of Umetsu et al. (1979), helped assure the stability of the carbosulfan, which is unstable and breaks down rapidly below pH 7.0. There was no evidence of decarbamylation of carbosulfan or carbofuran by the weakly basic buffer in sample extracts stored at room temperature for 1 week, which was sufficient time for analysis.

In order to ensure the stability of intact carbosulfan in soil samples, the soil samples should be frozen immediately after sampling and then kept frozen until analysis.

As additional precautions against decomposition, soil samples should not be put through the classical thawing, air-drying, and sieving process before analysis to obtain a uniform sample. The soil samples should be, however, ground and well-mixed while frozen.

Gel permeation was a useful tool for separating carbosulfan from the lipids in crop samples high in vegetable oil content but was not suitable for separating carbosulfan from the terpenes comprising citrus oils. Samples, such as citrus oil, with a high terpene content required the classical hexane–acetonitrile partition.

The hexane–acetonitrile partition adequately separated the terpenes from the pesticides. As an additional separation tool, an excess of hexane in a subsequent hexane–acetonitrile partition was used. At this point, the partition of carbosulfan is favored into the hexane.

In most cases the Darco–Attaclay plus aluminum oxide cleanup columns were used as described. When more cleanup was desired, such as for dry alfafa hay and citrus oil, a 2 g plus 4 g (60-mL elution) or a 5 g plus 7 g (125-mL elution) Darco–Attaclay plus aluminum oxide column was used.

Other liquid phases used routinely in the gas chromatograph included SE-52 (2%), Super Pak 20M (Analabs), and Ultrabond (Ultra Scientific, Inc.). The best peak shape and response were achieved by using the OV-101. The SE-52, however, was especially useful with soil and field water samples in separating carbosulfan from interferences. Super Pak 20M (or Ultrabond) was useful with soil samples in separating carbofuran from interferences. The Super Pak 20M and Ultrabond could also be used to separate carbosulfan from carbofuran isothermally in a single chromatogram.

The OV-101 could also be used to separate carbosulfan from carbofuran in a single chromatogram if the columns were temperature programmed. The packing needed extra care in conditioning to ensure a minimum of column bleed and a prohibitively steep base line during analysis. The column was temperature programmed at a rate of 3 °C/min, while disconnected from the detector, from ambient to 230 °C and held at 230 °C for 24 h. In use, the column was held at 170 °C for 2 min and then programmed at a rate of 10 °C/min to 225 °C, where the temperature was held for 1.0 min.

ACKNOWLEDGMENT

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Registry No. Carbosulfan, 55285-14-8; carbofuran, 1563-66-2; water, 7732-18-5.

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Metabolism of [^{14}C]Fosamine Ammonium in Brush and Turf

Robert L. Chrzanowski

The metabolism of ammonium ethyl [^{14}C]carbamoylphosphonate ([^{14}C]fosamine ammonium, the active ingredient in Du Pont Krenite Brush Control Agent) was studied at 13.4 kg of a.i./ha, on a pasture area consisting of a small pin oak surrounded by grass and clover. Fosamine ammonium had an average half-life of 7 days in the pasture flora. The only metabolites found were carbamoylphosphonic acid (CPA) and carboxyphosphonic acid which reached a maximum concentration after 2 weeks and then rapidly degraded. Twelve months after treatment, no fosamine ammonium, CPA, or carboxyphosphonic acid (<0.05 ppm) was found in pasture turf.

Du Pont Krenite Brush Control Agent when applied as a foliar spray in late summer or early fall controls and/or suppresses the growth of many woody species. Except for certain pines, susceptible species show little or no effect and defoliate normally at the end of the season. The following spring, these species fail to refoliate and eventually die or are severely retarded.

The metabolism of [^{14}C]fosamine ammonium in the rat (Chrzanowski et al., 1979) and its degradation in water and soil (Han, 1979) were reported previously.

This paper describes the metabolism of [^{14}C]fosamine ammonium in pasture flora and brush oak.

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EXPERIMENTAL PROCEDURES

The methodology for analyzing radioactive samples such as liquid scintillation (LSC), combustion analysis (CA), thin-layer chromatography (TLC), X-ray autoradiography, and gas chromatography/mass spectrometry (GC/MS) was described in a previous paper (Chrzanowski et al., 1979).

Materials. Ammonium ethyl [^{14}C]carbamoylphosphonate and [^{14}C]carbamoylphosphonic acid ([^{14}C]-CPA) were obtained as described by Chrzanowski et al. (1979). Unlabeled and ^{14}C-labeled carboxyphosphonic acid

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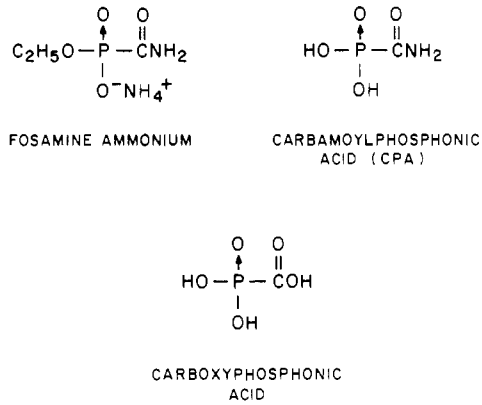

Figure 1. Chemical structures. The ^{14}C label is on the carbonyl carbon atom.

were synthesized according to the following schemes.

Synthesis of Carboxyphosphonic Acid Trisodium Salt. Carbamoylphosphonic acid diammonium salt (500 mg, 3.1 mmol) and 9.45 mL of 1 N sodium hydroxide (10 mmol) were dissolved in 5 mL of water and heated at reflux for 3 h. The reaction mixture was cooled to 25 °C and the solvent evaporated at 45 °C under vacuum. The crude product was recrystallized from water and methanol (50:50 v/v) to give white crystals of carboxyphosphonic acid trisodium salt hexahydrate (Naqui and Wheatley, 1971; Nylen, 1924). Anal. Calcd for $CO_5PNa_3 \cdot 6H_2O$: C, 4.0; H, 4.0; O, 58.7; P, 10.3; Na, 23.0. Found: C, 4.2; H, 3.2; O, 58.4; P, 11.2; Na, 22.3.

Synthesis of ^{14}C-Radiolabeled Carboxyphosphonic Acid Triammonium Salt. Radiolabeled [^{14}C]CPA diammonium salt (sp act. 1.6 mCi/mmol) was hydrolyzed with a 3-fold molar excess of 0.1 N NaOH as described above. The reaction mixture was then cooled to room temperature and applied to the top of a 2.5 × 50 cm glass column packed with 50–100-mesh activated 50W-X8 cation-exchange resin in the H^+ form (Bio-Rad Laboratories). After elution with 500 mL of distilled deionized water at room temperature, the eluant was immediately made basic with excess ammonium hydroxide and evaporated to dryness under vacuum at 45 °C; yield, 48% (200 μCi, sp act. 0.85 mCi/mmol) [^{14}C]carboxyphosphonic acid triammonium salt (radiochemical purity >99%).

Treatment. In late summer, outdoor pasture areas consisting of a pin oak (*Quercus palustris*) covering a soil area of about 0.56 m^2, and a 0.305 m^2 area each of fescue grass (*Festuca* sp.) and red clover (*Trifolium pratense*) at Newark, DE, were sprayed once to near runoff with a water–Du Pont Surfactant WK solution of ammonium ethyl [^{14}C]carbamoylphosphonate (fosamine ammonium, Figure 1). The spray solution, prepared shortly before application, consisted of 1000 mg of [^{14}C]fosamine ammonium (750 μCi) in a 200-mL volume (equivalent to 13.4 kg of a.i./ha) and 8 mL of Surfactant WK. The solution was applied uniformly from a hand-held sprayer held about 15 cm from the vegetation.

At selected intervals (0 day, 2 weeks, and 1, 3, 7, 9, and 12 months), representative samples of vegetation and soil to a depth of 8 cm were taken for analysis.

Fescue grass and red clover outside of the spray area were used as control plants.

Analytical characteristics of Keyport silt loam soil from the Newark, DE, plots were reported previously (Han, 1979).

Plant Analysis. A 1-g representative aliquot of fresh grass, clover, or brush was placed in a 10-mL centrifuge tube along with 5 mL of 0.3 M ammonium carbonate. The tube was stoppered and heated for 2 h in a steam bath. The mixture was centrifuged to separate the supernatant, and the solids were extracted once with 2 mL of methanol–water (50:50 v/v). The mixture was centrifuged again, the insoluble solids were air-dried, and an aliquot was combusted for total ^{14}C content. The remainder of the solids were saved for further analysis.

The extracts were combined, counted for ^{14}C by liquid scintillation counting (LSC), and evaporated to a 3-mL volume under a stream of dry nitrogen at 45 °C. The water fraction was then extracted once with 3 mL of ethyl acetate and both phases were counted for total ^{14}C. Aliquots of the water fraction, which contained >99% of the extracted ^{14}C, were analyzed by cochromatographic thin-layer chromatography (TLC) along with ^{14}C-labeled standards of fosamine ammonium, CPA diammonium salt, and carboxyphosphonic acid triammonium salt. The identities of the ^{14}C-labeled metabolites were established by a homogeneous mixing with the ^{14}C-labeled standards. Radioactive compounds were located by autoradiography using SB-5 X-ray film (Kodak).

The insoluble solids which still contain unextracted ^{14}C-labeled material were digested with 1.0 mL of 2.5 N sodium hydroxide for 3 days at 100 °C, centrifuged to remove the supernatant, and reextracted once with 3 mL of water. The insoluble residue was analyzed by combustion analysis (CA) for total ^{14}C, and the supernatants were combined and counted for ^{14}C by LSC. Extractable radiolabeled residues were chracterized by cochromatographic TLC (Chrzanowski et al., 1979) along with a ^{14}C-labeled standard of carboxyphosphonic acid triammonium salt. CPA and fosamine ammonium are unstable under these harsh extraction conditions and decompose completely (>99.9%) to carboxyphosphonic acid trisodium salt and *O*-ethyl carboxyphosphonic acid disodium salt, respectively.

Soil Analysis. Ten grams of soil was placed in a 250-mL centrifuge tube along with 60 mL of 0.3 M ammonium carbonate and heated on a steam bath for 2 h. The mixture was centrifuged to separate the supernatant and the solids were ultrasonically extracted once with 60 mL of water for 20 min. The mixture was centrifuged again, the residue was air-dried, and aliquots of the solid were combusted for total ^{14}C determination.

The extracts were combined, counted for total ^{14}C, and evaporated to dryness. The residue was redissolved in 10 mL of 0.05 M ammonium carbonate, and 90 mL of methanol was added dropwise to effect cleanup by precipitation of organic matter. The precipitate was washed with 20 mL of 90% methanol, dried in air, and combusted for ^{14}C determination. The soluble materials were combined, evaporated to a residue under vacuum, redissolved in a few milliliters of water, and analyzed by TLC along with standards.

Metabolite Identification. One month after application, a clover sample (120 g) was harvested and extracted 3 times with 300-mL portions of methanol–0.3 M ammonium carbonate (50:50 v/v) for 5 min in a Waring blender. The residue was separated by centrifugation after each extraction and then extracted a fourth time with 300 mL of 0.3 M ammonium carbonate at 100 °C for 2 h. The residue was separated by centrifugation, dried, and assayed by CA. The extracts were combined, counted for total ^{14}C by LSC, and evaporated to dryness under vacuum at 65 °C. The residue was dissolved in 50 mL of water and extracted 3 times with 50-mL portions of ethyl acetate which were discarded. All of the radioactivity remained in the aqueous phase. The major radioactive metabolite in the aqueous fraction was isolated and identified by TLC

Table I. Disappearance of Fosamine Ammonium and Metabolites from Grass, Clover, and Soil following Treatment with 13.4 kg of a.i./ha Radiolabeled Material

	ppm[a]				
fraction	total	fosamine ammonium	CPA	carboxy-phosphonic acid	unextracted
grass					
0 day	381	381	<0.05	<0.05	<0.05
2 weeks	106	56	24	3.3	23
1 month	53	20	9.0	2.0	22
3 months	7.3	0.5	1.6	0.05	5.2
7 months	3.2	<0.05	1.5	<0.05	1.7
9 months	3.5	<0.05	0.82	<0.05	2.7
12 months	0.4	<0.05	<0.05	<0.05	0.41
grass soil					
1 month	18	<0.05	8.6	<0.05	9.4
3 months	4.2	<0.05	3.0	<0.05	1.2
7 months	2.5	<0.05	1.1	<0.05	1.4
12 months	2.5	–[b]	–	–	–
clover					
0 day	483	483	<0.05	<0.05	<0.05
1 month	158	16	95	<0.05	47
3 months	2.2	<0.05	0.6	<0.05	1.6
7 months	1.5	<0.05	0.3	<0.05	1.2
9 months	0.5	<0.05	0.13	<0.05	0.39
12 months	0.4	<0.05	<0.05	<0.05	0.42
clover soil					
1 month	7.6	<0.05	3.6	<0.05	4.0
3 months	0.9	<0.05	0.4	<0.05	0.5
7 months	1.7	<0.05	0.7	<0.05	1.0
12 months	3.9	–	–	–	–
grass under pin oak					
9 months	4.8	<0.05	2.6	<0.05	2.2
12 months	0.4	<0.05	<0.05	<0.05	0.43

[a] All values were calculated as fosamine ammonium equivalents. [b] (–) Radioactive residues in samples were not characterized.

Table II. Disappearance of Fosamine Ammonium and Metabolites from Pin Oak Brush and Soil following Treatment with 13.4 kg of a.i./ha Radiolabeled Material

	ppm[a]				
fraction	total	fosamine ammonium	CPA	carboxy-phosphonic acid	unextracted
leaves					
0 day	434	434	<0.05	<0.05	<0.05
2 weeks	186	82	41	11	52
1 month	119	62	23	9	25
stems					
0 day	57	57	<0.05	<0.05	<0.05
1 month	41	8.8	9.1	2.1	21
3 months	34	2.0	9.0	3.0	20
7 months	50	<0.05	13	<0.05	37
9 months	12	–[b]	–	–	–
12 months	23	–	–	–	–
new pin oak growth					
12 months (leaves)	15	–	–	–	–
soil under pin oak					
2 weeks	0.1	–	–	–	–
1 month	2.8	<0.05	1.3	<0.05	1.5
3 months	0.6	<0.05	0.5	<0.05	0.1
7 months	1.2	<0.05	0.5	<0.05	0.7
9 months	1.0	–	–	–	–
12 months	0.8	–	–	–	–

[a] All values were calculated as fosamine ammonium equivalents. [b] (–) Radioactive residues in samples were not characterized.

and gas chromatographic/mass spectral (GC/MS) methods described previously (Chrzanowski et al., 1979). Materials not present in sufficient quantity for isolation were identified by comparing their TLC R_f values to standards.

RESULTS AND DISCUSSION

Pin oak, fescue grass, and red clover were treated with [^{14}C]fosamine ammonium (13.4 kg of a.i./ha) in Delaware on Sept 19, 1978. Samples from all plant species and soil in the treated areas were taken at selected intervals over the next 12 months and analyzed for total radioactive metabolite residues.

Total radioactivity was found to rapidly decline with time in the grass and clover species (Table I). Total ^{14}C-labeled residues in pin oak leaves and stems (Table II) did not immediately decline as rapidly since the plant went into dormancy shortly after spraying, whereas grass and clover continued growing until the onset of winter. The following spring, treated grass grew normally. Clover also showed regrowth, but there was some retardation com-

Table III. Local Climatological Data[a] (September 1978 to September 1979) for Test Site

test interval	rainfall (water equiv), in.	av daily temp, °F
0-2 weeks	0.80	61
2-4 weeks	0.99	54
1-3 months	6.19	46
3-7 months	21.70	35
7-9 months	7.47	64
9-12 months	15.70	73
total	52.9	

[a] Data compiled at Wilmington Delaware Airport for NOAA (National Oceanic and Atmospheric Administration, U.S. Department of Commerce).

pared to the control. The treated oak did not break dormancy until late summer when several twigs were observed to have a very small amount of severely retarded growth. Local climatological data during the 12 month test, commencing on Sept 19, 1978, is shown in Table III.

Fosamine ammonium and metabolites (Figure 1) found at various sampling intervals are listed in Tables I and II. The data show that fosamine ammonium was rapidly degraded to CPA and lesser amounts of carboxyphosphonic acid. The half-life of fosamine ammonium in the plant species was about 1 week. CPA reached a maximum concentration after 2–4 weeks and then degraded to carboxyphosphonic acid and bound residues. Twelve months after ^{14}C treatment, no CPA or carboxyphosphonic acid could be found in the grass and clover (<0.05 ppm); only bound residues (~0.41 ppm) were observed. Rigorous caustic hydrolysis of grass, clover, and brush liberated 98% of the bound radioactivity in 1-month samples as [^{14}C]-carboxyphosphonic acid trisodium salt.

In the soil (Keyport silt loam, Newark, DE), only CPA and bound residues were found after 1 month (Tables I and II). The average concentration of CPA reached a maximum in soil (8.6 ppm) 1 month after treatment and then declined to <1.1 ppm at 7 months. Field soil degradation studied by Han (1979) with fosamine ammonium on Keyport silt loam showed that after 6 months, >99% of the parent compound and CPA disappeared, leaving only ^{14}C-labeled reincorporation products in the soil organic fractions. In this case, the residual CPA found in pasture soil after 7 months may represent CPA which was extracted from plant roots and surface plant remains, since no efforts were made to remove these fractions from the soil prior to analysis.

Characterization of the radiolabeled residues in clover for most sampling intervals was made by comparison of TLC R_f values with those of authentic standards. However, for confirmation of identities, metabolites were isolated at the 1-month interval and confirmed by combination GC/MS using the previously described methodology (Chrzanowski et al., 1979). A characteristic radioscan of a TLC plate is shown in Figure 2. Because of the low levels of ^{14}C-labeled carboxyphosphonic acid in plant extracts, this metabolite could only be detected by exposing TLC plates to X-ray film. The mass spectra of isolated CPA (as methyl ester) and a standard are shown in Figure 3.

Carboxyphosphonic acid, a breakdown product of CPA, was isolated from turf and brush. Comparison with an authentic standard by cochromatography was the only confirmation of identity which could be achieved. This compound is only stable as a salt and spontaneously decarboxylates (half-life of <5 min at room temperature) when prepared as the free acid. Mass spectral analysis of

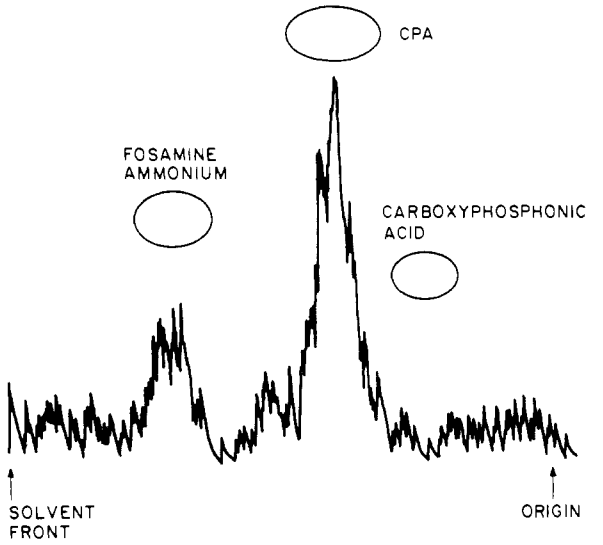

Figure 2. Ammonium carbonate 1-month clover extract; radioscan of TLC plate: cellulose; 0.5 M ammonium carbonate–methanol–water (5:60:35 v/v/v).

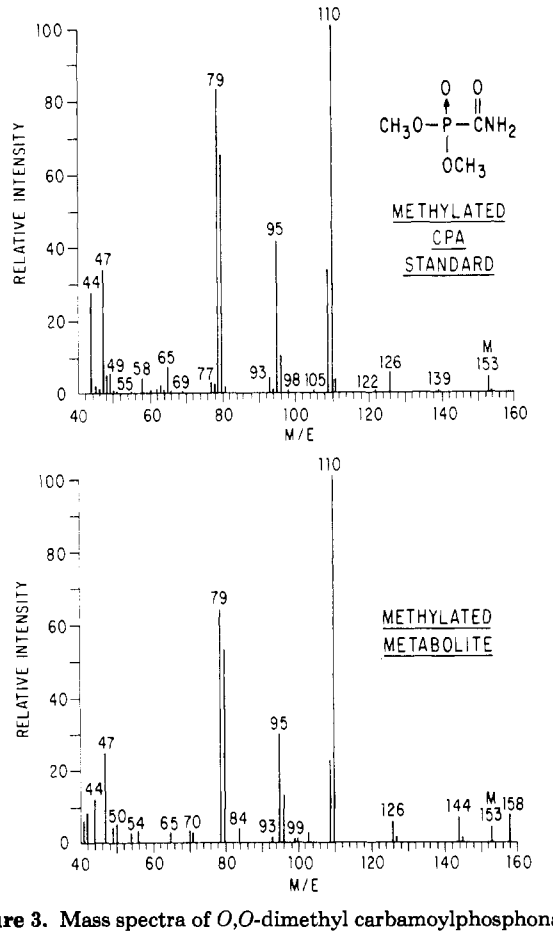

Figure 3. Mass spectra of *O,O*-dimethyl carbamoylphosphonate.

the silanized standard (triammonium salt) and the isolated metabolite produced only ions of phosphorus acid. However, even though mass spectral confirmation could not be achieved, the consistent TLC data and the ease with which carboxyphosphonic acid salts can be prepared from CPA leave little doubt of the identity of the isolated metabolite/breakdown product. It is possible that the rapid loss of ^{14}C-labeled residues from plants treated with [^{14}C]fosamine ammonium (Tables I and II) could be explained by the decarboxylation of the [^{14}C] carboxyphosphonic acid metabolite. However, no attempt was made to monitor the production of $^{14}CO_2$ during the experiment since the

test was conducted in an open outdoor field.

This study has shown that fosamine ammonium is rapidly degraded in pasture species. Twelve months after treatment at 13.4 kg of a.i./ha, no (<0.05 ppm) fosamine ammonium or its main metabolite (CPA) could be found in either grass or clover. The small amount of residues which did remain (~0.42 ppm) appeared to be bound carboxyphosphonic acid moieties.

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Registry No. CPA, 6874-57-3; CPA·3Na, 63585-09-1; CPA·3NH$_3$, 83665-50-3; fosamine ammonium, 25954-13-6; carboxyphosphonic acid, 4428-95-9.

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Diphenyl Ether Herbicides: Mutagenic Metabolites and Photoproducts of Nitrofen

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Nitrofen [2,4-dichloro-1-(4-nitrophenoxy)benzene] (1-NO_2; 1 = Cl_2PhOPh–) in thin films undergoes rapid photochemical reduction in near-UV light by the pathway 1-NO_2 → 1-NO → [1-NHOH] → 1-NH_2 and 1-N=N(O)-1. Rat liver enzyme preparations with NADPH reduce 1-NO_2 or 1-NO to 1-NH_2 under anaerobic conditions, confirming earlier in vivo studies of 1-NO_2 with rats and suggesting 1-NO and 1-NHOH as intermediary metabolites. This enzyme system in air oxidizes 1-NH_2 to 1-NO. Nitrofen's photoproducts and metabolites (1-NO, 1-NHOH, and 1-NH_2) are mutagens in the Ames *Salmonella typhimurium* (strain TA 100) assay with microsomal activation, i.e., 11–13 revertants/nmol in each case. Nitrofen is known to be a herbicide, teratogen, and carcinogen. The current study also identifies 1-NO_2 as a promutagen activated on nitro reduction. The 1-NO and 1-NHOH intermediary metabolites or their activated derivatives may be involved in the mutagenesis and perhaps in other aspects of the biological activity of nitrofen.

Diphenyl ethers (nitrofen or 1-NO_2 and related compounds) are one of the most important classes of herbicides, requiring light to disrupt membrane permeability, elicit biochemical changes, and kill plant cells (Matsunaka, 1969; Suzuki et al., 1981; Orr and Hess, 1981). The role of light in the herbicidal effect is not clearly defined (Matsunaka, 1969; Orr and Hess, 1981). 1-NO_2 is also a mutagen (Jeang and Li, 1980), carcinogen (Milman et al., 1978), and teratogen (Gray et al., 1982), properties not observed to date with other diphenyl ether herbicides. Definition of the mechanism of mutagenesis might contribute to an understanding of the carcinogenic action (Ames et al., 1975) and possibly other types of biological activity. As a first step in this direction the present study evaluates the possible activation of 1-NO_2 using photochemical and metabolic systems and the Ames *Salmonella typhimurium* mutagenesis assay. The compounds examined are indicated in Figure 1.

MATERIALS AND METHODS

Chromatography. Thin-layer chromatography (TLC) utilized 0.25-mm silica gel 60 F-254 plates (E. Merck), 0.25-mm aluminum oxide F-254 Type T plates (E. Merck), or 0.25-mm RPSF fluorescent reverse phase plates (Analtech, Inc.) developed in mobile phases as specified in chromatography tanks without liners; 0.5-mm layers were used for preparative isolations. Sorbed compounds were eluted with diethyl ether (apolar bands) or methanol–diethyl ether (polar bands). Photoproducts were determined by gas–liquid chromatography (GLC) with a Varian 1400 instrument fitted with a hydrogen flame ionization detector (FID) and a glass column (1 m × 2 mm i.d.) packed with Chromosorb W (60–80 mesh) coated with 5% SE-30: nitrogen carrier gas flow rate, 35 mL/min; hydrogen gas flow rate, 20 mL/min; air flow rate, 200 mL/min; column temperature, 180 °C; inlet temperature, 230 °C; detector temperature, 300 °C. Metabolites were analyzed with a Hewlett-Packard 5830A instrument fitted with a nickel-63 electron capture (EC) detector and a glass column (1.5 m × 4 mm i.d.) packed with GHP (80–100 mesh) coated with 5% OV-101; the carrier gas was 5% methane–95% argon with a flow rate of 28 mL/min; the operating temperatures were inlet 230 °C, column 230 °C, and detector 250 °C.

Spectroscopy. Chemical ionization mass spectra (CI-MS) were recorded with a Finnigan 3200 spectrometer interfaced with a System Industries 150 data system. Methane (0.8 torr) was used as the reagent gas and the ionization voltage was 70 eV. Samples were introduced with a solid probe or by GLC. Nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a 250-MHz Fourier transform instrument; compounds were dissolved in $CDCl_3$ containing 0.2% Me_4Si as the internal reference.

Chemicals. Table I gives the compounds considered and properties useful in their characterization as described below.

Pure 1-NO_2 (>99%) was obtained from the U.S. Environmental Protection Agency (Research Triangle Park, NC) or Chem Service (West Chester, PA) and technical

Pesticide Chemistry and Toxicology Laboratory, Department of Entomological Sciences, University of California, Berkeley, California 94720.

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