Natural occurrence of nivalenol in foods

Takumi YOSHIKAWA*

芳澤 宅實*：ニバレノールによる食品汚染

Isolation of nivalenol (NIV) from *Fusarium nivale* Fn-2B and its structural elucidation were reported in 1968 to 1970¹⁻³⁾. Thereafter deoxynivalenol (DON) was discovered, and its natural occurrence with NIV was firstly confirmed in 1972 to 1973^{4,5)}. Since these findings, more than a quarter century has passed, and thousands of papers related to these mycotoxins have been published. The two trichothecenes are produced mainly by *F. graminearum* Schwabe (teleomorph *Gibberella zeae* (Schw.) Petch.), one of the major causative phytopathogens of head blight disease in wheat and barley and rot disease in corn, and occur worldwide in these plant products intended for human and animal consumption⁶⁻⁸⁾.

Besides many published surveys for trichothecenes in foods, informations on the worldwide occurrence of NIV are limited, especially compared with DON, and how common it is and what significance it has for human and animal health are still not clear. Table 1, cited from IARC Monographs⁹⁾ with modifications, shows the worldwide occurrence of NIV in cereals. NIV has been reported extensively in Japanese and Korean grain samples, and concentrations up to 22.9 µg/kg have been found in Japanese cereals and 3.0 µg/kg in wheat from Korea. It has also been reported at relatively low levels in samples from Europe, southern Africa and Australia, whereas it is virtually unknown in grains in North and South America. Thus, there seems to be a

Table 1 Worldwide occurrence of nivalenol in cereals*.

Country or region	Product	Year	Positive/ total no.	Content (mg/kg)
Argentina	Cereals	1983	15/60	Mean, 0.03
Norway	Barley, wheat	1984	102/102	0.01-0.25
Poland	Wheat	1985	43/48	0.003-0.35
United Kingdom	Wheat, barley	1984	20/39	0.004-1.1
Transkei (S. Africa)	Maize	1985	44/96	0.01-15.2
China	Wheat	1989	7/30	0.01-0.02
	Wheat	NR	45/49	Mean, 0.04
Japan	Wheat	1984	7/18	0.05-0.44
	Barley	1970-80	73/89	0.06-22.9
Korea	Wheat, barley	1983-87	85/87	0.02-3.0
Taiwan	Wheat, barley	1984-85	14/26	0.005-0.98

* Cited from ref. 8.

* Department of Bioresource Science, Faculty of Agriculture, Kagawa University, Miki-cho (Kagawa 761-07)
香川大学農学部生物資源科学科 (〒761-07 香川県木田郡三木町)

Table 2 Occurrence of NIV and DON in Japanese wheat and barley grains (1989-1994).

	Total	Wheat	Barley
No. samples analyzed	245	151	94
No. positive	190	108	82
(%)	(78)	(72)	(87)
NIV positive	178	100	78
(%)	(73)	(66)	(83)
DON positive	153	82	71
(%)	(62)	(54)	(76)
NIV + DON	144	75	69
(% positive)	(76)	(69)	(84)
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NIV concentration,		136	218
mean (range), ng/g		(5-4,390)	(15-3,900)
DON concentration,		162	270
mean (range), ng/g		(5-1,620)	(5-3,780)

geographical difference in the NIV occurrence, whereas DON occurs worldwide in cereals of temperate regions⁸). Moreover, NIV has been found in corn from the Philippines even though at low levels⁹), indicating the probably wide distribution of NIV not only in temperates but also in tropics. Further efforts should be made to gain an appreciation of global aspect of the natural occurrence of NIV.

In Japan, DON and NIV are two major trichothecenes coincidentally occurring in domestic wheat and barley grains¹⁰). Recently, comprehensive studies on the geographic difference in the trichothecene occurrence and the distribution of toxigenic *G. zeae* (*F. graminearum*) in wheat and barley have been conducted in the author's laboratory¹¹⁻¹³). A total of 245 grain samples (151 wheat and 94 barley grains) were collected in 1984 to 1994 from 88 fields in 16 prefectures and analyzed for trichothecenes by GC-MS according to the previously reported procedure¹²). As summarized in Table 2, the trichothecenes were detected in 190 (78%) samples; NIV and DON were in 178 and 153 samples, respectively, and 144 samples were co-contaminated with both toxins. Analytical results indicated a regional difference in the DON and NIV contamination of Japanese wheat and barley. DON was the major trichothecene in the northern districts, Akita and Hokkaido (approximately 70% DON in concentration) and NIV in the central districts (over 80% NIV), whereas in the southern districts the DON levels was 30 to 50% in Shikoku district, and was slightly higher (55 to 65%) than the NIV level in Kyushu district. Several data¹⁴⁻¹⁷) previously obtained in Hokkaido, Kanto and Hokuriku districts were in line with the results obtained in this study. These results on the occurrence of NIV and DON were highly correlated to the geographic difference in the distribution of different chemotypes of *Fusarium* (*Gibberella*) species producing these trichothecenes in wheat and barley and also in fields of these crops in Japan.

Table 3 presented the natural co-occurrence of DON and NIV together with their acetylated derivatives in selected grain samples from different regions¹²). 3-ADON occurred together with

Table 3 Natural co-occurrence of trichothecenes (DON, NIV and their acetylated derivatives) and ZEA in Japanese wheat and barley grains.

Prefecture	Crop year	Cereal type	Sample code	Concentration of mycotoxin, ng/g				
				DON	3ADON/15ADON*	NIV	4-ANIV	ZEA
Hokkaido	1990	wheat	9067	323	tr	22	—	—
	1991	wheat	9141	1,510	10*	117	—	—
			9176	664	11/tr*	41	—	—
Akita	1990	barley	9055	6,120	437/522*	729	171	—
			9058	307	10	498	60	—
			9059	997	65/96*	254	tr	—
Tochigi	1990	wheat	9020	29	—	367	tr	—
Kyoto	1990	barley	9027	467	161	2,860	215	105
			9028	3,330	347	20,300	462	159
Kagawa	1990	barley	9012	653	112	878	—	—
		wheat	9013	368	41	645	—	—
Ehime	1989	barley	8904	448	85	226	57	—
			8915	418	93	116	tr	—
Fukuoka	1991	wheat	9134	11,700	920	4,390	—	505
		barley	9135	70,500	18,700	26,000	—	11,500
			9136	61,200	11,000	14,100	2,470	15,300
Oita	1991	wheat	9122	698	108	475	—	459
		barley	9124	2,460	210	1,170	—	661
			9125	752	170	668	87	—

* Concentration of 15-ADON. tr : below 10 ng/g.

DON in almost all prefectures, whereas 15-ADON was found mainly in the samples from northern prefectures, Hokkaido and Akita. These results may support the geographic difference in the distribution of different DON-chemotypes of *F. graminearum*. The presence of monoacetylated DON in cereal grains may be considered as an indication of the subclassified DON-producers involved in the field infection of cereals. On the other hand, the occurrence of 4-ANIV seems to be less frequent than that of 3-ADON, but it was found in most prefectures except Hokkaido and Kagawa. These results on the different profile on the occurrence of several trichothecenes are clearly correlated to the geographic difference in the distribution of different chemotypes of *F. graminearum* (3-ADON producer, 15-ADON producer and NIV producer) in Japan. In addition to the co-occurrence of DON and NIV, the presence of their acetylated toxins is of importance because they have been found in both feeds associated with field outbreaks of animal mycotoxicoses¹⁸⁾ and staple foods collected from high-risk areas of human chronic diseases¹⁹⁻²¹⁾. Furthermore, the estimated acute toxicities of the monoacetylated derivatives are greater than the parent toxins^{22,23)}. Therefore, more attention should be devoted to the natural occurrence of these acetylated trichothecenes together with DON and NIV and the combined effects of these toxins on human and animal health.

With regard to the occurrence of NIV in commercial foods, it was detected together with DON in commercial parched barley flour (Mugi-kogashi or hattaiko, in Japanese)²⁴⁾, which had been reported to be associated with a human intoxication. A similar situation in the contamination of trichothecenes in domestic foodstuffs can be pointed out from the data of surveys carried

out by other groups^{25,26}. However, informations on NIV in foods are limited compared with DON, which is frequently found in foodstuffs for human consumption in several countries^{7,27,28}. Since these informations are important to assess the human exposure and the possible risk to human health, much efforts should be made to clarify this point for NIV.

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