

of carbofuran from the nutrient solutions. Unconjugated metabolites were absent, and only a minor portion of the polar activity was identified as being glycosidic.

The activity in the insoluble plant residues was not identified except for possible traces of glycosidic conjugates.

The half-life of carbofuran, applied topically to the leaves of tobacco plants, was very much greater than 4 days. This, and a somewhat different pattern of metabolism, indicates that foliar-applied carbofuran does not readily penetrate the cuticle.

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Bux Insecticide Soil Metabolism

Beverly V. Tucker* and Donald E. Pack

Bux Insecticide [3 to 1 mixture of *m*-(1-methylbutyl)-phenyl methylcarbamate and *m*-(1-ethylpropyl)-phenyl methylcarbamate] is readily metabolized by soil organisms by attack at the carbamate ester linkage. Soils treated separately with *m*-(1-methylbutyl)-phenyl methylcarbamate-*carbonyl*-¹⁴C and *m*-(1-ethylpropyl)-phenyl methylcarbamate-*carbonyl*-¹⁴C evolved ¹⁴CO₂ as the parent carbamate content decreased. Each parent carbamate formed only one ¹⁴C metabolite in the soil and it was present

only in trace amounts. The main emphasis was placed on the major isomer of Bux Insecticide and its metabolite was identified as *m*-(1-hydroxy-1-methylbutyl)-phenyl methylcarbamate. This metabolite is not persistent in soil but is degraded at about the same rate as the parent carbamate (50% loss in 1 to 2 weeks under laboratory conditions at ambient temperature). Six hydroxylated derivatives of the major isomer of Bux Insecticide were synthesized to aid metabolite identification.

Bux Insecticide is a 3 to 1 mixture of *m*-(1-methylbutyl)-phenyl methylcarbamate and *m*-(1-ethylpropyl)-phenyl methylcarbamate which is used to control corn rootworm. It is presently available as a 10% granule and applied to the soil in a band at the time of planting. Soil samples from six test locations in Iowa and Nebraska contained less than 0.02 to 0.24 ppm of Bux Insecticide at corn harvest after a 2 lb/acre application at planting. The samples contained less than 0.02 ppm (limit of detection) of the phenolic hydrolysis product of Bux Insecticide. The average Bux Insecticide residue found was 0.08 ppm, which shows there is a minimum of 90% loss of Bux Insecticide from corn planting (treatment) to corn harvest (5 to 6 month interval). These tests were performed at twice the maximum anticipated commercial rate of 1 lb/acre. Bux Insecticide residues were determined by total *in vitro* acetylcholinesterase inhibition with thin-layer chromatography confirmation of residues. The phenolic hydrolysis product of Bux Insecticide was determined by thin-layer chromatography.

The phenolic hydrolysis product of Bux Insecticide is degraded rapidly in soils (50% loss in 24 hr). In laboratory tests the maximum amount of the phenol found in soils

treated with Bux Insecticide was 2% of the carbamate added and this was several days after treatment. Due to the non-persistence and low toxicity of the phenol, the fate of Bux Insecticide after the carbamate functional group is lost is of minor importance.

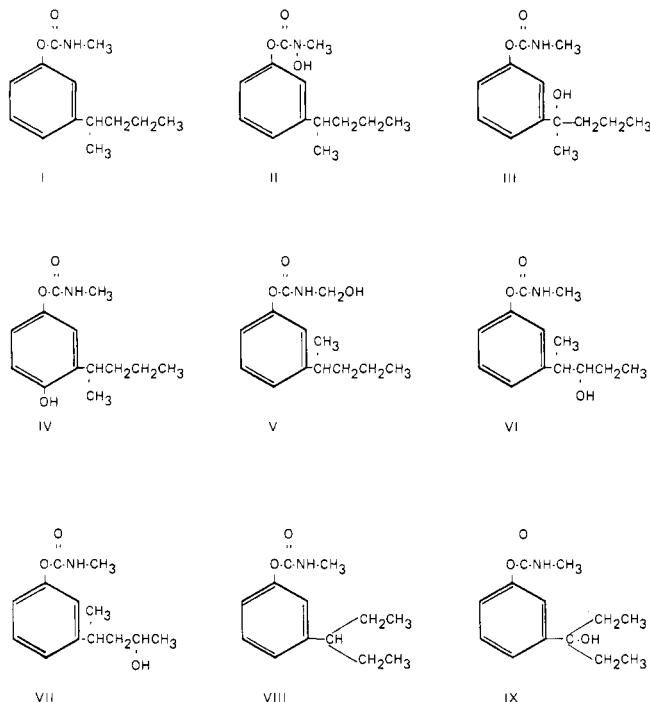
There are few reports in the literature concerning the soil metabolism of methylcarbamates. Kaufman (1967) reviewed the available knowledge on carbamate degradation in soil and postulated degradation mechanisms based on analogies with metabolic pathway of carbamates in other media. He postulates that methylcarbamates would be degraded by initial attack at the ester linkage, giving methylamine, carbon dioxide, and the phenol.

This paper is concerned with the metabolism of Bux Insecticide in soil. Carbonyl-¹⁴C-labeled carbamate was used so that the fate of the carbamate functional group could be followed. Radiotracer techniques were used in the studies and the fate of the molecule after the carbamate group was lost was not followed. Model compounds that were considered potential metabolites were synthesized to develop extraction and chromatography procedures for identifying actual metabolites. The model compounds were *m*-(1-methylbutyl)-phenyl *N*-hydroxy-*N*-methylcarbamate (II), *m*-(1-hydroxy-1-methylbutyl)-phenyl methylcarbamate (III), *p*-hydroxy-*m*-(1-methylbutyl)-phenyl methylcarbamate (IV), *m*-(1-methylbutyl)-phenyl *N*-hydroxymethylcarbamate (V), *m*-

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(2-hydroxy-1-methylbutyl)phenyl methylcarbamate (VI), and *m*-(3-hydroxy-1-methylbutyl)phenyl methylcarbamate (VII).

Since the two isomers of Bux Insecticide have similar chemical and biological properties, most of the work was conducted with the major isomer (I). However, some confirmatory work was performed with the minor isomer (VIII) and its side chain hydroxy derivative (IX).



EXPERIMENTAL

Apparatus and Reagents. The *m*-(1-methylbutyl)phenyl methylcarbamate carbonyl- ^{14}C and *m*-(1-ethylpropyl)phenyl methylcarbamate carbonyl- ^{14}C were obtained from New England Nuclear Corp. They were synthesized by reacting the respective phenols with methyl isocyanate- ^{14}C . Each had a specific activity of 4.71 mCi per mM and a radiochemical purity of at least 99.5%.

Samples were counted with a Model 6850 Nuclear-Chicago liquid scintillation counter. Counting solutions consisted of 8 ml of scintillation solution (8.25 g of PPO per liter of toluene) and 8 ml of methyl cellosolve or 4 ml of methyl cellosolve and 4 ml of carbon dioxide adsorbing solution.

Total ^{14}C content of samples was determined by wet combustion using an apparatus which was a modification of that described by Smith *et al.* (1964). Generated carbon dioxide was collected in 10 ml of 20% (v/v) ethanolamine in methyl cellosolve.

Silica gel G thin-layer plates (250 μ) were used for all thin-layer chromatography except when noted otherwise. For color development of phenols and carbamates, plates were first sprayed with a solution of 6 g of sodium hydroxide in 200 ml of methanol:*n*-butanol (1 to 1 v/v) until thoroughly wetted. After the plates were dry, they were sprayed with a solution of 50 mg of *p*-nitrobenzenediazonium fluoborate (Eastman Organic Chemicals) in 100 ml of methanol:ethyl ether (1 to 1 v/v).

Synthesis of Model Compounds. *m*-(1-METHYLBUTYL)-PHENYL *N*-HYDROXY-*N*-METHYLCARBAMATE. The sodium phenolate was prepared by treating 164 g of *m*-(1-methylbutyl)-phenol with 24 g of sodium hydride in toluene. The gelatinous fine suspension of phenolate was added dropwise to a cold solu-

tion of 300 g of phosgene in 1500 ml of toluene over a period of 1 hr. The mixture was kept at 5–10° C for 3 hr and then kept at room temperature overnight. The yellow solids were then filtered off and the toluene was evaporated under vacuum, leaving 180 ml of oil, which consisted of 30% *m*-(1-methylbutyl)phenyl chloroformate and 60% bis[*m*-(1-methylbutyl)phenyl]carbonate. The oil was distilled under vacuum and the main fraction collected at 67–70° C/0.15–0.25 mm. Forty grams of pure *m*-(1-methylbutyl)phenyl chloroformate were obtained.

A mixture of 17 g methyl hydroxylamine and 18 g of ammonium carbonate was dissolved in 150 ml of water. To this solution, 22 g of the *m*-(1-methylbutyl)phenyl chloroformate was added dropwise with agitation over a period of 1 hr. The mixture was allowed to react for 6 hr. It was then acidified with 10% hydrochloric acid and continuously extracted with ether for 15 hr. After evaporation of the ether, 22 g of colorless oil remained. Upon cooling in Dry Ice, the oil solidified.

The product was purified by column chromatography on silicic acid, using benzene-chloroform mixtures as eluents. The structure of the product was verified by nmr.

Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{O}_3\text{N}$: N, 5.91. Found: N, 6.01.

m-(1-HYDROXY-1-METHYLBUTYL)PHENYL METHYLCARBAMATE. A Grignard solution was prepared by adding 61.4 g of *n*-propyl bromide dissolved in an equal volume of ether to a suspension of 12 g of magnesium in 250 ml of dry ether over a period of 1 hr. The flask was then cooled to 1–10° C. A solution of 27.2 g of *m*-hydroxyacetophenone in 300 ml of ether was added dropwise over a period of 1.5 hr with vigorous stirring and without external cooling. Then 100 ml of aqueous saturated ammonium chloride was added to the reaction mixture. The ether phase was decanted and the aqueous phase extracted three times with 100 ml of ether. The combined ether phases were dried over magnesium sulfate and evaporated under vacuum. A brown oil (44 g) was obtained which crystallized upon standing overnight. The *m*-(1-hydroxy-1-methylbutyl)phenol was recrystallized from benzene-hexane, yielding 32.7 g of a brownish-white powder with a melting point of 91–93° C.

A solution of the *m*-(1-hydroxy-1-methylbutyl)phenol (9 g) in dimethoxyethane (30 ml) was placed in a glass ampoule and cooled in a Dry Ice-acetone bath. A few drops of triethylamine and 2.9 g of methyl isocyanate were added. The ampoule was sealed and kept at 55° C for 20 hr. After opening the ampoule, unreacted methyl isocyanate and dimethoxyethane were evaporated under vacuum. The resulting yellow-brown oil was stripped at 23° C/0.3 mm, leaving a viscous oil (11.5 g).

The product was purified by column chromatography on silicic acid using ether-hexane mixtures as eluents. The desired product was in the 50% ether-hexane fraction. The structure of the product was verified by ir.

Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{O}_3\text{N}$: N, 5.90. Found: N, 5.96.

p-HYDROXY-*m*-(1-METHYLBUTYL)PHENYL METHYLCARBAMATE. Dibenzylquinoacetophenone (Baltzly *et al.*, 1950) was prepared by adding 18.2 g of benzyl chloride and 12 g of 50% aqueous sodium hydroxide to a boiling suspension of 5.1 g of quinoacetophenone in 50 ml of ethanol. The mixture was refluxed overnight. Additional ethanol was then added and the mixture was kept at room temperature for 3 days. The almost solid mass was dissolved in 10% sodium hydroxide solution and the dibenzyl derivative extracted with ether. The monobenzyl derivative remained in the aqueous phase. The ether phase was dried over magnesium sulfate and evapo-

Table I. R_f Values of Carbamates and their Phenolic Hydrolysis Products

Sample ^a		Silica gel G		Cellulose 1 to 4 (v/v) methanol- water
		Ethyl ether	1 to 1 (v/v) Ethyl ether-benzene	
I and VIII	C	0.74	0.52	0.29
	P	0.81	0.67	0.30
II	C	0.34	0.26	0.44
	P	0.81	0.67	0.30
III	C	0.46	0.22	0.90
	P	0.65	0.38	0.90
IV	C	0.55	0.37	0.81
	P	0.62	0.42	0.63
V	C	0.41	0.21	0.54
	P	0.81	0.67	0.30
VI	C	0.39	0.21	0.90
	P	0.60	0.40	0.90
VII	C	0.48	0.11	0.90
	P	0.68	0.25	0.90
IX	C	0.48	0.24	0.91
	P	0.68	0.42	0.91

^a C is carbamate. P is phenolic hydrolysis product.

rated under reduced pressure, yielding a white crystalline solid. It was recrystallized from ethanol, giving 7.5 g, mp 78°C.

A Grignard solution was prepared by reacting 6.2 g of *n*-propyl bromide in 25 ml of ether with a suspension of 1.2 g of magnesium in 200 ml of ether under a nitrogen atmosphere. The mixture was cooled to 0–10°C and 8.3 g of dibenzylquinacetophenone dissolved in 100 ml of ether added over a period of 30 min. A saturated solution of ammonium chloride (25 ml) was added slowly. The ether phase was decanted, dried over magnesium sulfate, and the ether evaporated under reduced pressure. A yellow oil (9.2 g) was obtained.

A cold solution of 25 ml of concentrated HCl in 25 ml of dimethoxyethane was added to a solution of 4.5 g of the (1-hydroxyl-1-methylbutyl)dibenzylhydroquinone in 25 ml of dimethoxyethane. After a short time a lighter phase separated. The mixture was agitated for 20 hr, the phases were separated, and the aqueous phase was extracted two times with 50 ml of ether. The ether was combined with the organic phase and the solution dried over magnesium sulfate. The ether was then evaporated under reduced pressure, leaving 4.7 g of a yellow oil, which slowly solidified to give a semisolid product. The ir spectrum showed no OH peak.

Four grams of 5% Pd on charcoal (Baker) were hydrogenated in 30 ml of ethanol. Then 3.9 g of the (1-chloro-1-methylbutyl)dibenzylhydroquinone dissolved in 30 ml of ethanol was added. The hydrogen uptake was completed after approximately 4 hr. After filtration the ethanol was evaporated under vacuum and the resulting brown oil chromatographed on 10 g of silicic acid, using chloroform as the eluent. The first 30 ml was discarded and the next 230 ml contained the desired product. Approximately 1.6 g of semisolid product was obtained.

Two grams of the (1-methylbutyl)hydroquinone was dissolved in 50 ml of benzene, and a few drops of triethylamine were added. Methyl isocyanate (0.63 g) was added and the solution kept under nitrogen for 3 hr at room temperature. After stripping, the resulting brown oil showed the presence of three compounds as analyzed by tlc: starting material, monocarbamate, and dicarbamate. The monocarbamate was isolated by preparative thin-layer chromatography on

silica gel plates, 0.5 mm, run in 50% ether-benzene. The compound was faintly colored and noncrystalline. The structure of the compound was verified by nmr.

m-(1-METHYLBUTYL)PHENYL *N*-HYDROXYMETHYLCARBAMATE. This compound was prepared according to the procedure developed by Balba *et al.* (1968). It involved the catalytic hydrogenolysis of the *N*-benzyloxymethylcarbamate, prepared by reaction of the phenol with benzyloxymethyl isocyanate. The final product structure was verified by nmr.

m-(2-HYDROXY-1-METHYLBUTYL)PHENYL METHYLCARBAMATE AND *m*-(3-HYDROXY-1-METHYLBUTYL)PHENYL METHYLCARBAMATE. These compounds were prepared by reacting the respective phenols with methyl isocyanate (Kobzina, 1971).

m-(2-Hydroxy-1-methylbutyl)phenol was prepared by first benzylating *m*-hydroxyacetophenone. This was followed by a Wittig reaction with triphenylmethoxymethylphosphonium chloride. The resulting methylvinyl ether was hydrolyzed to the aldehyde, which was treated with ethyl Grignard reagent. Hydrogenation with a palladium-on-charcoal catalyst gave the desired phenolic compound.

The *m*-(3-hydroxy-1-methylbutyl)phenol was prepared by first benzylating *m*-hydroxyacetophenone. This was followed by condensation with the sodium salt of diethylcyanomethylphosphonate. The resulting nitrile was treated with methyl Grignard reagent, followed by acid hydrolysis to yield an unsaturated ketone. Hydrogenation with a palladium-on-charcoal catalyst followed by reduction with lithium aluminum hydride gave the desired phenolic compound.

Intermediate and final product structures were verified by ir and nmr.

Thin-Layer Chromatography R_f Values. The R_f values in several thin-layer systems for Bux Insecticide and the carbamate derivatives synthesized as potential metabolites are given in Table I. The R_f values of the respective phenolic hydrolysis products are also given.

Soil Metabolism. For soil fortification with a solution, a hexane or methanol solution of *m*-(1-methylbutyl)phenyl methylcarbamate-*carbonyl*- ^{14}C or *m*-(1-ethylpropyl)phenyl methylcarbamate-*carbonyl*- ^{14}C was added to the soil in small droplets with a syringe or pipet. For soil fortification with granules, a weighed quantity of granules was added to individual soil samples. The granules were prepared by coating Pikes Peak L-6 clay (15/30 mesh) with an acetone solution of *m*-(1-methylbutyl)phenyl methylcarbamate *carbonyl*- ^{14}C to give 10% (w/w) active chemical. The *m*-(1-methylbutyl)phenyl methylcarbamate *carbonyl*- ^{14}C used to coat the granules was prepared by diluting the 4.71 mCi per mM material tenfold with nonradioactive material.

For total ^{14}C accountability studies (Table III), the treated soil was placed in an Erlenmeyer flask fitted with an air inlet and outlet. Before entering the flask, the air passed through concentrated sulfuric acid, stannous chloride, and then water. After exiting the flask, the air passed through Drierite, a carbon dioxide absorber containing 8 ml of methylcellosolve 2 ml of ethanolamine, and then an absorber containing aqueous saturated barium hydroxide. The last absorber acted merely as an indicator that all of the carbon dioxide was being absorbed by the ethanolamine. The ethanolamine-methylcellosolve absorber was changed every 3 to 4 days and a 4-ml aliquot was counted. Samples of soil were removed at intervals for combustion, extraction, and moisture determination. To determine the total ^{14}C , 1 g of solid was combusted. Soil samples (10 g) were extracted twice with 50 ml of methanol for 15 min each in a Waring blender using microblender containers. The extract was filtered through granular

Table II. Chemical and Mechanical Analysis of Soils

Soil origin	% Clay	% Silt	% Sand	Soil type	Organic matter	Total cation exchange capacity Me g/100 g soil	pH
York	20	63	18	Silt loam	4.9	18.8	5.8
Nebraska Norwalk	2	93	6	Silt	5.2	27.4	6.5
Iowa							

Table III. Total ^{14}C Accountability from Metabolism of *m*-(1-Methylbutyl)phenyl Methylcarbamate Carbonyl- ^{14}C in Soil, Solution Application

Soil sample	Weeks after treatment	% of initial ^{14}C				
		Released as $^{14}\text{C-CO}_2$	Remaining in soil	Extracted with methanol	<i>m</i> -(1-Methylbutyl)phenyl methylcarbamate	Metabolite
Iowa silt fortified at 1.04 ppm	0	0	100	92	92	0
	1	33	58	48	44	5
	2	49	48	38	33	5
	3	59	35	20	17	3
	9	68	23	7	6	1

sodium sulfate into a 100 ml volumetric flask and brought to volume. The ^{14}C extracted was determined by counting 0.1 ml of the extract. Extracts were chromatographed on thin-layer plates developed in ethyl ether. Untreated soil extracts were used to co-spot standards. The chromatograms were exposed to X-ray film, the ^{14}C spots scraped off of the plate, and counted. The remainder of the plate was sprayed. Moisture content of soil samples was determined by heating 10 g of soil at 110°C overnight. All analyses were done in duplicate. The limit of detection was 1% of ^{14}C initially applied.

In the study comparing metabolism in sterile and nonsterile soil (Table IV), 20-g samples of soil were placed in individual Erlenmeyer flasks. Half of the samples were sterilized by autoclaving for three 1-hr periods at 15 psi. Samples were treated with 1 ml of $19\text{ }\mu\text{g}$ *m*-(1-methylbutyl)phenyl methylcarbamate carbonyl- ^{14}C per milliliter of sterilized water. The moisture content of the soils was adjusted to approximately 15% with sterilized water. Samples were incubated at 39°C . Initially and after 1 week samples were extracted with methanol, and the extract was counted and chromatographed as above.

To study the soil metabolism of *m*-(1-methylbutyl)phenyl methylcarbamate carbonyl- ^{14}C when applied coated on granules (Table V), 50-g samples of soil were placed in pint Mason jars and treated with 5 mg of the granules. The jars were capped and agitated to mix the treated soil. The samples were incubated at 39°C . Initially and at 2 and 4 weeks, samples were extracted with methanol and the extract was counted and chromatographed.

Chemical hydrolysis was used to help identify the ^{14}C metabolite in the soil extracts. The extract was streaked on a thin-layer plate, developed in ether, and exposed to X-ray film. The ^{14}C metabolite band was eluted from the plate using acetone and an aliquot of the acetone extract respot on a thin-layer plate. The origin of the plate was sprayed heavily with a solution containing 6 g of NaOH in 200 ml of 1 to 1 (v/v) methanol-butanol, allowed to dry, and sprayed

with 10% glacial acetic acid in ethyl ether. The remainder of the acetone extract plus carbamate and phenol standards was spotted, the plate developed in 1 to 1 (v/v) ethyl ether-benzene, and sprayed.

All soil samples were extracted twice with methanol. Recovery studies showed that methanol would efficiently extract *m*-(1-methylbutyl)phenyl methylcarbamate and its hydroxy-

Table IV. Comparison of *m*-(1-Methylbutyl)phenyl Methylcarbamate-carbonyl- ^{14}C in Sterile and Nonsterile Soil after 1 Week Incubation

Soil sample		% of initial ^{14}C		
		Extracted with methanol	<i>m</i> -(1-Methylbutyl)phenyl methylcarbamate	Metabolite
Iowa silt	Sterile	85	85	0
soil	Nonsterile	54	50	3
Nebraska silt loam	Sterile	95	95	0
soil	Nonsterile	42	40	2

Table V. Metabolism of *m*-(1-Methylbutyl)phenyl Methylcarbamate-carbonyl- ^{14}C when Applied as a Granule to Iowa Silt Soil (Fortified at 10 ppm)

Weeks treatment	% of initial ^{14}C		
	Extracted with methanol	<i>m</i> -(1-Methylbutyl)phenyl methylcarbamate	Metabolite
0	100	100	0
2	47	46	1
4	30	30	1

lated derivatives from soil. Recoveries were generally at least 80%.

RESULTS

Soil Metabolism. The soil metabolism of both isomers of Bux Insecticide was studied using carbonyl- ^{14}C -labeled material. However, after it was determined that both isomers are metabolized in the same manner, most of the work was concentrated on the major isomer. All of the tests were performed using a silt soil from Iowa or a silt loam soil from Nebraska. Both of these soils are from corn-growing areas where Bux Insecticide would be primarily used. The properties of these soils are given in Table II.

Data obtained from metabolism studies of *m*-(1-methylbutyl)phenyl methylcarbamate carbonyl- ^{14}C in the silt soil in the laboratory at ambient temperature are given in Table III. The percents of initial ^{14}C values given in Table III are based on the initial ^{14}C determined by combustion of the soil immediately after treatment. As the quantity of ^{14}C in the soil decreased, an essentially equivalent amount of ^{14}C was released as $^{14}\text{CO}_2$ and the quantity of the parent compound in the soil decreased. There was only one ^{14}C metabolite observed in the soil and it was present in only trace amounts. After 9 weeks, 23% of the initially applied ^{14}C remained in the silt soil, but only 7% was extracted, with 6% being the parent carbamate and 1% being the ^{14}C metabolite. The soil was extracted with methanol, which efficiently extracts polar compounds from soil, such as hydroxylated derivatives of the parent compound. The unextracted ^{14}C could be inorganic ^{14}C carbonates incorporated into the soil matrix.

The soil metabolism of the minor isomer of Bux Insecticide proceeds in the same manner and rate as the major isomer. A study of the silt soil fortified at approximately 1 ppm *m*-(1-ethylpropyl)phenyl methylcarbamate carbonyl- ^{14}C showed that $^{14}\text{CO}_2$ is the major ^{14}C decomposition product and only trace quantities of a ^{14}C metabolite are formed in the soil. Samples of the silt soil treated individually with each of the isomers of Bux Insecticide and incubated at 39° C in closed containers exhibited the same rate of loss for each isomer. The soil was fortified at approximately 1 ppm and showed approximately a 50% loss of each isomer in 1 week.

The ^{14}C metabolite of *m*-(1-methylbutyl)phenyl methylcarbamate in soil was identified as *m*-(1-hydroxy-1-methylbutyl)phenyl methylcarbamate. The ^{14}C soil metabolite and the latter carbamate chromatographed the same in several different chromatographic systems, using both one and two-dimensional systems. Identical R_f values were obtained on silica gel in 100% ethyl ether and in 2 to 1 (v/v) ethyl acetate-toluene and on cellulose in 1 to 4 (v/v) methanol-water. Also, the soil metabolite hydrolyzed to *m*-(1-hydroxy-1-methylbutyl)phenol as shown by thin-layer chromatography. The ^{14}C soil metabolites of both isomers of Bux Insecticide had similar R_f values; *m*-(1-hydroxy-1-methylbutyl)phenyl methylcarbamate and *m*-(1-hydroxy-1-ethylpropyl)phenyl methylcarbamate also had similar R_f values. The stability of the hydroxylated metabolite in soil is approximately the same as that of the parent compound. Silt soil treated at 1 ppm with *m*-(1-hydroxy-1-methylbutyl)phenyl methylcarbamate resulted in approximately 50% loss after 1 week.

It seemed logical that all of the volatile ^{14}C material released from the soil was carbon dioxide. However, tests were performed to confirm that this was the case and that the volatile ^{14}C material released from the soil was not partly the parent compound or a similar carbamate. Silt soil treated at 1 ppm *m*-(1-methylbutyl)phenyl methylcarbamate carbonyl-

^{14}C was gently flushed with air, which then passed through an absorber containing 10 ml of methylcellosolve and secondly through an absorber containing 2 ml of ethanolamine plus 8 ml of methylcellosolve. After 1 week, 24% of the ^{14}C applied to the soil was collected in the ethanolamine absorber, while less than 1% was collected in the first absorber containing methylcellosolve only. If the parent compound or similar carbamate were being volatilized from the treated soil, the methylcellosolve absorber would contain ^{14}C . When air was gently flushed through an absorber containing 5 μg of the ^{14}C -carbamate in methylcellosolve then through an absorber containing 2 ml of ethanolamine plus 8 ml of methylcellosolve, less than 1% of the ^{14}C was collected in the ethanolamine absorber after 1 week. The methylcellosolve absorber still contained 98% of the ^{14}C originally added to it. Also this shows that volatility is not a major cause for disappearance of the carbamate from soil. The soil was quite moist while being flushed with air. Kaufman (1967) reports moist soil is more conducive to loss by volatility than dry soil.

The decomposition of Bux Insecticide in soil is primarily due to soil microorganisms. Sterile and nonsterile soils treated at 1 ppm *m*-(1-methylbutyl)phenyl methylcarbamate and incubated at 39° C resulted in significantly different rates of decomposition of the carbamate. All soil samples contained approximately 15% moisture and were treated with a sterile water solution. It is seen in Table IV that the nonsterile soils contained only 40 to 50% of the parent compound after 1 week, while the sterile soils contained 85 to 95%. Also traces of the ^{14}C metabolite were present in the nonsterile soils, which were not present in the sterile soils.

All of the above studies were performed by treating the soil with a solution of the carbamate. In actual field practice, granules coated with Bux Insecticide are added to the soil. Bux Insecticide coated on granules decomposes more slowly in soil than when applied as a solution directly to the soil. However, the slower rate of decomposition does not give a different metabolism route. Silt was treated with *m*-(1-methylbutyl)phenyl methylcarbamate carbonyl- ^{14}C coated granules and incubated at 39° C. The results, given in Table V, show that the metabolic path with a granular application is the same as with a solution application. After 4 weeks, 70% of the parent compound had decomposed and the soil contained only one ^{14}C metabolite that was extractable with methanol. The metabolite was equivalent to only 1% of the initially applied ^{14}C and was *m*-(1-hydroxy-1-methylbutyl)phenyl methylcarbamate.

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