posits of the technical and formulated material and in water solution. The major identified photoproducts arise through established oxidative and hydrolytic mechanisms. Oxidation of the phenyl-*S*-methyl sulfur to sulfoxide and sulfone derivatives appeared to be the initial step in the degradation of 9306. Comparable photochemical oxidation of thioether moieties is known for both OP (Wendel and Bull, 1970) and carbamate (Abdel-Wahab et al., 1966) insecticides. Likewise, oxidative desulfuration and aryl ester cleavage of OP insecticides are previously reported photochemical pathways (Koivistoinen and Merilainen, 1962; Ohkawa et al., 1974).

The identified photoproducts of 9306 (Figure 2), which are formed through straightforward oxidative and hydrolytic reactions, are clearly not the terminal photodegradation residues to be expected in the environment because more polar products are rapidly generated both on surfaces and in water solution. While these polar derivatives remain uncharacterized, studies with rats indicate that they will not likely result in appreciable toxicological hazards to mammals. The compounds were rapidly excreted by rats and were not retained in the tissues. These studies thus indicate that 9306 will be of short persistence in the environment, and that the persisting terminal residues will likely be of little toxicological significance.

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Effects of Light on the Fate of Carbofuran during the Drying of Alfalfa

Thomas E. Archer

Carbofuran and related compounds as residues on alfalfa hay exposed to drying by sunlight, ultraviolet light, and air in the dark under controlled conditions were investigated using gas–liquid chromatography (GLC) and thin-layer chromatography (TLC) for the purpose of determining the fate, form, and removal of these residues from the hay. Maximum loss of carbofuran and related compounds calculated as total carbofuran occurred approximately 10 days after application from all the samples. Maximum losses of residue from lot I, lot II, and lot III were 83.6, 81.3, and 89.8%, respectively. Hydroxycarbofuran, 3-oxocarbofuran, 3,7-diol, and the 3-keto-7-phenol increased in all of the lots. The hydroxycarbofuran increased most dramatically in the dark drying experiment. This increase was evident because less volatility with plant moisture occurred as it was formed since the percent moisture loss from the alfalfa during days 2 to 10 in the dark experiment was less than in the ultraviolet light and sunlight experiments.

Carbofuran (Furadan) is used for the control of alfalfa weevil larvae and adults, Egyptian alfalfa weevil larvae, pea aphid, and lygus bugs. Furadan 4 Flowable (4 lb of active ingredient/gal) is applied to alfalfa as a foliar application in rates ranging from 0.5 pt to 1 qt/acre 7 days to 28 days preharvest.

Tolerances are established for combined residues of the insecticide carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl *N*-methylcarbamate), its carbamate metabolite (2,3-dihydro-2,2-dimethyl-3-hydroxy-7-benzofuranyl *N*-methylcarbamate), and its phenolic metabolites (2,3-dihydro-2,2-dimethyl-7-benzofuranol, 2,3-dihydro-2,2-dimethyl-3-oxo-7-benzofuranol, and 2,3-dihydro-2,2-dimethyl-3,7-benzofurandiol) in or on alfalfa as follows: 40 ppm in or on alfalfa hay (of which not more than 20 ppm is carbamates); 10 ppm in or on fresh alfalfa (of which not more than 5 ppm is carbamates).

It has been shown of six insecticides applied before and after alfalfa weevil adults oviposited on alfalfa in the spring of 1969 in New York that carbofuran gave by far the best control in both experiments (Summers et al., 1971). The metabolism of carbofuran residues in alfalfa and bean plants and in the dairy cow has been discussed (Knaak et al., 1970a,b). The persistence of carbofuran and 3-hydroxycarbofuran on alfalfa has been discussed by Shaw et al. (1969). Fahey et al. (1970) showed that carbofuran residues on green alfalfa were not found 14 days after treatment at the rates of 0.5 and 1.0 lb/acre in 20 gal of spray in Indiana, and dehydration of the alfalfa in a drum-type commercial dehydrator reduced the carbofuran residues by 65%. The effect of drying harvested mature alfalfa plants by sunlight, ultraviolet light, and air in the dark on residues of DDT and related chlorinated hydrocarbon residues (Archer, 1969), toxaphene residues (Archer, 1971), and endosulfan residues (Archer, 1973) has been published.

The present investigations were undertaken to determine the effect on the residues of drying in the dark and under natural and artificial light conditions harvested alfalfa containing carbofuran and related compounds residues (Figure 1). The dark and artificial ultraviolet light experiments were conducted as relative experiments to the normal sunlight drying to determine the fates of the pesticide residues on nonliving alfalfa plants under con-

Department of Environmental Toxicology, University of California, Davis, California 95616.

trolled light exposure conditions other than the normal drying procedures.

MATERIALS AND METHODS

Apparatus. The Blak-Ray Ultraviolet Intensity Meter was obtained from Ultraviolet Products, Inc., Model J 227 metering unit; J 226 short wavelength cell. Ultraviolet lamps were General Electric germicidial lamps (G15T8). The fluorescence spectrophotometer was a Baird-Atomic, Inc., Model SF-1.

Reagents. All solvents were reagent grade freshly distilled before use. Florisil was obtained from the Floridin Co., Berkeley Springs, W. Va., and was used without further activation.

Pentafluorobenzyl bromide (PFB) and trifluoroacetic anhydride (TFA) reagents were obtained from the Aldrich Chemical Co., Milwaukee, Wis.

Procedure. *Experimental Alfalfa Sample and Carbofuran Application.* Nine kilograms of alfalfa stalks, approximately 46 cm long, were cut near ground level of an alfalfa field over a 27 × 90 m strip in August. The alfalfa was well mixed and divided into three equal lots. The alfalfa contained no detectable carbofuran residues and 83.3% moisture.

A mixture of 8 g of Furadan 4 Flowable (active ingredient, 43.8%; inert ingredients, 56.2%) was prepared in 3.8 l. of distilled water (3.5 g of active ingredient). Three kilograms of subsampled alfalfa was sprayed with 1 l. of this spray mixture (0.921 g of active ingredient).

The previously subdivided alfalfa lots were individually placed in a spray compartment 158 × 68 × 10 cm, composed of 2.5-cm chicken wire netting, supported on 30.5-cm uprights. The alfalfa was sprayed out-of-doors with 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 i.d. flexible neoprene, Teflon-lined rubber tubing for chemical inertness was attached between the pressure tank and the Roto-Spray Nozzle. During the application of the spray, the plant material was turned several times to attempt uniform and even coverage with the chemical.

After carbofuran application, the alfalfa was dried for 10 min at ambient temperature, mixed to ensure uniform sampling, and transferred to the light treatment areas.

Alfalfa Light Treatment. Lot I was transferred to an aluminum foil lined carton of such size that the alfalfa could be spread in a 4-cm layer for drying which decreased in thickness as drying occurred. The plant material was mixed twice daily. The sample was placed in a well-ventilated laboratory in a dark area near a hood at temperatures ranging from 21 to 24 °C and covered with a double layer of cheesecloth to protect it from light. After 10 days, a portion was transferred to ultraviolet lamp and sunlight treatment for 10 days.

It was necessary to cut lot II into 2 to 3 cm pieces with a paper cutter in order to achieve adequate artificial ultraviolet light irradiation. The sample was transferred to an aluminum foil lined carton in a 4-cm layer thickness and exposed to ultraviolet lamp treatment at temperatures ranging from 29 to 35 °C for 11 days. The layer decreased to less than 0.5 cm as drying occurred. The lamps were arranged to cover the plant samples to minimize ventilation and ambient drafts. Subsequently, a portion was transferred to a sunlight exposure for 10 days at temperatures ranging from 26 to 43 °C. The plant material was mixed twice daily to ensure uniform exposure to the light irradiation. The two 15-W ultraviolet lamps had an effective length of 25.56 cm and a diameter of 2.54 cm. They were placed 5.08 cm above the alfalfa in such a manner as to equally illuminate the entire sample. Ultraviolet light intensity was measured with a Blak-Ray Ultraviolet Intensity Meter measuring microwatts per square centimeter, $\mu W/cm^2$, with an accuracy of ±5% and converted to ergs per square centimeter intensity. Readings were made at a 5-cm distance from the lamp at the surface of the treated sample. The meter and measuring cell were calibrated against a Fluorispec fluorescence spectrophotometer. The xenon lamp excitation monochromator provided an irradiation source with a 32-nm bandwidth.

Lot III was distributed on the spray compartment previously described and allowed to remain continuously out-of-doors at temperatures ranging from 26 to 43 °C for 10 days. The loosely distributed plant material thickness decreased to less than 1 cm as drying occurred. The plant material was mixed twice daily to ensure uniform exposure to the sunlight. After this treatment a portion was transferred to ultraviolet lamp treatment for 10 days at temperatures ranging from 29 to 35 °C. Some dew was observed on the green sunlight treatment sample during early morning hours but not to the excess of dripping, and no dew was observed on the sample after the second day of exposure.

Precautions were taken to representatively sample so that the proper ratio of leaves to stems of the alfalfa plant material was maintained.

Extraction of the Alfalfa Plant Material. The extraction procedure was based on the method of Cassil et al. (1969) with the following modifications. Twenty-five grams of chopped green alfalfa or 5 g of chopped dry alfalfa was extracted using 250 ml of 0.25 N hydrochloric acid. This extraction procedure does not apparently alter the compounds under investigation as determined by recovery studies. Twenty-five 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 dichloromethane. After the dichloromethane extraction the aqueous phase was extracted with 25 ml of anhydrous diethyl ether, the aqueous phase was discarded, the ether was washed with 10 ml of saturated sodium chloride, and it was filtered and pooled with the dichloromethane extracts. This step was necessary to recover the phenolic compounds. The filter paper and sodium sulfate were washed with 25 ml of diethyl ether and 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 to 0.5 ml to remove all traces of dichloromethane. Five milliliters of hexane was added to the concentrated sample in preparation for the column chromatography cleanup.

Sample Extract Cleanup by Column Chromatography on Florisil. The sample cleanup was based on the procedure of Knaak et al. (1970a) 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 Florisil activated as received from the supplier, and 0.5 g of anhydrous sodium sulfate. The column was wet with 25 ml of hexane. The 5 ml of hexane containing the crop extract (1 g or less of alfalfa extract) 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. The receiver was changed and separate eluate collections of 50 ml of 10% ethyl acetate–90% hexane and 50 ml of 20% ethyl acetate–80% hexane were pooled. The receiver was again changed and 50 ml of 30% ethyl acetate–70% hexane was added and collected followed by 40% ethyl acetate–60%

Table I. Retention Times and R_f Values of Carbofuran and Related Products under the Experimental Conditions Employed[a]

Compounds	t_R, min[b]	R_f values[c]
Carbofuran	7.0	0.49
Hydroxycarbofuran	8.0	0.35
3-Oxocarbofuran	10.0	0.47
7-Phenol	10.5	0.68
3,7-Diol	1.5	0.53
3-Keto-7-phenol	1.5	0.57

[a] Method sensitivity 0.1 ppm; column temperature 140 °C. [b] Nanograms detectable by GLC 4, 1, 1, 0.5, 0.1, and 1, respectively. [c] Micrograms detectable by TLC are 2 for the carbamates and 1 for the phenols.

hexane which was pooled. The first eluate of hexane was discarded.

The remaining pooled eluates were each evaporated in vacuo on a rotary evaporator at 50 to 60 °C to 0.5 ml; 25 ml of benzene was added and evaporated to remove all traces of ethyl acetate. Each fraction of the cleaned-up alfalfa extract was finally adjusted to a 10-ml volume with benzene and stored for further analytical procedures.

Thin-Layer Separation of the Compounds. Thin-layer plates were prepared by spreading a water slurry of silica gel H, 250 μm thick, on 20 × 20 cm glass plates. The slurry was allowed to air dry and the plates were heated at 100 °C for 30 min, allowed to cool to room temperature, and stored in a TLC plate desiccator. The compounds spotted on the TLC plate were separated with a solvent system composed of 25% benzene–75% diethyl ether (v/v). The time of spot development was approximately 20 min or until the solvent front had travelled 15 cm from the spot origin. After plate development, the solvent was evaporated from the plate for approximately 5 min in a hood. The reference standards were detected with a chromogenic spray consisting of 2 N sodium hydroxide in absolute methyl alcohol followed by a spray composed of 5 mg of *p*-nitrobenzenediazonium fluoroborate dissolved in 25 ml of absolute methyl alcohol plus 25 ml of diethyl ether. The spots were pink in color against a white background. Silica gel squares approximately 2 in. × 2 in. containing compound standards and cleaned-up sample extracts with R_f values relative to the known compound standards were extracted without chromogenic detection with 3 ml of ethyl acetate in 10-ml hexagonal base volumetric flasks for 5 min on a wrist-action Burrell shaker. The solvent was made to 10 ml and aliquots were analyzed on the GLC after derivatization. The R_f values are shown in Table I.

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, the injector 215 °C, and the 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 ×. The compounds were separated on the GLC as the TFA derivatives with the exception of the 7-phenol which was the PFB derivative and the t_R minutes are listed in Table I. Quantitation of sample peak areas relative to standards was by measurement of peak areas with a polar planimeter. All results were based on sample dry weights with a method sensitivity of 0.1 ppm, and all residue interpretations of carbofuran and related products on the alfalfa were relative to day zero.

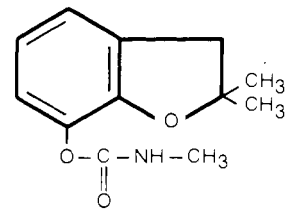
Sample Derivatization as the Pentafluorobenzyl Ether (PFB) or Trifluoroacetate (TFA). The pentafluorobenzyl ether derivatization was based on the procedure of Johnson (1973) with the following modifications. Not more than 50 μg of insecticide (1 g of sample extract) was dissolved in ethyl acetate in 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 pentafluorobenzyl bromide (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 Florisil 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 5 ml of hexane and the rinse was transferred to the column. 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 of 75% benzene in hexane. A final 5 ml of 100% benzene was added; the sample was adjusted to an appropriate volume and analyzed on the GLC.

The trifluoroacetate derivatization of the carbofuran and related compounds was based on the method of Seiber (1972) with the following modification. The derivatized sample was transferred to a 60-ml separatory funnel with a Teflon stopcock and washed with 3 rinses of 5 ml of distilled water. The water washes were pooled in a 60-ml separatory funnel and extracted with three 1-ml washes of redistilled hexane. The organic solvents were pooled, adjusted to appropriate volumes, 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. Recoveries of carbofuran and related compounds through the entire procedure of extraction, cleanup, TLC, and final analysis by GLC ranged from 77 to 100% at fortification levels of 1 and 10 ppm.

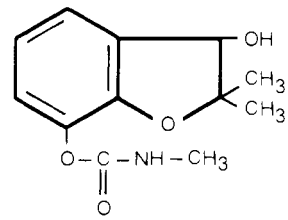
RESULTS AND DISCUSSION

The active ingredients by analysis using the procedures previously discussed 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 molecular structures of carbofuran and related compounds are shown in Figure 1.

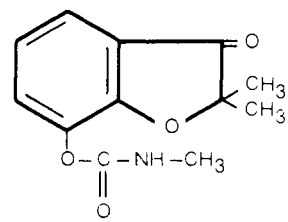
Figure 2 shows the decline of carbofuran and related products calculated as carbofuran on the alfalfa from day zero to 10 days' drying treatment during dark (lot I), ultraviolet light (lot II), and sunlight (lot III) exposure. Maximum loss of residue (lot I, 83.6%; II, 81.3%; and III, 89.8%) occurred 10 days after carbofuran application. However, most of the residue loss in lot II (72.2%; moisture, 7.8%) had occurred by day 6 of continuous exposure to ultraviolet light at temperatures ranging from 29 to 35 °C while the maximum residue loss in lot I was after 10 days' exposure to no light at temperatures ranging from 21 to 24 °C and the maximum residue loss in lot III was after a 10-day exposure to sunlight at temperatures ranging from 26 to 43 °C during daylight hours only. The moisture contents of the alfalfa plant material at these respective time periods were approximately: lot I, 16%; lot II, 8%; and lot III, 20%. Since the rate of residue losses on the plant material in lots II and III decreased significantly by the 8th day of the experiment, the plant samples including lot I were interchanged to other light treatments.



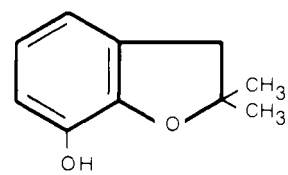
2, 3–Dihydro–2, 2–dimethyl–7–benzofuranyl N–methylcarbamate (Carbofuran)



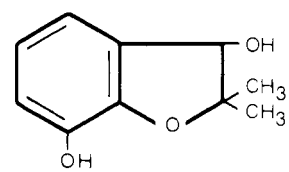
2, 3–Dihydro–2, 2–dimethyl–3–hydroxy–7–benzofuranyl N–methylcarbamate (OH-Carbofuran)



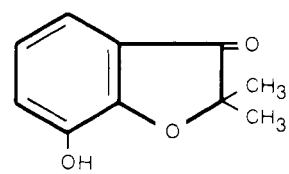
2,3–Dihydro–2, 2–dimethyl–3–oxo–7–benzofuranyl N–methylcarbamate (3-Oxocarbofuran)



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.

Table II shows the levels on the treated plant material from 0 to 10 days for the carbofuran, hydroxycarbofuran, 3-oxocarbofuran, 7-phenol, 3,7-diol, and the 3-keto-7-phenol. Lot I (dark) sample had a very significant increase in the amounts of the hydroxycarbofuran (day 0, 15 ppm; day 5, 72 ppm; day 10, 23 ppm), the 3,7-diol (day 0, <0.1 ppm; days 1 and 2, 0.2 ppm; day 3 and later, <0.1 ppm) and the 3-keto-7-phenol (day 0, 1.5 ppm; day 3, 12.3 ppm; decline by day 10, 2.2 ppm). Lot II (ultraviolet light) sample had a very significant increase in the amounts of the 3-oxocarbofuran (day 0, 4.4 ppm; day 6, 9.8 ppm; decline to day 10, 3.2 ppm), the 3,7-diol (day 0, <0.1 ppm; day 5, 0.4 ppm; decline to days 8 through 10, <0.1 ppm), and the 3-keto-7-phenol (day 0, 0.2 ppm; day 5, 3.3 ppm; day 10, <0.1 ppm). Lot III (sunlight) sample had a very significant increase in the amounts of the 3,7-diol (day 0, <0.1 ppm; day 3, 2.5 ppm; by day 10, 0.4 ppm) and the 3-keto-7-phenol (day 0, 1.5 ppm; day 2, 8.6 ppm; declined by day 10, 0.7 ppm).

In all lots the hydroxycarbofuran, 3-oxocarbofuran, 3,7-diol, and the 3-keto-7-phenol increased. The hydroxycarbofuran increased most dramatically in the dark

Table II. Residue Changes (Milligrams per Kilogram)[a] of the Various Carbofuran-Related Compounds on Alfalfa during 10-Day Light Treatments

Time, days	Moisture	Carbofuran	Hydroxy-carbofuran	3-Oxo-carbofuran	7-Phenol	3,7-Diol	3-Keto-7-phenol
			Lot I (Dark Drying[a]; Temp Range 21-24 °C)				
0	83.3	604	15.2	5.97	19.1	<0.010	1.49
1	80.3	541	17.7	7.29	19.5	0.224	2.85
2	77.2	466	31.7	8.10	13.2	0.196	8.36
3	71.8	392	50.4	7.29	6.88	0.096	12.3
4	58.0	332	68.0	6.86	4.85	0.057	9.62
5	46.6	301	71.6	7.54	2.92	0.075	7.10
6	25.5	279	61.4	8.43	1.42	0.129	5.72
7	20.2	241	55.3	7.95	0.851	0.091	4.71
8	18.7	212	47.4	6.17	0.560	0.030	3.83
9	17.1	166	35.6	3.95	0.362	0.021	3.00
10	15.7	80.8	22.9	1.63	0.187	0.018	2.18
			Lot II (Ultraviolet Light Drying[b]; Temp Range 29-35 °C)				
0	83.3	557	20.7	4.35	14.3	<0.010	<0.010
1	79.9	361	14.4	4.53	12.0	0.099	0.420
2	50.9	260	16.7	4.64	9.52	0.158	0.659
3	19.3	205	16.8	6.06	6.85	0.251	1.50
4	8.9	172	12.5	7.51	4.25	0.332	3.57
5	11.5	153	11.1	9.40	2.36	0.365	3.29
6	7.9	143	12.6	9.84	1.18	0.317	1.14
7	7.7	130	9.97	7.56	0.489	0.188	0.496
8	9.3	115	11.0	5.99	0.232	0.094	0.256
9	8.2	105	13.2	4.96	0.119	0.048	0.099
10	8.6	97.2	12.2	3.20	0.04	0.021	0.016
			Lot III (Sunlight Drying[c]; Temp Range 26-43 °C)				
0	83.3	636	3.37	7.59	16.1	<0.100	1.49
1	47.6	555	2.02	7.54	10.5	0.693	5.02
2	28.9	461	1.52	6.35	4.44	1.59	8.55
3	19.0	369	1.46	4.36	2.29	2.53	5.32
4	16.2	288	1.60	2.75	1.53	2.42	3.66
5	13.7	219	1.52	2.30	1.42	1.84	2.99
6	12.2	172	1.38	2.13	1.99	1.09	1.87
7	11.1	130	1.35	2.16	1.67	0.794	1.38
8	14.5	95.1	1.49	2.07	1.49	1.20	1.38
9	18.2	76.9	1.65	1.87	1.32	1.11	1.15
10	21.2	62.2	1.76	1.78	1.14	0.429	0.712

[a] All milligrams per kilogram data are by dry weight. [b] Ultraviolet light exposed (254 nm) at approximately 1.6×10^4 ergs/cm^2. [c] Sunlight exposure to nondefined type ultraviolet light at $> 5 \times 10^4$ ergs/cm^2.

Table III. Carbofuran and Related Products Calculated as Total Carbofuran after Drying in the Dark, Sunlight, and Ultraviolet Light and Interchanged to Further Sunlight and Ultraviolet Light Exposure[a]

	Lot I to lot III, dark to sunlight,[c] 26 to 43 °C in sunlight		Lot II to lot III, ultraviolet[b] to sunlight, 26 to 43 °C in sunlight		Lot III to lot II, sunlight to ultraviolet light,[b] 29 to 35 °C in ultraviolet light		Lot I to lot III, dark to ultraviolet light,[b] 29 to 35 °C in ultraviolet light	
Exposure, days	Moisture, %	Carbofuran, mg/kg	Moisture, %	Carbofuran, mg/kg	Moisture, %	Carbofuran, mg/kg	Moisture, %	Carbofuran, mg/kg
10	15.7	107	8.9	112	21.2	68.5	15.7	107
10 + 3	15.6	100	15.2	84.3	6.7	63.0	8.8	98.3
10 + 6	17.0	69.1	15.0	53.2	6.7	59.4	9.5	85.0
10 + 10	16.0	35.6	14.1	25.3	8.7	53.2	13.0	69.3

[a] All milligrams per kilogram data are by dry weight. [b] Ultraviolet light exposed (254 nm) at approximately 1.6×10^4 ergs/cm^2. [c] Sunlight exposure to nondefined type ultraviolet light at $> 5 \times 10^4$ ergs/cm^2.

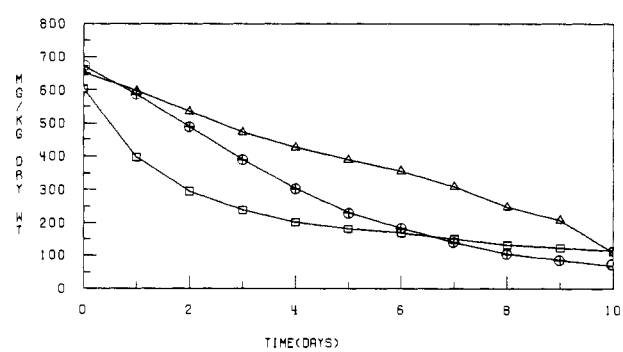


Figure 2. Changes in carbofuran compounds calculated as carbofuran on alfalfa with time: (△) dried in the dark; (□) ultraviolet light lamp; (⊕) sunlight.

drying experiment and was most evident because less volatility probably occurred as it was formed as is shown by the percent moisture content of the alfalfa plant material from day 2 to day 10 of the dark experiment relative to the ultraviolet light and sunlight experiments. The 3-oxocarbofuran in all lots increased to the maximum by day 6 or 7 and remained either constant or declined slowly to day 10. The 3,7-diol reached the maximum concentration by days 2 (lot I), 5 (lot II), and 8 (lot III) and declined to day 10. The 3-keto-7-phenol increased to the maximum concentration by days 3 (lot I), 5 (lot II), and 2 (lot III) and declined slowly to day 10.

Upon an additional 10 days' exposure of lot I to sunlight (Table III), there was a loss of 66.7% of the total residues remaining after the initial 10-day treatment. Upon ex-

posure of lot I to ultraviolet light (Table III), there was a loss of 35.2% of the residues remaining after the 10 days' dark treatment.

After an additional 10 days' exposure of lot II to sunlight (Table III), 77.4% of the residue remaining on lot II after the initial 10-day treatment with ultraviolet light was lost.

When lot III was exposed to ultraviolet light for an additional 10 days (Table III) after the initial 10-day sunlight exposure, a loss of 22.3% of the total residues occurred.

During the 10-day subsequent light exposures, no significant changes occurred in the carbofuran-related degradation products on the plant material other than losses due to temperature effects except with the following compounds: lot I to sunlight, the 3-oxocarbofuran increased from 1.6 to 2.4 ppm and the 7-phenol increased from approximately 0.2 to 2.9 ppm; lot I to ultraviolet light, the 3-oxocarbofuran increased from 1.6 to 2.5 ppm and the 7-phenol increased from approximately 0.2 to 1.5 ppm; lot II to sunlight, the 7-phenol increased from approximately 0.1 to 2.3 ppm and the 3-keto-7-phenol increased from approximately 0.1 to 0.3 ppm.

The presence of ultraviolet light or its absence significantly affected the interconversion of certain of the carbofuran related compounds while increased temperature effects greatly influenced the loss of all residues probably due to volatility from the plant material.

The practical relevence of these findings is that carbofuran and related compounds are removed or decreased in concentration during the drying of alfalfa by conventional sunlight as well as by artificial ultraviolet light irradiation. Losses of pesticide residues from the plant material probably also occur as volatilization with moisture.

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Photodegradation of Polybromobiphenyls (PBB)

L. Octavio Ruzo,[1] Göran Sundström, Otto Hutzinger,* and Stephen Safe

A series of polybrominated biphenyls (PBB) ranging from 2 to 8 atoms in bromine content was studied in regard to their ultraviolet properties and photochemical reactivity. The compounds containing bromine atoms in positions ortho to the biphenyl linkage were found to have greater ease of debromination in hexane and methanol solutions at wavelengths >290 nm. Debromination at the ortho positions was preferred in all cases. No substitution products were detected in methanol or water–acetonitrile solutions. The sensitizing effect of benzophenone and the slight quenching observed in air-saturated solutions suggest a triplet excited state intermediate.

Recently, polybrominated biphenyls (PBB) have aroused considerable interest among environmental chemists and biologists. This interest is based on the structural similarity of PBBs to the well-known pollutants polychlorinated biphenyls (PCB), combined with the extensive use of PBBs as fire retardants, thereby making their entry into the ecosystem (via sewage, household waste, etc.) a good possibility. Polybrominated biphenyls have not as yet been reported to be present in the environment; however, severe poisonings of livestock have occurred in the U.S. when feed was accidently mixed with technical PBB (*Chem. Eng. News*, 1975). Investigations have shown that hexabromobiphenyl preparations induce hepatic porphyria in birds in a manner similar to PCB and HCB (hexachlorobenzene) (Strik and Wit, 1972; Strik, 1973). The toxicity of PBBs and some other biological effects have also been studied (Cecil et al., 1975; Norris et al., 1975).

Degradations of PBBs in the environment may occur either by metabolic (Safe, 1975) or photochemical (Ruzo and Zabik, 1975) pathways. Generally, photodegradation of aromatic bromo compounds has received little attention (Maatsura and Omura, 1966; Párkány and Lee, 1974); however, in a recent paper Bunce et al. (1976) reported some mechanistic data on the photolysis of monobromobiphenyls. This study showed that bromobiphenyls follow the same order of photoreactivity as the PCBs (Ruzo et al., 1974a) in that cleavage of bromine atoms ortho to

Laboratory of Environmental Chemistry, Nieuwe Achtergracht 166, University of Amsterdam, The Netherlands (L.O.R., G.S., O.H.), and the Department of Chemistry, University of Guelph, Guelph, Ontario, Canada (S.S.).

[1]Present address: Division of Entomology and Parasitology, University of California, Berkeley, Calif.