

A Research Note N-Nitrosothiazolidine in Cured Meat Products

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ABSTRACT

Since N-nitrosothiazolidine (NTHZ) formation in cure-pumped bacon has recently been linked to the heating-smoking step in bacon processing, a survey of other smoked cured meat products was conducted. Nitrosothiazolidine was detected in 23 of 70 products, other than cure-pumped bacon, in concentrations ranging from 1.7–19.0 ppb. No correlation of NTHZ values with either residual sodium nitrite or with product type was found.

INTRODUCTION

WE RECENTLY REPORTED that uncooked bacon contained higher amounts of N-nitrosothiazolidine (NTHZ) than either fried bacon or its drippings, and that NTHZ formation in bacon was not affected by cooking method (Pensabene and Fiddler, 1983). N-Nitrosothiazolidine differs from the other nitrosamines normally found in bacon, N-nitrosopyrrolidine and N-nitrosodimethylamine, in that the latter are absent in raw bacon and are detected only after cooking. The analysis of pork bellies for NTHZ during the various processing stages showed that NTHZ was formed during the heating-smoking step (Pensabene and Fiddler, 1983). We also found that the presence of NTHZ was not limited to bacon, since up to 34 ppb NTHZ was detected and confirmed in smoked pork butts (Pensabene and Fiddler, 1983). Accordingly, we undertook a survey of other smoked meat products to determine the prevalence of NTHZ. A second survey was conducted to gather information on the extent of NTHZ contamination in cure-pumped bacon. The results of these surveys are reported herein.

MATERIALS & METHODS

Materials

Bacon samples were obtained from local processors and retail stores or from the Food Safety and Inspection Service (FSIS). Other cured meat products were purchased from local retail stores. NTHZ and N-nitrosothiomorpholine (NTMOR) were synthesized from their corresponding amines and sodium nitrite, and purified by fractional vacuum distillation as described previously (Pensabene et al., 1972). All other reagents needed for the analysis of NTHZ in cured meat products have been reported elsewhere (Pensabene and Fiddler, 1982).

N-nitrosothiazolidine analysis

Uncooked cured meat samples were ground and mixed thoroughly prior to analysis. The complete details of the procedure have been described elsewhere (Pensabene and Fiddler, 1982). All NTHZ values reported herein have been corrected for the recovery of NTMOR internal standard in each individual sample. "N.D." denotes "none detected" or <1 ppb, the minimum level of reliable measurement based on the gas chromatography-Thermal Energy Analyzer system response. Since NTHZ concentrations in general were less than 10 ppb, the samples were not subjected to

mass spectral confirmation. Mass spectral (Kimoto et al., 1982) and $\mu\nu$ photolytic (Doerr and Fiddler, 1977) confirmatory procedures have been carried-out on other samples so that there was a high degree of certainty that NTHZ was also present in the survey samples. Despite this, the NTHZ values reported in this paper should be considered "apparent," since the nitrosamine was not identified with absolute certainty. Note: NTHZ and NTMOR are potential carcinogens; exercise care in handling these materials.

Sodium nitrite analysis

Residual sodium nitrite (NaNO_2) content was determined in 10g of raw comminuted sample by the modified Griess-Saltzman procedure (Fiddler, 1977).

Statistical analysis

Statistical analyses were carried-out according to the methods of Snedecor and Cochran (1979).

RESULTS & DISCUSSION

N-NITROSOTHIAZOLIDINE has been detected in bacon analyzed by both the mineral oil distillation method (Gray et al., 1982) and by the dual column chromatographic procedure (Kimoto et al., 1982; Pensabene and Fiddler, 1982). Although the dual column method, as originally published, was found to give excellent results for NTHZ in fried bacon, its applicability to uncooked meat products of varying fat to lean ratios was unknown. Therefore, uncooked products were first subjected to a ruggedness test designed along recommendations of AOAC in which combinations of varying grinding, packing, solvent elution, and flow rate techniques were used to assess their effect on measured NTHZ. Results indicated that at the 10 ppb spiking level the only significant difference was caused by packing of the Celite column more tightly than recommended. This step was also noted as a potential source of error in the ERRC dry column method for NPYR in fried bacon (Pensabene et al., 1982). Next, a within-laboratory repeatability of the method was determined after triplicate analysis of six different products having varying fat to lean ratios and pH. Analysis of variance of the results showed that repeatability of NTHZ determination was 0.33 ppb (0.26 ppb corrected with recovery of internal standard). This was better than the 1.35 repeatability reported for NTHZ in fried bacon (Pensabene and Fiddler, 1982). The repeatability of recovery of the NTMOR internal standard was 5.16%. Finally, to determine if erroneous results could be obtained because of artifactual nitrosamine formation, particularly in those fermented products having a relatively low pH, 10 ppm morpholine was added to four different products prior to analysis. No nitrosomorpholine was detected.

The results of our survey of cured meat products for NTHZ are shown in Table 1. From 1.7–19.0 ppb NTHZ was detected in 23 of 70 samples, other than cure-pumped bacon. Since we had previously indicated that NTHZ resulted from the smoking step during bacon processing, we expected a product like Lebanon bologna to have high NTHZ values. This product has a pH <5, which may favor nitrosamine formation, and is subjected to a lengthy smoking step to help impart its characteristic flavor. However, NTHZ was detected in only 3 of 6 samples analyzed

Table 1—N-nitrosothiazolidine in cured meat products

| Sample type | Residual ^a NaNO ₂ (ppm) | Nitrosothiazolidine, ppb ^b | | |
|----------------------|--|---------------------------------------|-------------------|----------------------|
| | | No. posi- tive/total | Range | Average ^c |
| Lebanon bologna | 8 | 3/6 | 1.7–4.4 | 3.1 |
| Cure-pumped ham | 13 | 2/5 | 2.9, 10.8 | 6.9 |
| Dry-cured ham | 3 | 0/3 | N.D. ^d | N.D. |
| Poultry franks. ham | 46 | 0/6 | N.D. | N.D. |
| Pepperoni | 5 | 4/9 | 2.0–3.6 | 2.7 |
| Salami | 6 | 0/4 | N.D. | N.D. |
| Canadian bacon | 16 | 3/5 | 2.0–6.5 | 4.1 |
| Hot dogs | 13 | 1/6 | 3.7 | 3.7 |
| Beef, pork strips | 10 | 5/7 | 3.3–9.5 | 5.6 |
| Cure-pumped bacon | 19 | 30/42 | 1.6–31.9 | 10.0 |
| Dry-cured bacon | 36 | 3/3 | 5.3–19.0 | 9.9 |
| Other cured products | 22 | 2/16 | 1.7, 1.8 | 1.8 |

^a Average values

^b Corrected for recovery of NTMOR internal std.

^c Average for positive samples

^d N.D. none detected (< ppb)

in concentrations ranging from 1.7–4.4 ppb (average 3.1 ppb). These results were comparable to those positive samples found with other cured products that normally have higher pH and are only lightly smoked, such as, pepperoni (average 2.7 ppb), Canadian bacon (average 4.1 ppb), cured-pumped ham (average 6.9 ppb), or in a single positive hot dog sample (3.7 ppb).

We detected NTHZ in 6 of 8 samples of beef or pork breakfast strips in concentrations ranging from 3.3–9.5 ppb (average 5.6 ppb). These formed products however, are not usually smoked directly, but instead incorporate a liquid smoke flavoring into the formulation. These survey results were similar to those we found in bacon processed only with liquid smoke, where NTHZ was detected in both nitrite-containing and nitrite-free bacon (Pensabene and Fiddler, 1983). Since we have previously shown that commercial liquid smoke concentrates contain varying amounts of NTHZ (Pensabene and Fiddler, 1983), detection of NTHZ in cured meat products processed with liquid smoke was not unexpected.

Finally, we conducted a survey of cure-pumped bacon for NTHZ, whose overall results are shown in Table 1. Since the initial finding of NTHZ was in bacon from a small producer (Pensabene and Fiddler, 1983), we analyzed the product from the same and other small processors and found NTHZ values ranging from 1.6–31.9 ppb, with an average of 11.8 ppb. However, samples from the major bacon producers gave NTHZ values ranging from N.D. to

11.5 ppb, with an average of 5.0 ppb. These results probably reflect the general content of NTHZ in bacon at the retail level compared to the higher average found in bacon from small producers. Analysis of all survey data indicated no correlation between NTHZ and residual NaNO₂ in either bacon or other cured meat products existed. Our findings do show, however, that bacon is unusual in that it has specific nitrosamines associated with both processing and cooking treatments.

While we have previously shown that NTHZ formation in bacon is associated with the heating-smoking step during processing (Pensabene and Fiddler, 1983), our survey data indicates no apparent correlation between product type and NTHZ formation. This results probably from both the variation in processing techniques and from the type of smoke (liquid or wood) used by the different processors. Results strongly suggest that NTHZ is formed as a result of smoking, since it is present in a variety of uncooked cured meat products that are smoked by conventional means or subjected to only a liquid smoke treatment.

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