

N-Nitrosodimethylamine in Brazilian, U.S. Domestic, and U.S. Imported Beers

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N-Nitrosodimethylamine (NDMA) was determined in beers manufactured in Brazil and in the United States as well as in beers imported into the United States from 20 countries. Among the 166 beers analyzed, 54% contained NDMA at levels ranging from 0.05 to 0.55 $\mu\text{g}/\text{kg}$, with an overall mean level of 0.07 $\mu\text{g}/\text{kg}$. NDMA levels in Brazilian beers were investigated for the first time. The average daily intake of NDMA per person from consumption of beer was estimated to be 0.002 and 0.01 μg in Brazil and in the United States, respectively. The NDMA levels reported in this study are similar to those given in other recent reports from a number of countries. They indicate that malting and brewing industries have reduced NDMA levels in beers to a few percent of what the levels were 15 years ago.

Keywords: *N*-Nitrosodimethylamine; NDMA; beer

INTRODUCTION

Following initial reports of *N*-nitrosodimethylamine (NDMA) in beers approximately 15 years ago, investigators from a number of countries reported mean NDMA values of 1–6 $\mu\text{g}/\text{kg}$ (Spiegelhalder *et al.*, 1979; Fazio *et al.*, 1980; Kann *et al.*, 1980; Kawabata *et al.*, 1980; Scanlan *et al.*, 1980). It was found that NDMA was formed during the direct-fired drying of malt, and preventive strategies focused on the modification of that process (O'Brien *et al.*, 1980; McWeeny, 1983). Although introduction of sulfur dioxide into the drying air of direct-fired kilns reduced nitrosamine formation, conversion of kilns to the indirect-fired type was found to be the most effective approach (O'Brien *et al.*, 1980; Hardwick *et al.*, 1981). Consequently, most maltsters converted their kilns from the direct- to the indirect-fired type to reduce nitrosamine formation.

A survey of beers from the United States and Canada in 1990 by Scanlan *et al.* indicated that NDMA levels ranged from none detected to 0.58 $\mu\text{g}/\text{kg}$, approximately 1–5% of what the levels were in 1980. Other countries also reported reduced NDMA levels in beer, among them Germany, France, Japan, and Italy (Yamamoto *et al.*, 1984; Gavinelli *et al.*, 1988; Frommberger, 1989; Mavelle *et al.*, 1991). Data are very scarce, however, on current NDMA levels in beers from some countries such as Brazil. Accurate information is important for investigators attempting to elucidate the role of various dietary carcinogens such as NDMA in the etiology of cancer.

The purpose of this investigation was to provide current information on NDMA levels in beers produced and purchased in Brazil as well as in both domestic and imported beers available in the U.S. market.

MATERIALS AND METHODS

Samples. Canned or bottled beers from Brazil were obtained at retail stores in Belo Horizonte, Minas Gerais,

Brazil. Samples of beers produced in the United States and imported into the United States were purchased at retail outlets in Corvallis, OR. We readily recognize that the beer samples in this study are not a representative sampling of either beer production or sales throughout the United States or Brazil. Rather, the beers sampled were those available in several commercial outlets in both countries between May 1994 and March 1995.

Analysis. Samples were analyzed for volatile nitrosamines using a Celite column procedure described by Hotchkiss *et al.* (1981) and Marinelli (1981). The sample size was increased from 25.0 to 50.0 g, which allowed a detection level of 0.05 $\mu\text{g}/\text{kg}$. Detection was by gas chromatography–thermal energy analysis (Marinelli, 1981). NDMA was corrected for recovery by use of *N*-nitrosodipropylamine as an internal standard (Scanlan *et al.*, 1982).

Safety. Nitrosamines are potent carcinogens in many animal species and must be handled with appropriate safety precautions.

RESULTS AND DISCUSSION

Among the 166 beers analyzed for volatile nitrosamines, 89 (54%) contained NDMA at levels ranging from 0.05 (detection limit) to 0.55 $\mu\text{g}/\text{kg}$. The mean concentration of NDMA in all samples, calculated by using zero for samples in which NDMA was not detected, was 0.07 $\mu\text{g}/\text{kg}$. There was variability among NDMA levels as the coefficient of variation (CV) was high (143%). Frommberger (1989) also observed variance on NDMA results for German beers and suggested that it was a reflection of the varying levels of NDMA in different malt batches.

Brazilian Beers. Among Brazilian samples analyzed (Table 1), 43% contained NDMA at levels ranging from the lower detection limit to 0.32 $\mu\text{g}/\text{kg}$. The overall mean value was 0.06 $\mu\text{g}/\text{kg}$ (CV = 133%). Nitrosamines in Brazilian beers were investigated for the first time. NDMA levels detected are similar to those detected in beers produced in countries where efforts have been made to reduce NDMA formation.

No NDMA was detected in nonalcohol beers (light beers). Significantly higher NDMA levels (Duncan test, $p \leq 0.05$) were observed in bock beers compared to other types. Higher NDMA levels are to be expected since

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Table 1. N-Nitrosodimethylamine Levels in Brazilian Beers

type of beer	no. of samples	no. of samples with NDMA levels of					NDMA ^a
		<0.05 μg/kg	0.05–0.09 μg/kg	0.10–0.19 μg/kg	0.20–0.29 μg/kg	0.30–0.32 μg/kg	
lager	34	23	8	3	0	0	0.02 ± 0.04 ^b
light	5	5	0	0	0	0	0.00 ± 0.00 ^c
bock	14	2	0	8	2	2	0.16 ± 0.10 ^a
ale	7	4	3	0	0	0	0.02 ± 0.03 ^b
total	60	34	11	11	2	2	

^a Mean ± standard deviation. Zero was used for ND (none detected) NDMA levels < 0.05 μg/kg. Values with the same superscript do not differ significantly (Duncan test, $p \leq 0.05$).

Table 2. N-Nitrosodimethylamine Levels in U.S. Beers

type of beer	no. of samples	no. of samples with NDMA levels of					NDMA ^a
		<0.05 μg/kg	0.05–0.09 μg/kg	0.10–0.19 μg/kg	0.20–0.29 μg/kg	0.30–0.50 μg/kg	
lager	9	5	2	2	0	0	0.04 ± 0.05
light	6	4	0	2	0	0	0.02 ± 0.04
ale	12	5	1	4	1	1	0.10 ± 0.14
clear malt	1	0	1	0	0	0	0.08
total	28	14	4	8	1	1	

^a Mean ± standard deviation. Zero was used for ND (none detected) NDMA levels < 0.05 μg/kg.

Table 3. N-Nitrosodimethylamine Levels in Beers Imported into the United States

type of beer	no. of samples	no. of samples with NDMA levels of					NDMA ^a
		<0.05 μg/kg	0.05–0.09 μg/kg	0.10–0.19 μg/kg	0.20–0.29 μg/kg	0.30–0.55 μg/kg	
lager	49	17	11	16	3	2	0.09 ± 0.11
ale	29	12	5	7	2	3	0.10 ± 0.12
total	78	29	16	23	5	5	0.09 ± 0.11

^a Mean ± standard deviation. Zero was used for ND (none detected) NDMA levels < 0.05 μg/kg.

bock beer is manufactured with 50% more malt as compared to the other types of beer depicted in Table 1.

U.S. Domestic Beers. The levels of NDMA in the different types of U.S. beers are indicated in Table 2. NDMA was detected in 50% of the beers at levels ranging from 0.05 to 0.50 μg/kg, with mean value of 0.07 μg/kg (CV = 143%). These results are similar to those reported by Scanlan *et al.* (1990); therefore, no change has been observed in NDMA levels in U.S. beers within the past 5 years. No significant difference was observed among the different types of beer (analysis of variance, $p = 0.198$).

Beers Imported into the United States. The NDMA levels in imported beers purchased in the United States are shown in Table 3. NDMA was detected in 63% of the samples analyzed with levels up to 0.55 μg/kg. The mean NDMA value was 0.09 μg/kg. There was variability among NDMA mean values from different countries (CV = 99%) as well as among samples from the same country (CV ≤ 200%).

A comparison of results obtained for some countries included in this study (Table 4) with data reported in the literature showed that similar NDMA levels have been observed for beers from Germany and Canada (Frommberger, 1989; Scanlan *et al.*, 1990). Levels of NDMA detected in samples from Italy, France, England, Japan, Holland, New Zealand, and China, however, are lower than those observed in previous investigations (Maki *et al.*, 1980; Spiegelhalder *et al.*, 1980; Stephany and Schuller, 1980; Klein *et al.*, 1982; Yin *et al.*, 1982; Weston, 1983; Gavinelli *et al.*, 1988; Mavelle *et al.*, 1991). Therefore, it seems likely that volatile nitros-

Table 4. N-Nitrosodimethylamine Levels of Beers Imported from Different Countries into the United States

country	no. of samples	NDMA levels (μg/kg)	
		range	mean ^a
Australia	3	ND	0
Canada	6	ND–0.21	0.10 ± 0.07
China	4	0.05–0.26	0.16 ± 0.12
Denmark	3	ND	0
England	10	0.05–0.39	0.21 ± 0.12
France	3	0.06–0.10	0.08 ± 0.02
Germany	4	0.08–0.15	0.11 ± 0.03
Holland	4	0.08–0.13	0.10 ± 0.02
Ireland	3	ND	0
Italy	3	ND	0
Jamaica	4	ND–0.10	0.07 ± 0.05
Japan	5	0.09–0.55	0.21 ± 0.20
Korea	2	0.07–0.11	0.09 ± 0.03
Mexico	7	ND–0.18	0.04 ± 0.08
New Zealand	1	ND	0
Norway	5	ND–0.10	0.02 ± 0.04
Scotland	2	ND–0.43	0.22 ± 0.30
Singapore	5	ND–0.12	0.08 ± 0.05
Thailand	2	ND–0.05	0.03 ± 0.04
Vietnam	2	ND	0
total	78	ND–0.55	0.09 ± 0.11

^a Mean ± standard deviation. Zero was used for ND (none detected) NDMA levels < 0.05 μg/kg.

amines in beers from most of these countries have been reduced through efforts to decrease NDMA levels in malt.

Daily Intake. According to Reid (1996), the average daily consumption of beer in the United States per person is 0.22 L, and the U.S. beer market share by category is represented by 52% lager, 33.6% light, 8.8% ale, and 5.6% imported beer. On the basis of these

percentages, the average daily intake of NDMA in the United States is estimated to be 0.01 μg per person.

The average daily beer consumption in Brazil is 0.11 L (Sant'anna, 1992). Unfortunately, market share by category is not available for Brazilian beer. Therefore, the average per capita daily intake of NDMA, assuming that all beer consumed in Brazil is lager, is estimated to be 0.002 μg per person.

Caution is urged in making inferences from daily intake data. These data assume that all members of the population consume the same amount of beer on a daily basis. Undoubtedly, the population contains subgroups that consume larger than average amounts of beer and others that consume no beer.

The data from this study demonstrate that NDMA in beers commercially available in Brazil and in the United States contain only a few percent of NDMA levels which commonly occurred in beers 15 years ago. The diligent efforts responsible for the reduction in NDMA levels need to be continued since NDMA and many other *N*-nitroso compounds have been shown to be potent carcinogens in a variety of animals. Additional research will be required to elucidate the health effects of low levels of nitrosamines in the human diet.

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Received for review July 15, 1996. Revised manuscript received December 9, 1996. Accepted December 13, 1996. © Technical Paper 11 010 from the Oregon Agricultural Experiment Station.

JF960523J

© Abstract published in *Advance ACS Abstracts*, February 1, 1997.