Effect of Boiling on the Formation of Ethylenethiourea in Zineb-Treated Foods

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Introduction

Ethylenethiourea (ETU) has been reported as a decomposition product of a group of fungicides known as ethylenebisdithiocarbamates (1,2). Since ETU has been found goiterogenic in rats (3) and tumorigenic in mice (4), concern has arisen regarding its possible occurrence in the food supply. Although the mechanism of decomposition of ethylenebisdithiocarbamates to ETU is unknown at present, a study of various parameters governing its formation has revealed that boiling of foods containing the parent compound can result in increased levels of ETU.

Materials and Methods

Zinc ethylenebisdithiocarbamate employed in all experiments was a commercial preparation of zineb containing 82.9% active ingredient. For experiments with carrots and spinach, the vegetable was sprayed with a suspension (1.0 mg/ml) of the material in distilled water. After permitting the vegetables to dry until free of surface moisture by standing in the laboratory, samples (5.0 g) were taken for boiling.

Boiling was carried out by placing the samples and water (15 ml) into 125 ml flasks equipped with reflux condensers. The samples were then refluxed for 15 min, after which time the solids were removed by filtration on Whatman No. 1 filter paper. The solids were extracted by homogenizing with ethanol (50 ml) and filtered through Whatman No. 1 filter paper under slight negative pressure. Ethanol extracts were diluted to 100 ml with distilled water and aliquots (20 ml) taken for ETU analysis.

The cooking water obtained by filtration from the solids was made to 50 ml with distilled water, then diluted to 100 ml with ethanol and aliquots (20 ml) taken for ETU analysis.

Uncooked samples (5.0 g) were extracted and analysed for ETU as described for cooked solids.

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Apple or tomato samples (5.0 g) were fortified with zineb (50 ppm) and treated in a manner similar to carrot and spinach, but were boiled in 5.0 ml of water prior to extraction with ethanol. Combined solids and water from cooked and uncooked samples were homogenized with ethanol (50 ml), filtered, and the filtrate made to 100 ml with distilled water. Aliquots (20 ml) were analysed for ETU.

For the time course experiment, flasks containing carrot (5.0 g), zineb (250 µg), and water (15 ml) were refluxed for various time intervals. At the end of the reflux interval the solids were removed from the water immediately by filtration and analysed for ETU after extraction as previously described.

ETU was quantitated by gas-liquid chromatography of the trifluoroacetylated S-benzyl derivative as previously described for apples (5). Recoveries from vegetables and fruit fortified with ETU were similar to those obtained from apple.

Results and Discussion

The effect of boiling carrot or spinach treated with zineb on the content of ETU is shown in Table I. The ETU found in uncooked samples represents that originally present in the zineb plus that presumably formed on aeration which accompanies suspension of the solid and application by spraying (6).

TABLE I

ETU formed by boiling zineb treated carrot or spinach[a]

		Carrot	Spinach
Uncooked		0.073±0.004	0.182±0.009
Cooked	solids	0.248±0.002	0.880±0.120
	filtrate	0.838±0.039	2.70 ±0.040

a - values (in ppm) are the means of duplicate determinations

It is evident from the data that cooking promotes decomposition of the parent compound to ETU. Much of the formed ETU is removed in the cooking water, but compared to the uncooked samples, increased amounts remain in the solids.

Similarly, as shown in Table II, apple or tomato originally containing 50 ppm of zineb can accumulate several times the level of ETU when cooked as compared to uncooked.

TABLE II

Effect of boiling on the ETU content of zineb treated apple or tomato[a]

	Apple	Tomato
Uncooked	0.033±0.001	0.067±0.001
Cooked	0.300±0.032	0.311±0.025

a - values (in ppm) are the means of duplicate determinations.

From the data presented in Figure 1, it is seen that the amount of ETU formed increases in approximately a linear manner with cooking time over an interval of at least 1 hour.

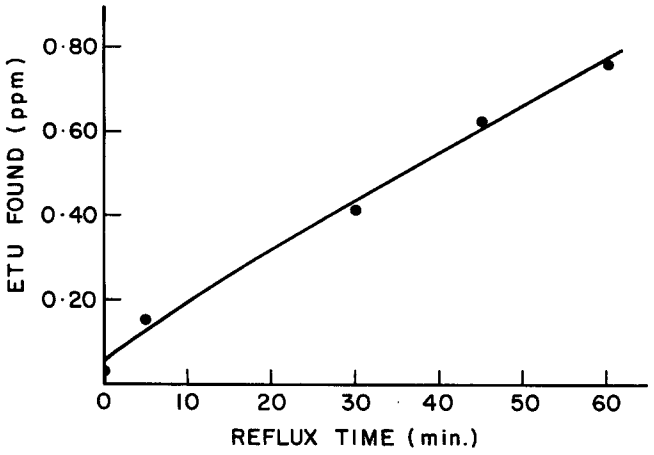

Figure 1. Effect of refluxing time on the amount of ETU formed in carrot treated with 50 ppm of zineb

It has been shown that ETU does not accumulate on some crops following the field application of ethylenebisdithiocarbamate (7). However, from the above results it is evident that residues of the parent compound on foods represent a potential source of ETU when subjected to cooking.

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