[e]	48	ND	82
AF-B_2	Tr	46	ND	87
AF-G_1	ND[f]	Tr	ND	37
AF-G_2	ND	Tr	ND	53
ZEM	ND	96	ND	98
DON[c]	Tr	84	Tr	91
NIV[d]	Tr	78	Tr	88

[a]AF; aflatoxin
[b]ZEN; zearalenone
[c]DON; deoxynivalenol
[d]; nivalenol
[e]Tr; trace (below 0.1%)
[f]ND; not detected

also found in wheat products such as spaghetti, macroni and biscuit. It is noteworthy that coix seeds were frequently contaminated with both aflatoxins and *Fusarium* mycotoxins such as zearlaenone. Popcorn grains imported from America are very frequently contaminated with deoxynivalenol. Thus, popcorn should be checked carefully in the future. Deoxynivalenol was also found in corn grits, canned corn and other products.

FATE OF MYCOTOXINS DURING COOKING AND MANUFACTURING PROCESSES

1. Heat stability of mycotoxins

Heat stability curves showing the relationship between the residual amount of mycotoxins and temperature are shown in Fig. 1. Aflatoxins and *Fusarium* mycotoxins are quite stable to heat, and cannot be decomposed or removed under home-cooking conditions. The usual temperature for boiling and frying is around 100°C to 150°C, at which mycotoxins are hardly decomposed. At the temperature for deep frying, that is 180°C, mycotoxins can be gradually decomposed. At the temperature for grilling, 210°C, trichothecene-type mycotoxins can be decomposed within 30 minutes. However, it became clear that within the usual range of cooking time at home, mycotoxins cannot be effectively decomposed by either boiling, deep-frying or grilling.

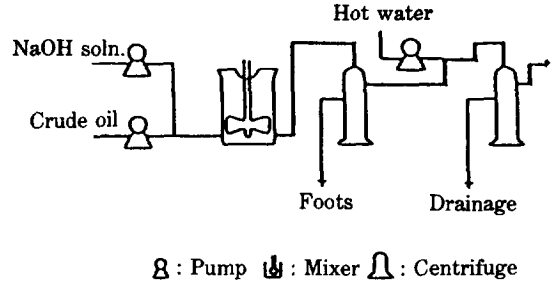

Fig. 2. Diagram of neutralization process of crude oil

2. Decomposition by cooking

Mycotoxins were added artificially to raw materials, whcih were then processed. In the case of buckwheat noodles, only 10 to 12% of the added aflatoxins were transferred into water. Bread and noodles made using flour artificially contaminated with *Fusarium* mycotoxins still contained some mycotoxins. These experiments indicate that there is a high probability of intake of mycotoxins from such cooked foods.

Buckwheat noodles were prepared using naturally contaminated buckwheat flour. Before cooking, the contents of aflatoxin B_1, B_2 and G_1 were 162 ng, 12 ng and 12 ng, respectively. After being boiled, the buckwheat noodles contained 136 ng of B_1, 9 ng of B_2 and 6 ng of G_1, while 22 ng of B_1, 1.6 ng of B_2 and 1.2 ng of G_1 were detected in the water. Aflatoxins are scarcely decomposed by cooking.

Other foods were made from spaghetti which was naturally contaminated with deoxynivalenol, from coix seed which was naturally contaminated with zearalenone, from barley which was naturally contaminated with deoxynivalenol, nivalenol and zearalenone, and from popcorn which was naturally contaminated with deoxynivalenol. As shown in Table 4. the contents of these mycotoxins were essentially unaffected by cooking.

3. Behavior of mycotoxins during manufacturing processes

The possibility that mycotoxins may be removed in manufacturing processes was investigated. Edi-

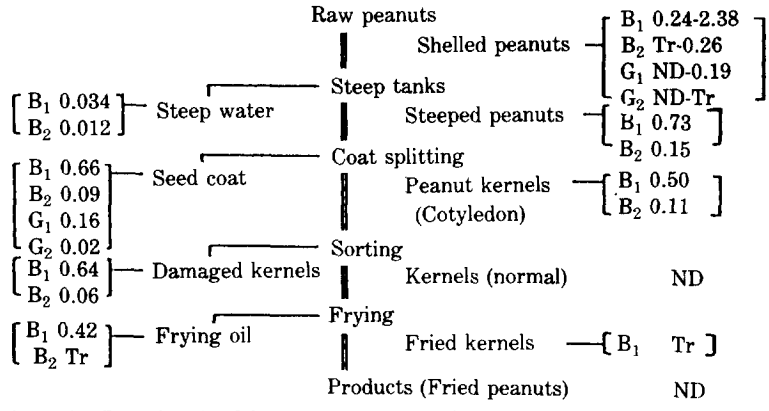

Fig. 3. Distribution of aflatoxins in fried-peanuts processing

ble oil at various stage of the manufacturing process was examined to determine the fate of mycotoxins (Table 5). The flow-sheet of the deacidification process is shown in Fig. 2. In the deacidification process, crude oil is mixed with alkali, stirred, centrifuged to remove foots and washed with warm water until the pH becomes neutral. The foots layer and washing were examined. When the oil and foots layer were separated, a major part of mycotoxins was found to have moved to the foots layer and, after washing with water, mycotoxins were found to have moved exclusively into the washing. Thus the manufacturing processes generally used in Japan leave no mycotoxins in the edible oil finally produced. Therefore, even if the crude oil is contaminated with aflatoxins and/or *Fusarium* mycotoxins, they can be completely removed during manufacture.

The fate of aflatoxins in the manufacturing process of fried peanuts made of aflatoxin-contaminated American raw peanuts which belong to the florunner species was examined. The results are shown in Fig. 3. In the raw peanuts, 0.24 to 2.38 ppb of aflatoxin B_1 was detected, while the content of aflatoxin after steeping was 0.73 ppb in kernels and 0.03 ppb in the water. After coat splitting, the content of aflatoxin B_1 was 0.50 ppb in kernels, 0.66 ppb in coats and 0.64 ppb in damaged kernels. After frying, the oil contained 0.42 ppb of aflatoxin B_1, but the fried kernels contained only a trace of aflatoxins and no aflatoxins were found in the end-products. From this investigation, it is clear that the content of aflatoxin is decreased in the steeping and coat splitting processes and also that the selection process is effective to decrease the amount of aflatoxin. To prevent secondary con-tamination of products, it is important to change the water frequently in the steeping process and to change the oil in the frying process.

I believe that we can prevent aflatoxin contamination in products if inferior kernels can be effectively excluded by human eye or by machine. Unfortunately, a part of the contaminated products may be missed in the selection processes in practice, and mycotoxins thus left in the raw materials may not be completely removed during the food manufacturing processes. In this case, decomposition and removal of mycotoxins by using food additives should be considered.

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