Table V. Degradation of Carbofuran by a Bacterium Isolated from Flooded Alluvial Soil

Incubation, days	μg of carbofuran recovered/20 mL of incubation medium[a]	
	Uninoculated	Inoculated
0	320	320
10	295	250
20	278	150
40	223	trace

[a] Mean of two replicates. Carbofuran added to 20 mL of medium, 360 μg.

IV). During a 40-day incubation period, about 62 to 75% carbofuran was decomposed in nonautoclaved soils as compared with only 18 to 27% loss in autoclaved soils. The slow rate of degradation until 20 days followed by more rapid loss between 20 and 40 days in nonautoclaved soils is indicative of microbial involvement in carbofuran degradation.

More direct evidence for microbial role in carbofuran degradation in flooded soil was provided when a bacterium, isolated from a flooded soil by enrichment culture technique, degraded carbofuran under static conditions (Table V). At the end of 40 days after inoculation with the bacterium, carbofuran residues in 20 mL of incubation medium decreased from 320 μg to negligible levels; in uninoculated media, during the same period, no appreciable degradation of the insecticide occurred. Carbofuran was supplied to the bacterium as sole source of carbon and nitrogen.

In a recent study (Getzin, 1973), liberation of $^{14}CO_2$ from ring labeled [^{14}C]carbofuran in a nonflooded soil system indicated microbial degradation since microorganisms are implicated in ring cleavage of organic molecules. Similarly, in nonflooded soils, more rapid mineralization of ^{14}C-carbonyl-labeled carbofuran to $^{14}CO_2$ occurred in nonsterile conditions (Williams et al., 1976). Among the microorganisms isolated from carbofuran-amended soils, actinomycetes were particularly active in converting carbofuran to CO_2. The data on the increased persistence of carbofuran in sterile soils (Table IV) and its degradation by a bacterium isolated from flooded soils (Table V) lead to the conclusion that, as in nonflooded soils, microorganisms participate in the rapid loss of carbofuran in flooded soils.

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Fate of Carbofuran and Its Metabolites on Strawberries in the Environment

Thomas E. Archer,* James D. Stokes, and Royce S. Bringhurst

Three varieties of strawberries, Day-Neutral, Tioga, and Tufts, were sprayed once with carbofuran (Furadan 4-Flowable) at the rates of (4 and 8 oz of active ingredient)/acre during fruit maturation. The berries and leaves were sampled, and the residues of carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) and its metabolites were determined. The combined residues on the berries never exceeded the tolerance level of 0.5 ppm nor did the carbamate fraction exceed 0.2 ppm 6 days after application. In some instances, the amounts of the metabolites 3,7-diol and 3-oxocarbofuran increased until 7 days after application but then decreased in amounts to harvest. Reduction of residues probably resulted from dilution by plant growth and volatilization from the plant tissue surfaces.

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) has been registered for use as an insecticide or nematicide on various crops, alfalfa, field corn, peanuts, rice, sweet peppers, sugarcane, bananas, tobacco (Furadan, 1974), and more recently to control root weevils, *Brachyrhinus*, *Nemocestes*, *Perifelinus*, and *Sciopithes* spp. on strawberries. The registered formulation, Furadan 4-Flowable (64 oz of active ingredient (a.i.)/gal), is applied at 2.6 to 5.1 fluid oz per 1000 linear feet of row once in a 10- to 12-in. band over the rows, spaced 42 in. apart, after last harvest but before Oct 1. The established tolerance for carbofuran and its carbamic and phenolic metabolites

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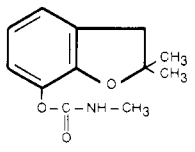
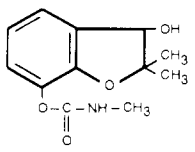


2, 3-Dihydro-2, 2-dimethyl-7-benzofuranyl-N-methyl carbamate (Carbofuran)



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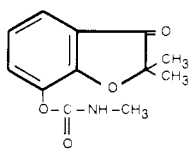
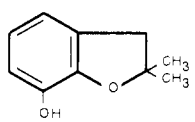
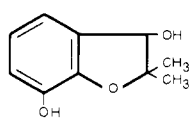


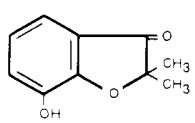
2,3-Dihydro-2, 2-dimethyl-3-oxo-7-benzofuranyl-N-methyl carbamate (3-Oxocarbofuran)



2, 3-Dihydro-2, 2-dimethyl-7-benzofuranol (7-Phenol)



2, 3-Dihydro-2, 2-dimethyl-3, 7-benzofurandiol (3,7-Diol)



2, 3-Dihydro-2, 2-dimethyl-3-oxo-7-benzofuranol (3-Keto-7-Phenol)

Figure 1. Molecular structures of carbofuran and related compounds.

(Figure 1) in or on raw strawberries is 0.5 ppm, of which not more than 0.2 ppm may be carbamates (Fed. Regist., 1975).

Previous literature reports (Williams and Cram, 1971) have stated that carbofuran applied to strawberries at up to (32 oz of a.i.)/acre as a pre-bloom spray gave residues below 0.3 ppm. In actual practice they stated that applications need be made at only (8 to 16 oz of a.i.)/acre for adequate control of root weevil adults in strawberries. Williams and Brown (1973) described a gas chromatographic method using a Coulson conductivity detector in the nitrogen mode for the determination of carbofuran and 3-hydroxycarbofuran residues in small fruits including strawberries with recoveries averaging greater than 86% over the range of 0.2 to 5.0 ppm.

The present investigation was undertaken to determine the fate of carbofuran and its metabolites on three varieties of strawberries (Everbearers, Tiogas, and Tufts) when the carbofuran was applied as a spray at the green stage 14 days before harvest. These residues were also studied on the leaves of the strawberry plants.

MATERIALS AND METHODS

Apparatus. The following equipment were used: A Hudson Climax 6335 Simplex Sprayer, 8.5-L capacity, equipped with a Hudson 149-403 spray control valve and a nozzle extension; a 0.95-cm inner diameter flexible neoprene, with Teflon-lined rubber tubing for chemical inertness, attached between the pressure tank and the Roto-Spray Nozzle; an Ohaus moisture balance Model No. 6010.

Reagents. All solvents were reagent grade freshly distilled before use.

Silica gel, grade 923, 100–200 mesh, specification MIL-D-3716, was obtained from the Davison Chemical Division, W.R. Grace and Co., Baltimore, Md. and was used as received from the manufacturer without further activation.

Pentafluorobenzyl bromide (PFB) and trifluoroacetic anhydride (TFA) reagents were obtained from the Aldrich Chemical Co., Milwaukee, Wisc. Stock pentafluorobenzyl bromide solution was prepared by dissolving 1 g of pentafluorobenzyl bromide in 50 mL of acetone.

Procedure. *Carbofuran Applications and Sampling of the Experimental Strawberry Plots.* Duplicate plots (42 × 112 in.) of three strawberry varieties, Day-Neutral, Tioga, and Tufts, were sprayed with a Hudson hand-sprayer at a rate of (4 and 8 oz of active ingredient of carbofuran)/acre. The formulation used for spray application was Furadan 4-Flowable (active ingredient, 43.8%; inert ingredients, 56.2%). The active ingredients by analyses in Furadan 4-Flowable were 99.4% carbofuran, 0.2% hydroxycarbofuran, and 0.4% 7-phenol. The other carbofuran related products, if present at all, were only in trace amounts. The strawberry plants and berries were sprayed in Aug 1975 in Davis, Calif. An unsprayed control plot was maintained for each variety.

Two sets of experimental plots were treated. One set of plots was treated for sampling from the day of application of the pesticide through 14 days of sampling. The strawberries were green at the date of spray application and were mature ripe at the harvest period 14 days after spraying. A second set of plots was sprayed as described above when the strawberries were at a stage of maturity 7 days before harvest. These plots were sampled at the time of pesticide application and for a total of 7 days after spray application. Berries and leaves were randomly sampled for the 14-day experiment and berries only were sampled for the 7-day experiments. Each experimental sampling of the Day-Neutral strawberries variety was weighed and counted, and moisture determinations were made on the berries. The average weight per berry at day 1 was 0.9 g, day 7 was 3.2 g, and day 14 was 6.0 g, and the average moisture content was 89.8%. The samples from the field were extracted immediately and the extracts were stored in the cold for analyses. An (8 oz of a.i.)/acre spray application to the strawberries was not done in the 7-day experiment since this type of information could be extrapolated from the other experiments. The average moisture content of the leaves in the experiments was 76.4%.

Extraction of the Strawberries and Leaves. The extraction procedure was based on the method of Cassil et al. (1969) with the following modifications. Ten grams of berries or leaves was blended for 15 s in a Waring blender in 50 mL of 0.25 N hydrochloric acid. The mixture was transferred quantitatively to a 500-mL, round-bottomed flask with an additional 50 mL of acid and was refluxed 1 h. This extraction procedure does not apparently alter the compounds under investigation as determined by recovery studies. Ten milliliters of the aqueous acid plant extract was added to a 125-mL separatory funnel with a Teflon stopcock, and the residues were partitioned into 25 mL of dichloromethane three times. After the dichloromethane extraction, the aqueous phase was extracted with 25 mL of anhydrous diethyl ether followed by 25 mL of a mixture of 50% ethyl acetate and 50% hexane. The

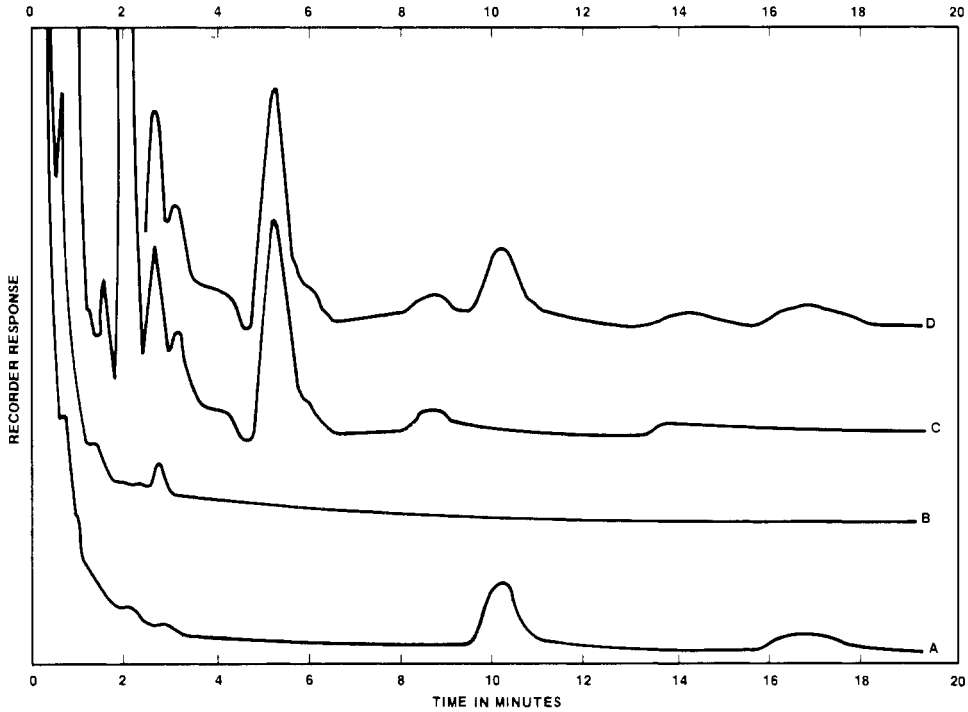


Figure 2. GLC traces of PFB derivatives of reagent blank, control strawberries, standard compounds, and fortified controls (fraction 1: (curve A) 0.1 ng of 7-phenol; 0.1 ng of 3-keto-7-phenol; retention time (R_t), 10 and 17 min; (curve B) reagent blank; (curve C) 10 mg of strawberry (Everbearer) control; (curve D) 10 mg of control plus 0.01 ppm 7-phenol and 3-keto-7-phenol.

extraction solvents were pooled and filtered through anhydrous sodium sulfate. The aqueous phase was discarded. The filter paper and sodium sulfate were washed with 25 mL of a mixture of 50% ethyl acetate and 50% hexane which was combined with the other solvents. The solvents were evaporated in vacuo on a rotary vacuum evaporator at 50 to 60 °C to 0.5 mL, 25 mL of hexane was added, and the sample was evaporated just to dryness to remove all traces of dichloromethane and ethyl acetate. The presence of a keeper was not necessary during solvent concentration for the prevention of compound losses during evaporation. Five milliliters of hexane was added to the concentrated sample in preparation for the column chromatography cleanup.

Sample Extract Cleanup by Column Chromatography on Silica Gel. The sample cleanup was based on the procedure of Knaak et al. (1970) with the following modifications. To a glass column 10 × 220 mm with a 125-mL reservoir at the top was added a glass wool plug, 3 g of silica gel used as received from the manufacturer without further activation, and 0.5 g of anhydrous sodium sulfate. The column was wet with 25 mL of hexane, and the solvent was discarded. Five milliliters of hexane containing the crop extract (1 g or less of strawberries or leaves) was transferred to the top of the column. The extract container was washed with 50 mL of hexane which was transferred to the column, and the eluate was collected in a receiver and discarded. The receiver was changed, and 100 mL of a mixture of 90% hexane and 10% ethyl acetate containing the 7-phenol and 3-keto-7-phenol in the eluate was collected. The receiver was changed, and 50 mL of a mixture of 80% hexane and 20% ethyl acetate followed by 50 mL of a mixture of 70% hexane and 30% ethyl acetate containing the carbofuran, 3-oxocarbofuran, and the 3,7-diol in the eluate was collected. The receiver was changed, and 50 mL of a mixture of 60% hexane and 40% ethyl acetate followed by 50 mL of a mixture of 50% hexane and 50% ethyl acetate which contained the hydroxycarbofuran in the eluate was finally collected. Thus three major fractions were collected from the silica gel cleanup column. Fraction 1 contained the 7-phenol and 3-keto-7-phenol. Fraction 2 contained the carbofuran, 3-oxocarbofuran, and the 3,7-diol. Fraction 3 contained the hydroxycarbofuran.

Each of the eluate fractions was evaporated in vacuo on a rotary evaporator at 50 to 60 °C to 0.5 mL and 25 mL of isooctane was added and evaporated to remove all traces of ethyl acetate. The concentrated extracts were transferred quantitatively to centrifuge tubes with hexane and evaporated just to dryness under a stream of nitrogen gas. The samples that were to be derivatized with pentafluorobenzyl ether (PFB) had 50 mg of potassium carbonate added to the tube before final evaporation.

Gas Chromatographic Separation of the Compounds. The gas chromatograph was a Varian-Aerograph Model 1200 equipped with an electron-capture detector. The column was Pyrex glass, $^1/_8$ in. × 8 ft, coiled, and packed with Gas Chrom Q 60–80 mesh coated with 5% SE-30 gum rubber plus 5% Dow 710 silicone fluid. The operating temperatures were: for the column, 140 °C; injector, 215 °C; and detector, 200 °C. The nitrogen carrier gas flow rate was 30 mL/min and the electrometer range was 1 with the attenuator set at 8×. All the compounds were separated by GLC as the TFA derivatives with the exception of the 7-phenol and the 3-keto-7-phenol which were the PFB derivatives. The GLC retention times (in minutes) were: for carbofuran, 7.0; hydroxycarbofuran, 9.0; 3-oxocarbofuran, 10.0; 7-phenol, 10.0; 3,7-diol, 1.0; and 3-keto-7-phenol, 17.0. The retention times are as the TFA derivatives with the exceptions of the 7-phenol and 3-keto-7-phenol which were the PFB derivatives. Quantitation of sample peak areas relative to standards was by measurement of peak areas with a polar planimeter. All results were based on fresh weights with a method sensitivity of 0.05 ppm for carbofuran and 0.01 ppm for the other compounds. All residue interpretations of carbofuran and related products on the strawberries and leaves were relative to day zero. Figure 2 shows the PFB derivatives

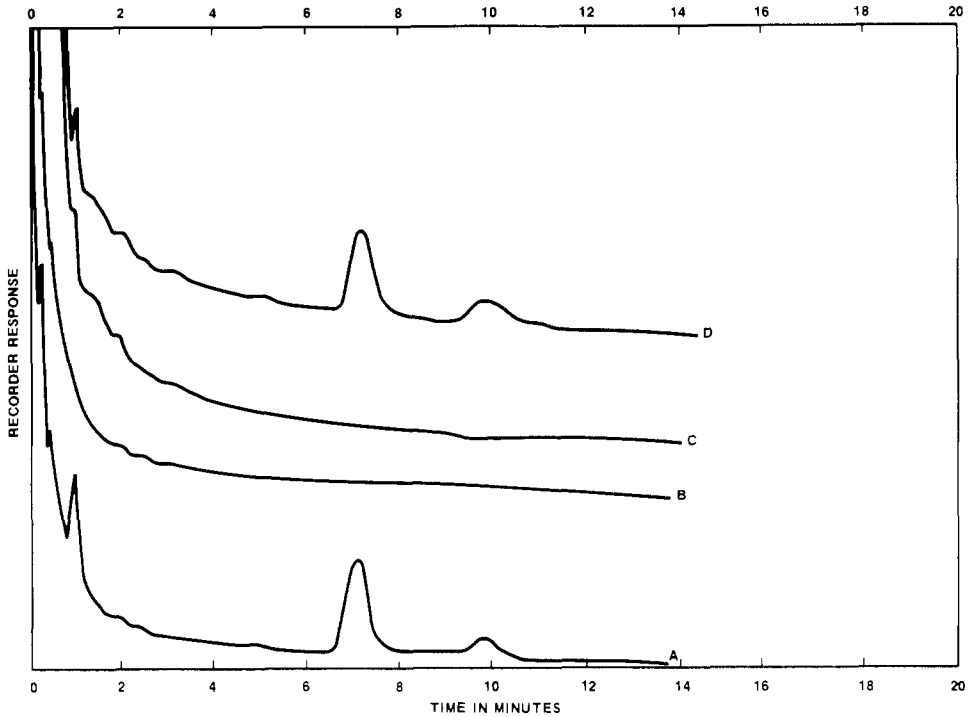


Figure 3. GLC traces of TFA derivatives of reagent blank, control strawberries, standard compounds, and fortified controls (fraction 2): (curve A) 0.1 ng of 3,7-diol; 0.5 ng of carbofuran; 0.1 ng of 3-oxocarbofuran; R_t 1, 7, and 10 min; (curve B) reagent blank; (curve C) 10 mg of strawberry (Everbearer) control; (curve D) 10 mg of control plus 0.05 ppm carbofuran and 0.01 ppm 3,7-diol and 3-oxocarbofuran.

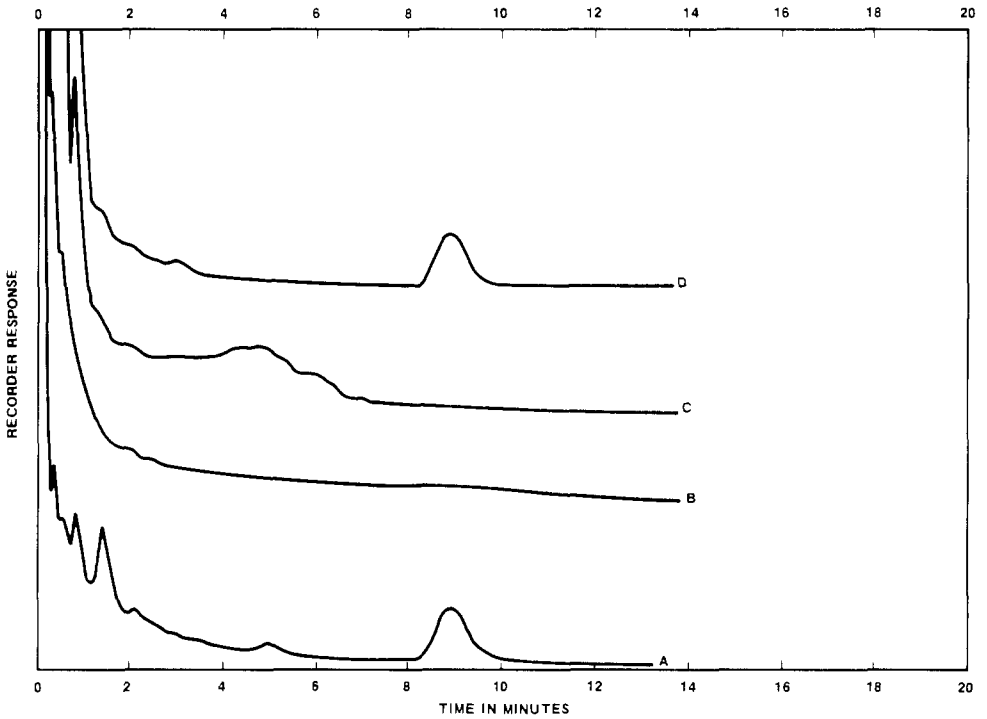


Figure 4. GLC traces of TFA derivatives of reagent blank, control strawberries, standard compounds, and fortified controls (fraction 3): (curve A) 0.1 ng of hydroxycarbofuran; R_t 9 min; (curve B) reagent blank; (curve C) 10 mg of strawberry (Everbearer) control; (curve D) 10 mg of control plus 0.01 ppm hydroxycarbofuran.

of control strawberries, reagent blank, 7-phenol, 3-keto-7-phenol, and fortified controls at the 0.01 ppm level. Figure 3 shows the TFA derivatives of control strawberries, reagent blank, carbofuran, 3,7-diol, the 3-keto-carbofuran, and fortified controls at 0.05 ppm for carbofuran and 0.01 ppm for the other compounds. Figure 4 shows the TFA derivatives of the control strawberries, the reagent blank, hydroxycarbofuran, and fortified control at the 0.01 ppm level. Figure 2 represents the eluate fraction 1, Figure 3 represents the eluate fraction 2, and Figure 4 represents the eluate fraction 3 from the silica gel cleanup column after derivatizations.

Sample Derivatization as the Pentafluorobenzyl Ether (PFB) or Trifluoroacetate (TFA). The pentafluorobenzyl ether derivatization was based on the procedure of Johnson (1973) with the following modifications. Not more than

Table I. Residues[a] (ppm) of Carbofuran and Its Metabolites on Day-Neutral Strawberries Applied at Two Rates 7 and 14 Days before Maturation

	Rate of Application									
	(4 oz of a.i.)/acre					(8 oz of a.i.)/acre				
	Carbamates				Phenol	Carbamates				Phenol
Day	Carbofuran	3-OH	3-Oxo	Total	3,7-Diol	Carbofuran	3-OH	3-Oxo	Total	3,7-Diol
					Seven Days					
1	0.420	<0.01	0.103	0.523	0.073	0.740	0.012	0.014	0.766	0.094
2	0.152	<0.01	0.033	0.185	0.018	0.338	<0.010	<0.010	0.338	0.033
3	0.110	<0.01	0.015	0.125	0.010	0.183	<0.010	<0.010	0.183	0.010
4	0.073	<0.01	<0.010	0.073	0.010	0.124	<0.010	0.044	0.168	0.011
5	0.050	<0.01	<0.010	0.060	0.012	0.075	<0.010	0.054	0.129	0.011
6	<0.050	<0.01	<0.010	<0.050	0.029	0.076	<0.010	0.025	0.101	<0.010
7	<0.050	<0.01	<0.010	<0.050	0.025	0.056	<0.010	<0.010	0.056	<0.010
					Fourteen Days					
1	0.337	0.011	0.021	0.369	0.029	0.808	0.027	0.024	0.859	0.063
2	0.265	0.011	0.030	0.306	0.029	0.741	0.020	0.021	0.782	0.032
3	0.217	0.015	0.040	0.272	0.025	0.554	0.016	0.031	0.601	0.022
4	0.160	0.018	0.053	0.231	0.025	0.408	0.021	0.036	0.465	0.015
5	0.109	0.023	0.058	0.190	0.033	0.297	0.020	0.031	0.348	<0.010
6	0.087	0.016	0.058	0.161	0.050	0.156	0.015	0.023	0.194	<0.010
7	0.050	0.021	0.068	0.139	0.056	0.084	0.018	0.016	0.118	<0.010
8	<0.050	0.017	0.061	0.078	0.040	0.077	0.014	0.011	0.102	<0.010
10	<0.050	0.024	0.058	0.082	0.023	0.052	<0.010	<0.010	0.052	<0.010
12	<0.050	0.029	0.048	0.077	0.013	<0.050	<0.010	<0.010	<0.050	<0.010
14	<0.050	0.017	<0.010	<0.050	<0.010	<0.050	<0.010	<0.010	<0.050	<0.010

[a] Method sensitivity for carbofuran, 0.05 ppm; for metabolites, 0.01 ppm.

Table II. Residues[a] (ppm) of Carbofuran and Its Metabolites on Leaves of Day-Neutral Strawberries after Application at Two Rates 14 Days before Maturation

					Phenols			
	Carbamates						3-Keto-7	
Day	Carbofuran	3-OH	3-Oxo	Total	7-Phenol	3,7-Diol	phenol	Total
				(4 oz of a.i.)/acre				
1	11.1	0.448	0.013	11.6	0.027	0.536	<0.010	0.563
2	8.77	0.280	0.082	9.13	0.039	1.09	<0.010	1.13
3	6.72	0.146	0.094	6.96	0.028	1.49	<0.010	1.52
4	5.31	0.067	0.068	5.44	0.015	1.74	<0.010	1.76
5	4.14	0.035	0.041	4.22	0.013	1.83	<0.010	1.84
10	2.78	0.077	0.025	2.88	0.016	1.79	<0.010	1.81
12	1.56	0.144	0.017	1.72	0.037	1.36	<0.010	1.40
14	0.344	0.187	0.010	0.531	0.068	0.459	<0.010	0.527
				(8 oz of a.i.)/acre				
1	17.2	0.260	0.018	17.5	0.563	5.05	<0.010	5.61
2	12.0	0.105	0.028	12.1	0.761	7.54	<0.010	8.30
3	7.38	0.044	0.036	7.46	0.624	8.06	<0.010	8.18
4	5.04	0.068	0.028	5.14	0.472	8.27	0.010	8.75
5	4.10	0.119	<0.010	4.22	0.363	8.95	0.014	9.33
10	2.71	0.127	<0.010	2.84	0.236	6.08	<0.010	6.32
12	1.66	0.103	<0.010	1.76	0.116	5.23	<0.010	5.35
14	0.347	0.061	<0.010	0.408	0.014	4.50	<0.010	4.51

[a] Method sensitivity for carbofuran, 0.05 ppm; for metabolites, 0.01 ppm.

50 μg of insecticide (1-g sample extract) were dissolved in hexane in a 15-mL centrifuge tube. Approximately 50 mg of potassium carbonate was added to the tube, the solvent was evaporated just to dryness, and 1 mL of PFB solution was added, and the mixture was heated for 15 min at 50 °C in a water bath. One and one-half milliliters of isooctane was added and evaporated to 0.5 mL. The sample was diluted with the addition of 1 mL of hexane. The excess pentafluorobenzyl bromide reagent was eliminated as follows. The tip of a 10 × 220 mm glass chromatographic column was plugged with glass wool, and 1 g of silica gel used as received from the manufacturer without further activation was added. The column packing was wet with 5 mL of hexane. A 25-mL test tube was placed under the column, and the 1.5 mL of derivatized sample was transferred to the column. The sample tube was rinsed with 1 mL of hexane, and the rinse was transferred to the column, and the column was washed with 8 mL of 5% benzene and 95% hexane. A clean 25-mL test tube was placed under the column, and the column was eluted with 6 mL of 25% benzene in hexane, followed by 8 mL 75% benzene in hexane. A final 5 mL of 100% benzene was added and the sample was adjusted to an appropriate volume and analyzed by GLC.

The trifluoroacetate derivatization of the carbofuran and related compounds was based on the method of Shafik et al. (1972) as described by Sherma and Shafik (1975) and analyzed by GLC. The 7-phenol was analyzed as the PFB

derivative since derivatization with TFA in our laboratory did not result in reproducible results with the desired analytical sensitivity and recovery. The 3-keto-7-phenol was also analyzed as the PFB derivative since it was in the same silica gel column eluate as the 7-phenol. Recoveries of carbofuran and related compounds through the entire procedure of extraction, cleanup, and final analysis by GLC ranged from 78 to 91 with an average of 83% at fortification levels of 0.1 and 1.0 ppm.

RESULTS AND DISCUSSION

The molecular structures of carbofuran and related compounds under discussion in the present experiments are shown in Figure 1.

The levels of carbofuran and its metabolites on Day-Neutral (Everbearer) strawberries when sprayed at the rates of (4 and 8 oz of a.i.)/acre 7 and 14 days before harvest are shown in Table I. If we assume that a tolerance level for carbofuran, hydroxycarbofuran, and its phenolic metabolites (7-phenol, 3,7-diol, and 3-keto-7-phenol) could be 0.5 ppm total residue with not more than 0.2 ppm as the total carbamate residue, then the carbamate tolerance level in the strawberries in ppm was achieved by day 5 or 6 in this experiment. The phenolic residues at no time reached 0.3 ppm, and the levels of the 7-phenol and 3-keto-7-phenol were <0.01 ppm. The leaves, however, had much higher amounts of the carbamates (day 1, 11.6 ppm; day 14, 0.531 ppm) and phenolic compounds (day 1, 0.563; day 14, 0.527 ppm). The 3,7-diol increased from day 1 on both the berries (Table I) and leaves (Table II) to a maximum at approximately day 6 and then gradually decreased in amount to day 14. The 3-oxocarbofuran also followed a similar pattern of increase and decrease as the 3,7-diol. The other compounds either decreased gradually from day 1 to day 14 or were not present in detectable quantities. The compound levels in all cases on the berries sprayed at the rate of (4 oz of a.i.)/acre 14 days before harvest were at the level of the method sensitivity at the harvest date. On day 5 or 6, the total carbamate residues were below 0.2 ppm and all compounds except the 3-oxocarbofuran on the berries and leaves and the 3,7-diol on the leaves decreased gradually from day 1 to day 14. The berries at harvest date (14 days) had much lower residues than the leaves.

The Day-Neutral strawberries were much larger and closer to maturity when sprayed 7 days before harvest at the (4 and 8 oz of a.i.)/acre rate (Table I) than in the 14-day experiment previously discussed. The total carbamate levels dropped to approximately 0.1 ppm by day 4 on the berries at the (4 oz of a.i.)/acre rate of application and day 6 to 7 at the (8 oz of a.i.)/acre rate. Neither the 3-oxocarbofuran nor 3,7-diol increased in significant amounts in this experiment because of the short period of exposure of the compounds to the plant tissue. A slight increase in the 3-oxocarbofuran was observed on day 5 at the (8 oz of a.i.)/acre rate of application. Most of the compounds decreased in amounts from day 1 through day 7 and were near the level of method sensitivity at harvest date.

The levels of carbofuran and its metabolites on Tioga and Tufts strawberries sprayed 7 and 14 days before harvest at (4 and 8 oz of a.i.)/acre followed similar patterns as those residues on the Day-Neutral variety. In general, little, if any, significant differences could be detected or attributed to the strawberry plant varieties on the metabolism of the chemicals and their residue levels.

When three varieties of strawberries, Day-Neutral, Tioga, and Tufts, were sprayed once with Furadan 4-Flowable either 7 or 14 days before harvest at rates of (4 or 8 oz of a.i.)/acre, sampled, and analyzed for carbofuran and its metabolites, the residues were below 0.1 ppm or near the level of the method sensitivity for detection. Much higher residues of these chemicals were detected on the leaves. Reduction of the chemical residues on the plant tissues probably resulted from dilution by plant growth and volatilization from the plant tissue surfaces.

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