Distribution of Ethylene Dibromide Residues in Whole Corn and Milled Corn Products[1]

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ABSTRACT

Corn, which had been artificially fumigated with a commercial fumigant containing ethylene dibromide (EDB), was processed at approximately 0, 30, and 180 days after treatment by milling to recover the normal milled products and after treatment of the whole corn to prepare products such as hominy and masa flour. EDB residues were determined on the mill fractions and processed whole corn products, as well as on typical cooked and baked products from fractions recovered from the milling process. The amounts of residual EDB in the recovered fractions from both dry and wet milling were within the EPA allowance limits. EDB appeared to concentrate largely in the germ, with some increased values in the hull fraction from dry milling and in steep water from wet milling. When germ fractions were extracted to recover the oil, the EDB values for the crude oils were further reduced. Refining of the crude oil reduced EDB even further. Hominy, masa, and tortillas from the masa had little or no residual EDB.

Although ethylene dibromide (EDB) has been used as a fumigant for soils, citrus, and grain for many years, it is only in recent times that it has been recognized as a potential carcinogen in rats and mice. On February 3, 1984, the Environmental Protection Agency halted the use of EDB as a grain fumigant and set guidelines calling for no more than 900 parts per billion (ppb) in raw grain for human consumption, 150 ppb in consumed products requiring cooking or baking, and 30 ppb in consumer products that are "ready to eat." They also asked the Agricultural Research Service to conduct studies to determine the distribution and persistence of EDB in corn and processed corn products. It is the purpose of this paper to report results of this study, which involved processing raw corn by the different means commonly used to provide corn products for human consumption.

MATERIALS AND METHODS

Materials

Corn, obtained at harvest from a local farmer, was treated with a commercial liquid fumigant at the U.S. Grain Marketing Research Laboratory, Manhattan, KS. The fumigant formulation contained the following ingredients (% by weight): carbon tetrachloride, 80.9%; carbon disulfide, 16.0%; sulfur dioxide, 1.5%; ethylene dibromide, 1.2%; pentane, 0.4%.

Methods

Fumigation. Two-hundred pounds of corn was treated at 25° C by applying, as uniformly as possible, the liquid fumigant at a dosage level of 3 gallons per 1,000 bushels (40.5 ml per 90.9 kg [200 lbs]) to the grain in a stainless steel drum fitted with a sealed lid. Exposure time was five days. Following this, the sample was thoroughly blended on a drum roller and subdivided into four equal parts in a precision divider. Each sample was placed in a burlap bag, and two lots were shipped to the Northern Regional Research Center (NRRC), Peoria, IL; one for immediate processing (initial sample), and the second placed in storage for 30 days under controlled conditions at 23° C and 50% relative humidity (stored sample A). The third and fourth lots were stored at Manhattan under ambient conditions for 30 (stored sample B) and 180 days (stored sample C). The stored samples were processed in the same manner as the initial sample.

Processing. The treated corn samples were processed by dry and wet milling and by treating whole corn with alkali and lime to simulate preparation of hominy and masa, respectively.

The NRRC standard dry-milling procedure, which involves tempering, degerminating, roller milling, and separating fractions by sifting and aspirating, was used to recover such products as grits, meal, flour, germ, and feed fractions (Brekke et al 1972). Wet milling of treated corn for recovery of starch, germ, and feed fractions was done according to the NRRC bench-scale wet-milling procedure (Anderson 1963). None of the milling equipment was treated with the fumigant containing EDB. Our laboratory and pilot plant procedures are designed to simulate large-scale production of the particular fractions and products but should not be construed as duplicating commercial operations. Typical cooked and baked products were prepared from dry-milled grits and meal. Corn grits were prepared by cooking 50 g of grits in boiling water for 2 min with constant stirring, then simmering for 8 min on reduced heat with stirring. Corn bread was prepared by the procedure developed by Bookwalter et al (1971). Simulated corn flakes were prepared by autoclaving the first-break grits for 3 hr at 121° C (250° F), followed by drying cooked grits to 20% moisture. The temperature of these grits was adjusted to about 66° C (150° F) and flakes produced on rolls spaced at 0.15 mm (0.006 in.). Flakes were toasted in an oven for 3 min at 274° C (525° F). Crude oil was recovered from germ fractions by extraction of flaked germs with hexane. The oil was further refined using the conventional alkali treatment. No bleaching or deodorization was done.

Whole corn hominy was prepared by cooking the corn (900 g) for 40 min in a lye solution (1.2%) at 60° C to loosen hulls, removing hulls, washing for 1 hr, and soaking the grain for 2 hr. After the water was drained, the corn was placed in cans to within 1/2 in. from the top, covered with salt water to 1/4 in. from the top, and exhausted by heating at 93° C for 8 min. The cans were then sealed, processed at 121° C for 1 1/4 hr, and cooled.

To prepare whole corn masa, corn was cooked (1,360 g) for 1 hr in a near-boiling lime solution (0.5%) and then held overnight at 25° C. The grain was then washed four times and finally ground to a pasty dough. To make a tortilla, the masa dough (45 g) was blended with a small amount of water (10–12 ml), flattened to a thin cake, and baked for 3 min on each side at 205° C (Bressani et al 1958).

Analytical

Sample preparation. Twenty grams of sample was weighed accurately into a 1-L round-bottom flask, and 200 ml of distilled water added, followed by the addition of 8 ml of HPLC-grade *n*-hexane (already established to be EDB free by gas chromatography [GC]), without agitation. The sample was allowed to stand at least 16 hr. A 10-ml capacity Bidwell-Sterling distillation receiver was placed on the flask and a water-cooled

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condenser inserted on top of the receiver. The collection portion of the receiver was submerged in ice water during distillation. Hexane was distilled first and collected in the graduated portion of the receiver. After all the hexane had been distilled, about 0.5 ml of water was collected in the bottom of the receiver and the receiver removed from the flask. The exact volume (ml) of hexane collected was carefully noted. Most of the hexane layer was then transferred to a 10-ml stoppered volumetric flask using a pasteur pipette for subsequent analyses by GC.

Gas chromatography. EDB content of the hexane distillate was analyzed by GC (Rains and Holder 1981). A Spectrophysics model 7100 equipped with ^{63}Ni detector and a 1.83-m (6 ft) × 2 mm i.d. glass column packed with 3% OV-1 on Gas Chrom Q (100–120 mesh) was used and operated under the following conditions: column 60° C, injector 120° C, detector 260° C, nitrogen flow 20 ml/min; 8 pg EDB gave full-scale deflection with a 1 mV recorder. The GC was standardized with working standards of 50 and 500 ng EDB per milliliter hexane, which was prepared by serial dilution of a stock standard. The stock standard was made by weighing accurately 0.5 g Eastman EDB into a 100-ml volumetric flask and diluting to volume with Fisher HPLC-grade hexane (previously checked by GC for purity). The protocol specified that duplicate analyses be conducted on about 20% of the samples on a spot check basis. Based on the 20% of samples duplicated, the relative standard deviations were 9.2 ppb for whole corn and 32.2 for ground fractions.

RESULTS AND DISCUSSION

Corn Samples

The corn treated with fumigant at Manhattan had an initial EDB content of 20 ppb. The theoretical level of EDB after application of the fumigant to the corn was calculated to be approximately 8 ppm. Approximately 10 days after start of fumigation the first two treated samples received at NRRC in Peoria had EDB contents of 805 and 879 ppb, respectively, for the initial sample (processed without storage) and for the sample placed in controlled atmosphere storage (stored sample A). The third sample of treated corn (stored sample B), stored under ambient conditions for 30 days at Manhattan before shipment, had 433 ppb of EDB when received. Similarly, the 180-day treated sample (stored sample C), contained 16 ppb EDB on receipt from Manhattan.

TABLE I
Ethylene Dibromide (EDB) Residues in Dry-Milled Corn Fractions

	Sample (Storage Conditions)					
	Initial (None)	**Stored - A (23° C, 50% rh)**		**Stored - B (Ambient)**		**Stored - C (Ambient)**
Time lapse between fumigation and processing (days)	10	45	55	38	65	186
			EDB (ppb)[a]			
Whole corn	805,879	577	667	433	ND[b]	16
First-break grits	20	31	28	55	25	2
Second- and third-break grits	19	27	24	53	20	2
Low fat meal	15	44	20	39	13	<1
Low fat flour	6	16	15	28	11	<1
High fat meal	29	20	25	34	12	<1
High fat flour	14	13	22	26	9	<1
Bran meal	10	28	34	48	18	<1
Hulls	70	37	47	105	17	<1
Degerminator fines	8	11	11	19	8	<1
Germ	55	45	80	68	21	0
Crude oil extracted from germ	10	7	3	17	3[c]	ND
Alkali refined crude oil	10	4	ND	5	ND	ND

[a]Relative standard deviation: Whole corn 9.2, ground fractions 32.2.
[b]ND = not determined.
[c]Pressed from germ.

TABLE II
Ethylene Dibromide (EDB) Residues in Wet-Milled Corn Fractions

	Sample (Storage Conditions)					
	Inital (None)	**Stored - A (23° C, 50% rh)**		**Stored - B (Ambient)**		**Stored - C (Ambient)**
Time lapse between fumigation and processing (days)	24	59	45	80	82	199
			EDB (ppb)[a]			
Whole corn	805	667	433	ND[b]	ND[b]	16
Coarse fiber	2	<1	1	<1	<1	0
Fine fiber	4	<1	2	<1	0	0
Germ	277	52	273	24	37	1
Starch	1	<1	3	2	<1	0
Gluten	<1	<1	3	<1	<1	0
Process water	2	<1	8	<1	1	<1
Steep water	65	155	324	47	62	2
Crude oil from solvent-extracted germ	111	11	48	9[c]		ND

[a]Relative standard deviation: Whole corn 9.2; ground fractions 32.2.
[b]ND = Not determined.
[c]Germ was combined from 80- and 82-day tests and oil extracted from combined germ.

TABLE III
Ethylene Dibromide (EDB) Residues in Products Prepared from Whole Corn and Dry Milled Fractions

	Sample (Storage Conditions)			
	Initial (None)	Stored - A (23° C, 50% rh)	Stored - B (Ambient)	Stored - C (Ambient)
Time lapse between fumigation and processing (days)	12–21	60–70	60–70	193–196
	EDB (ppb)[a]			
Whole corn	805	667	433	16
Hominy	8	0	<1	0
Masa	0	30	35	0
Tortilla, from masa	0	3	2	0
First-break grits	20	28	55	2
Corn flakes from grits	0	0	1	0
Second- and third-break grits	19	24	53	2
Cooked products from grits	2	2	5	0
Low fat meal	15	20	39	<1
Corn bread	2	<1	<1	0

[a] Relative standard deviation: Whole corn 9.2, ground fractions 32.2.

All corn samples were shipped without any special treatment with respect to containers, etc. This permitted the EDB to disperse as it might do when corn is moved from farm to elevator to plant. All samples were processed in a like manner as soon as possible after they were received or removed from storage. There were some time lags in processing, and these are noted in the results.

Dry Milling

When the treated and stored samples were dry milled, EDB was found in varying amounts in all of the milled fractions (Table I). Note that the EDB content of whole corn from stored sample A had fallen from 879 to 577 ppb after 45 days and to 667 ppb after 55 days. Stored sample B, the 30-day sample stored under ambient conditions, had an EDB level of 433 ppb at 38 days. After 180 days of ambient storage, EDB content of whole corn was 16 ppb. Higher levels of EDB were present in the germ and hull fractions from corns stored at 30 days or less, but this was not observed in the same fractions from corn stored for 6 months. When oil was recovered from the germ by extraction with hexane, the EDB contents of the crude oils were very low. Alkali refining of selected crude oils resulted in even less EDB in the oil.

Wet Milling

Products of wet milling of treated corn had very low levels of EDB except for the germ and steep water (Table II). EDB contents varied between samples of both germ and steep water. We have no explanation, other than possible sampling inadequacies, for the variability in the data obtained for the 45-day test of stored sample B. High values for EDB in germ and steep water are not in line with values obtained in repeat tests. All products from the extended storage corn samples showed extremely low levels of EDB. EDB levels in crude oils extracted from germ were quite low, except for initial sample and stored sample B. Alkali refining of crude oil from the corn stored 80 and 82 days reduced the EDB level from 9 to 5 ppb.

Products Prepared from Whole Corn and Dry Milled Fractions

Whole corn and three dry-milled fractions were further processed by cooking or baking to prepare ready-to-eat products. EDB contents of prepared products are listed in Table III. Hominy prepared from treated corns contained very little EDB, as did tortillas prepared from masa processed from EDB-treated corn. There was essentially no EDB in simulated corn flakes prepared from first-break grits recovered by dry milling. Levels of EDB in other cooked products from dry-milled fractions, i.e., second- and third-break grits and meal, were also very low. The application of chemical and/or heat treatments reduced all EDB levels to very low values, much below the EPA-acceptable levels.

CONCLUSIONS

Processing of corn samples treated with EDB reduced levels in most of the processed fractions to much below those established as acceptable by the EPA. EDB was concentrated in germ and hull fractions from dry milling, and the germ and steep water from wet milling, in the initial and 30-day storage samples but not in the treated corn sample stored for six months. It is apparent that EDB disperses from the corn itself while in storage over extended periods. Further processing of selected fractions by chemical and/or heat treatment to prepare ready-to-eat products reduced EDB levels in finished products to well below 30 ppb.

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