

Degradation of Carboxin (Vitavax) in Water and Soil

Wei-Tsung Chin, Gracie M. Stone, and Allen E. Smith

Carboxin (5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide) is oxidized to its sulfoxide (5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide 4-oxide) in water and soil, but hydrolysis has never been detected in either case. The oxidation of carboxin in water is retarded by high pH. At pH's of 2 and 4, traces of a further oxidation product, the

sulfone (5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide 4,4-dioxide) were detected after several weeks. The oxidation of carboxin in soil to its sulfoxide is complete two weeks after application under greenhouse conditions, but no sulfone was detected.

Carboxin (5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide) is the first synthetic fungicide for systemic control of barley and wheat loose smut. Its actions on some sensitive and resistant fungi have been studied by von Schmeling (1966), Edgington and coworkers (1966, 1967a,b), Hardison (1966), Mathre (1968), and Rowell (1967). In this investigation only its degradation in water and soil is presented.

EXPERIMENTAL

Thin-Layer Chromatography (tlc). Carboxin and six possible degradation products (Figure 1) were prepared for thin-layer chromatography. Standard solutions (0.1 g per 100 ml of CHCl_3) were spotted on Eastman chromatogram sheets (6061, Silica gel, without fluorescent indicator) and developed in 3.5-l. jars. Five solvent systems were studied. The R_f values were evaluated by spraying a 0.05% Fluorescein methanol solution and observed under UV light. Results are summarized in Table I. In this work, Chromatosprayer (Warner-Chilcott Laboratories, Instruments Division, 201 Tabor Road, Morris Plains, N.J.) and Chromato-VUE Viewer (Ultra Violet Products, Inc., San Gabriel, Calif.) were used. The shortwave length (2537 Å) gave much better identification than the longer wavelength for this investigation.

Degradation of Carboxin in Water. Buffer solutions of pH 2, 4, 6, 8, and 10 were prepared according to Clark-Lubs' formula 9 (Handbook of Chemistry and Physics, 1961) and adjusted with a pH meter. Saturated solutions of carboxin were prepared in the buffer solution. After filtration, the carboxin saturated buffer solutions were stored in 1-l. jars at room temperature without sterilization. About 30 ml of the above solutions were extracted with 10 ml of CHCl_3 at different time intervals. The CHCl_3 layer was separated, dried over Na_2SO_4 , and checked by tlc. Each aqueous solution was subjected to a second extraction as follows. The acidic solutions (pH 2, 4, and 6) were made basic with 0.2N NaOH and the basic solutions (pH 8 and 10) were made acidic with 0.2N HCl before the second CHCl_3 extraction. These extracts were also checked by tlc.

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Degradation of Carboxin in Soil. Nine hundred grams of dry sand was mixed with 850 mg of formulated carboxin (75% wettable powder) and made up to 31.5 kg with potting soil. This well-mixed soil (equivalent to 20.0 ppm of chemical in the soil) was put in 21 6-in. pots and set in the greenhouse. At each time interval, two pots were used for planting Pinto bean seeds, and a third one was used for soil extraction with benzene and tlc analysis. Rust spores were sprayed on the seedlings 10 days after planting. In another experiment, 25 g of organic soil with 5 ml water were mixed well in 250 ml Erlenmeyer flasks. These flasks were stoppered with cotton

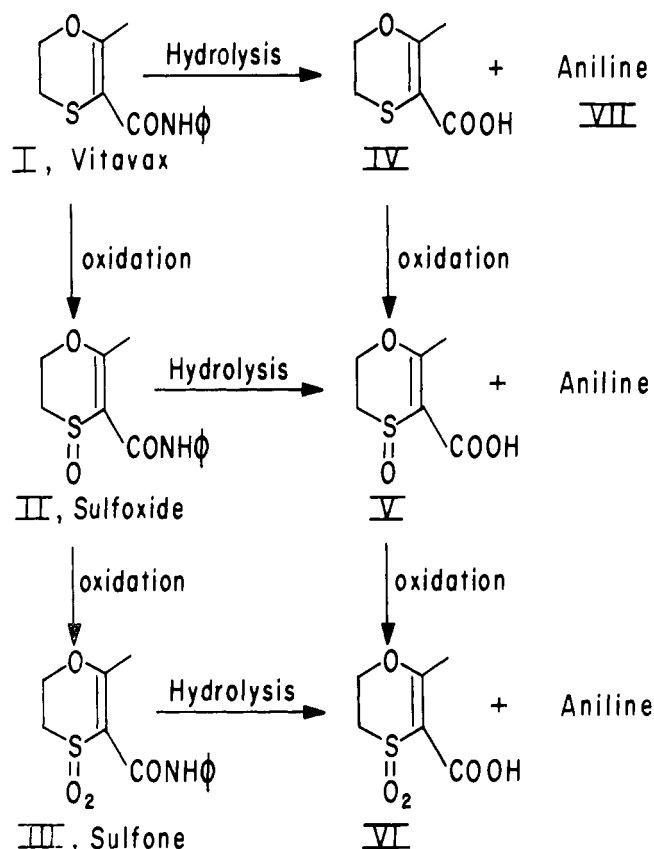


Figure 1. Carboxin (Vitavax) and its possible degradation products

Table I. R_f Values of Tlc of Carboxin and Related Compounds

Compounds	Methanol	Methanol-acetone (2:8 v/v)	Chloroform	Benzene	Acetone
I					
Carboxin					
5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide	0.6	0.9	0.8	0.1	0.9
II					
The sulfoxide					
5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide 4-oxide	0.6	0.7	0.1	0.0	0.6
III					
The sulfone					
5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide 4,4-dioxide	0.6	0.9	0.4	0.0	0.9
IV					
5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxylic acid	0.8	0.9	0.1	0.1	0.7
V					
5,6-dihydro-2-methyl-1,4-oxathiin 4-oxide-3-carboxylic acid	0.7	0.2	0.0	0.0	0.0
VI					
5,6-dihydro-2-methyl-1,4-oxathiin 4,4-dioxide-3-carboxylic acid	0.7	0.4	0.0	0.0	0.0
VII					
Aniline	0.6	0.9	0.7	0.2	0.9

Table II. pH Influence on Carboxin in Water

Time Elapsed	pH	Observation ^a
1st day	2-10	Only I in all solutions
2nd day	2-10	No change
1st week	2-10	No change
2nd week	2	Possible change
	4-10	No change
3rd week	2	Mainly I, trace II was detected
	4-10	No change
4th week	2	Mainly I, both II and III were detected in trace amounts
	4-10	No change
10th week	2	I almost disappeared, mainly II, trace III
	4-10	No change
27th week	2	No I, mainly II, III slightly increased
	4	Mainly I, little II, trace III
	6-8	Mainly I, trace II, no III
	10	No change

^a Compounds I, II and III are specified in Table II.

Table III. Degradation of Carboxin in Soil under Greenhouse Conditions

Time of Planting (Days)	% Control			% Carboxin Left by tlc Estimates	% II Produced by tlc Estimates
	Rep. I	Rep. II	Ave.		
0	99	99	99	100	0
3	95	95	95	80	15
7	30	50	40	50	50
10	10	20	15	5	90
14	0	0	0	0	100
21	0	0	0	0	100
28	0	0	0	0	100

and autoclaved at 120° C for 30 min. After taking out of the autoclave, the flasks were sealed immediately in plastic bags which were sterilized with excess absolute alcohol and cooled to room temperature. An aliquot of 750 µg of carboxin in 250 µl of ethyl alcohol was injected into the flask and mixed well with the soil. Duplicates, checks, and non-sterilized samples were also prepared.

RESULTS AND DISCUSSION

The degradation of carboxin in water was studied for 27 weeks, as summarized in Table II. This experiment indicated that the main change of carboxin in water was oxidation to its sulfoxide. The oxidation rate was found to be retarded by higher pH. At pH's of 2 and 4, further but slower oxidation to the sulfone was detected. Hydrolysis was not detected under any of these conditions. Results of the degradation of carboxin in soil are summarized in Table III. The rapid decrease in activity of carboxin was due to its quick oxidation to the less active sulfoxide in the soil. In this experiment, neither hydrolysis nor further oxidation to sulfone were detected by tlc. In a separate experiment, the sterilized soil was extracted 7 days after fortification and standing at room temperature. By tlc detection, it was found that about 20% of carboxin was oxidized to the sulfoxide. This would indicate that microbial activity is not an essential factor for this conversion. This idea is supported by the fact that oxidation of carboxin to sulfoxide was observed in dilute solutions in several organic solvents.

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