Effects of Cooking on Ethylenebisdithiocarbamate Degradation to Ethylene Thiourea

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The recent report of Blazquez (1973) and prior work in our laboratory on EBDC-ETU methodology suggest the possibility that cooking of foods containing ethylenebisdithiocarbamate (EBDC) residues would cause breakdown to ethylene thiourea (ETU). Blazquez reported that heating extracts containing maneb, zineb, or Dithane M-45 caused degradation largely to ethylene thiourea. Since EBDC fungicides have legal tolerances ranging from 0.1 to 25.0 ppm on fruits and vegetables, and up to 65 ppm on other crops, the amount of ETU produced in cooking could be quite significant.

The purpose of this study was to confirm Blazquez's findings and to show whether ETU is formed from EBDC residues during cooking of vegetables. For this investigation three crops were fortified at 10.0 ppm with EBDC compounds both before and after cooking and were analyzed by the modified method of Onley and Yip[1] (1971) using GLC with flame photometric detection (S-mode). Additionally the same EBDC compounds were boiled in water without a crop and ETU determined.

Materials and Methods

Spinach, carrots, and potatoes were chopped, composited, and 100 g samples were held frozen. Samples were analyzed in pairs by first cooking one sample, cooling, and then fortifying at 10 ppm (1 mg) with EBDC. The second sample was fortified with 10 ppm EBDC just prior to cooking. The EBDC compounds used were maneb (manganous ethylene bisdithiocarbamate); Dithane M-45 and Manzate 200 (coordination products of zinc ion and maneb); and Polyram (a mixture of 5.2 parts by weight of ammoniates of [ethylenebis (dithiocarbamate)]zinc and ethylenebis [dithiocarbamic acid] bimolecular and trimolecular cyclic anhydrosulfides and disulfides). All fortification standards were weighed on a Cahn Gram Electrobalance(R).

Procedure

A 100 g thawed sample was placed in a 600 ml beaker with 50 ml water and the total weight was recorded. The beaker was covered with a watch glass and boiled for 15 minutes on a hot plate. The cooked sample was cooled, the cover removed and

[1]Procedure currently being studied for AOAC collaboration.

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beaker re-weighed. Water was added to exactly compensate for loss during cooking. The sample weight to volume ratio was thus maintained for subsequent aliquot calculations. The sample was quantitatively transferred to a blender with 200 ml methanol and extracted by the modified method of Onley and Yip.

The study of the effects of boiling EBDC compounds in water without a crop present was done in a similar manner except, after boiling, the cooled solution was diluted to a definite volume. Standards of one milligram amounts were boiled in 60 ml water for 15 minutes. The sample was cooled and diluted to 200 ml with methanol. A 100 ml aliquot was analyzed as before.

Results and Discussion

The effects of cooking a vegetable containing fortified residues of an EBDC fungicide may be seen in Table 1. Samples were analyzed in pairs fortified before and after cooking so that any difference in ETU content could be directly attributed to a cooking effect. The amount of ETU formed (see explanatory footnote in Table I) by cooking ranged from 11.2% for maneb in potatoes to 26.5% for Polyram in spinach. All EBDC compounds produced significant amounts of ETU.

One pair of spinach samples was also fortified at 10.0 ppm with ETU before and after cooking to see if ETU was stable in a boiling food sample. Recoveries were 87 and 85 per cent respectively thus indicating cooking does not diminish ETU *per se*.

The four EBDC compounds were also boiled in water 15 minutes to determine the ETU magnitude when no crop was present. The results as per cent ETU formed (see explanatory footnote 2 in Table 1) are as follows: maneb, 25.5%; Polyram, 27.8%; Manzate 200, 17.0%; and Dithane M-45, 24.3%. These results compared to Table 1 indicate a similar magnitude of ETU production while boiling without a crop.

In conclusion, the results corroborate the findings of Blazquez and show normal home cooking of vegetables containing residues of maneb, Dithane M-45, Manzate 200, or Polyram at or near tolerance level will result in production of ETU and subsequent human consumption. It should be recognized that the tolerances for EBDC compounds represent levels based on CS_2 equivalents determined by the regulatory method and do not necessarily represent levels of EBDC *per se*. Certain metabolites of EBDC other than ETU are also known to be measured by the CS_2 evolution method. However, significant residues of parent EBDC would be expected on many agricultural commodities. The findings therefore show the EBDC content of a food should be of concern in addition to ETU residues on the raw agricultural commodities for any realistic evaluation of ETU exposure.

TABLE I

ETU produced from cooking vegetables fortified with 10.0 ppm EBDC compound.

Crop	EBDC	PPM ETU found[1] Fortified after cooking	PPM ETU found[1] Fortified before cooking	Per cent ETU[2] formed by cooking
Spinach	Maneb	0.16	1.82	16.6
	Dithane M-45	0.15	2.17	20.2
	Manzate 200	0.11	2.42	23.1
	Polyram	0.07	2.72	26.5
Potato	Polyram	0.08	1.43	13.5
	Maneb	0.08	1.20	11.2
Carrot	Polyram	0.09	1.42	13.3
	Maneb	0.08	1.42	13.4

[1]Results are corrected for blanks as follows: spinach, 0.003 ppm; potato, 0.008 ppm; and carrot, 0.002 ppm ETU.

[2]Because neither the EBDC molecular structures nor the reactions producing ETU are fully known, the % ETU formed as shown in table 1 is not based on stoichiometric equivalents but on a weight/weight basis of ETU/EBDC.

References

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