Table I. Comparison of Results from MID and Electron Capture GLC Methods for a Series of Benefin and Trifluralin Soil Residues

Sample no.	MID assay, ppm			Electron capture-GLC,[a] ppm
	Benefin	Trifluralin	Total	Total
1	0.026	0.038	0.06	0.07
2	0.010	0.025	0.04	0.04
3	0.012	0.014	0.03	0.025
4	0.016	0.050	0.07	0.08
5	<0.01	<0.01	<0.01	<0.01
6	0.018	0.018	0.04	0.04
7	0.010	0.01	0.02	<0.01
8	<0.01	<0.01	<0.01	<0.01

[a] Not able to determine individual levels.

total benefin and trifluralin residue levels in sandy loam and sandy soil is obtained, only the MID method giving individual benefin and trifluralin residues. Although eight replicate injections of a standard solution indicate the internal standard method (coefficient of variation = 1.7%) is considerably more precise than the alternative method (benefin, coefficient of variation = 3.4%; trifluralin, coefficient of variation = 2.0%), both methods are satisfactory for the analysis of soil residues. A further indication of the selectivity of the MID approach can be seen by comparison of a GLC and MID output (Figure 2). No decrease in sensitivity or deterioration in column performance was observed during use of the assay. In consequence it can be expected that residue samples for MID analysis will need less cleanup than those for electron-capture GLC analysis and include sample extracts too impure to assay by GLC.

A more general application of quantitative mass spectrometry to crop residue analysis is limited by cost. As both chromatographic and sample workup times are reduced by the MID method, the technique is very suitable for laboratories handling large numbers of samples. In our hands the mass spectrometer is more reliable and less susceptible to contamination than is a gas chromatograph fitted with an electron-capture detector. Short retention times, minimal delay for elution of highly retentive peaks, and less sample cleanup are all factors contributing to a faster assay turnover. The assay has been used successfully over a period of several months.

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Volatilization and Photodecomposition of Plictran Miticide

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Recently, a new organic tin product, Plictran miticide containing tricyclohexyltin hydroxide, has been developed for the control of mites in apples, pears, and citrus fruits. Photodecomposition and volatility studies were conducted with this miticide. The results indicate that tricyclohexyltin hydroxide rapidly undergoes photodecomposition, the main products being inorganic tin (80%) with traces of dicyclohexyltin oxide, cyclohexylstannoic acid, and tricyclohexyltin hydroxide unchanged. The traces of tetracyclohexyltin which were present in the samples as an impurity were not affected by irradiation. The amount of tricyclohexyltin hydroxide depends on the length of exposure and the intensity of the sunlight. The longer the exposure and the more intense the light the more tricyclohexyltin hydroxide will be decomposed. Volatility studies indicate that tricyclohexyltin hydroxide is not volatile from the dry state, but that the compound can be lost from a moist surface by co-distillation. The rate at which the miticide will be lost depends on the temperature and quantity of water evaporated. The dicyclohexyltin oxide is volatile from the dry state and can co-distill with water.

Plictran miticide, a new product containing tricyclohexyltin hydroxide, recently has been introduced and found to be extremely effective for the control of plant feeding mites, yet not harmful to predacious mites. The commercial applications of this miticide are for apples, pears, and citrus fruits (Kenaga, 1966; Allison et al., 1968).

The miticide is sprayed onto the trees and thus deposited on the surfaces of the leaves and fruit. Under these conditions, the chemical is subjected to photodecomposition by the sunlight irradiation and to the environmental conditions which will influence the volatility of the compound.

Studies were undertaken to determine how rapidly this miticide would undergo photodecomposition and how rapidly it could be lost from the surfaces of leaves and fruit by volatilization. In the initial studies with this miticide, it was found that part of the products formed by photodecomposition were insoluble and could not be easily removed from various surfaces. To account for this insoluble residue, it was necessary to combust the tissue and to determine the tin by colorimetric methods. This was a very time-consuming operation and did not indicate what chemical form the tin was present in on the surface of the fruit. It was also difficult to determine the true tin blank. To overcome these difficulties, a glass slide technique was employed using radioactive tricyclohexyltin-^{119}Sn hydroxide. The ^{119}Sn isotope was used instead of the ^{113}Sn

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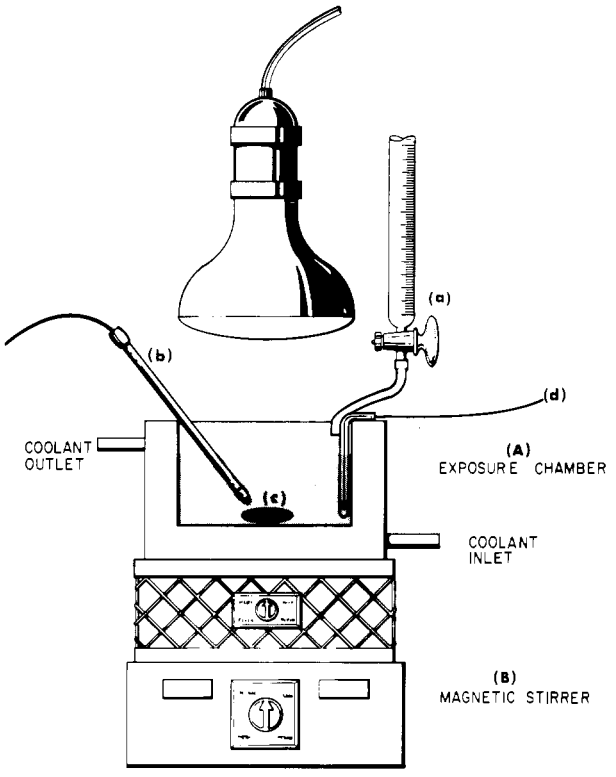

Figure 1. Exposure chamber.

to minimize the problems with radioactive decay and the number of radioactive daughter isotopes which could be formed. With the radioactive compounds it was possible to count the slides and determine the amount of compound present, even though it was not possible to extract the compounds from the slide.

EXPERIMENTAL SECTION

The radioactive labeled compound was prepared by New England Nuclear Corporation using ^{119}Sn. The compound was a white powder which had a specific activity of 0.26 mCi/g. Chromatographic analysis (Smith, 1976) indicated that the compound contained 95.8% tricyclohexyltin hydroxide, 2.4% dicyclohexyltin oxide, 0.3% monocyclohexylstannoic acid, 0.8% tetracyclohexyltin, and 0.7% inorganic tin.

Pyrex glass slides (1 × 4 cm) were used in the photodecomposition studies. These slides were small enough to be placed directly into the scintillation vials for counting. The slides were thoroughly cleaned by allowing them to stand overnight in chromate cleaning solution, washed in water, and allowed to stand overnight in saturated sodium bicarbonate. The slides were then washed with distilled water and allowed to stand overnight in distilled water. The slides were dried in an oven at 100 °C.

Two types of slides were used; in one series the slides were coated on one side with a chloroform solution of the radioactive tricyclohexyltin-^{119}Sn hydroxide. A measured amount of the solution was applied to each slide and spread uniformly over the surface of the slide.

In the second series, the slides were first coated with the waxy material off the surface of apples. The waxy material was obtained by extracting whole apples with *n*-hexane. The hexane solution was concentrated by flash evaporation until the majority of the hexane was removed. The slides were repeatedly dipped into the concentrated wax solution until they were completely covered as indicated by physical observations. The tricyclohexyltin hydroxide was applied to these slides using a methanol solution without disturbing the waxy coating on the slide. The slides were placed in the exposure chamber shown in Figure 1. In this chamber the slides were exposed to a contant source of light white being maintained at a constant temperature and relative humidity. A G.E. sunlamp was used. Triplicate slides were removed at each time interval. The slides were first extracted with a solution of 5% glacial acetic acid in *n*-hexane. This extraction removed the organic tin compounds and part of the inorganic tin compounds. The activity remaining on the slide was inorganic tin, which could only be removed with concentrated sodium hydroxide. In this investigation, the inorganic tin on the slides was determined by direct counting rather than by the sodium hydroxide extraction procedure.

Table I. Identification of Tin Compounds on Thin-Layer Chromatography Sheets by Color Formation

Compounds	Structure	Color with diphenylthiocarbazone	$R_f \times 100$[a]
Tricyclohexyltin hydroxide	$(C_6H_{11})_3SnOH$	Yellow	40
Dicyclohexyltin oxide	$(C_6H_{11})_2SnO$	Orange	30
Cyclohexylstannoic acid	$C_6H_{11}SnOOH$	Salmon-pink	5
Tin tetrachloride	$SnCl_4$	Pink	0
Tin oxide	SnO_2	White	0

[a] Silica gel plates with solvent system of 5% acetic acid in hexane.

The hexane extract was concentrated to a few milliliters and spotted on Eastman silica gel Chromagram sheets No. 6060, which contained a fluorescent indicator. The sheets were developed in an Eastman Chromagram development apparatus using a solution of 5% glacial acetic acid in *n*-hexane. Each sheet was developed three times to give complete separation of the compounds. After air drying, the sheets were viewed under uv light (2540 Å) to locate the spots. The spots were marked and autoradiographs prepared of each sheet to locate the radioactive spots. The radioactive spots were marked and the sheets sprayed with a solution of 20 mg of diphenylthiocarbazone (Eastman No. 3092) in 100 ml of chloroform and 2 ml of glacial acetic acid. When the sheets were air dried, each compound gave a characteristic colored spot (Table I) (Smith, 1975).

The radioactive spots were then cut from the sheet and placed in scintillation vials for counting. The scintillation solution used for counting contained 0.3 g of POPOP (1,4-bis[2-(5-phenyloxazolyl)]benzene) (scintillation grade), 6 g of PPO (2,5-diphenyloxazole) (scintillation grade), 30 g of naphthalene, 100 ml of Cellosolve ether, and 500 ml of dioxane. The samples were counted in a Nuclear-Chicago Corporation scintillation system Mark II with an external standard. All counts were corrected for background, efficiency, quenching, etc.

After the slides had been extracted, they were air-dried and placed directly in the scintillation vials for counting, to determine the amount of the radioactive compounds still remaining on the slides.

The R_f values of the various decomposition products gave a partial identification of the various products. Further identification was obtained by spraying the sheets with the diphenylthiocarbazone reagent. By combining R_f values, color reactions, and radiochemical analyses, it was possible to obtain both a positive identification of each compound as well as a determination of the amount present.

In the volatility studies, two techniques were employed. Radioactive tricyclohexyltin hydroxide, dicyclohexyltin oxide, or cyclohexylstannoic acid was dissolved in chlo-

roform and plated out in the concavities of a microscope slide. The slides were then placed in a Meseran instrument and counted. The slides were stored at room temperature and counted every 3 to 4 days for a period of 100 days. Radioactive tricyclohexyltin hydroxide was added to the commercial formulation of the miticide; a sample was plated on the glass slide which was also counted at various time intervals for 100 days.

The Meseran instrument used in these studies is based on the principle of an internal flow counter in which the sample is placed inside the counting tube with a constant flow of counting gas. In studying the volatility of compounds with the Meseran instrument, there are several steps which must be taken to ensure obtaining satisfactory results. It is first necessary to use a pure compound. Secondly, the sample must be counted over a sufficient period of time so that it is possible to distinguish the loss of the compound by volatilization and adsorption on the glass slide. Finally, it is necessary to recover the sample from the slide to determine if decomposition has occurred during the operation. The breakdown products may be more volatile than the parent compound. In the present studies, the radioactive compounds were produced by photodecomposition of the tricyclohexyltin hydroxide. The individual compounds were then separated by solvent distribution and further purified by TLC. The radiochemical purity was determined by TLC combined with scintillation counting. The chemical form and purity were determined by ir and mass spectroscopic analyses to ensure that the compounds were in the correct chemical form.

In the present studies the radioactive compound obtained from New England Nuclear Corporation contained about 5% impurities. These impurities were removed by chromatographing the sample repeatedly on an Eastman Silica Chromagram sheet using a solvent system containing 5% acetic acid in hexane. When no other compound besides the tricyclohexyltin hydroxide could be detected it was assumed that the compound was pure enough for these studies.

The other derivatives were obtained by irradiating a sample of the tricyclohexyltin hydroxide and separating the components by TLC chromatography using the procedure described above. All the samples were checked by ir and mass spectroscopic methods to be sure that the compounds were in the correct chemical form. At the conclusion of the experiment, the samples were again checked for chemical and radiochemical purity.

From time to time, there have been speculations that if a compound is mixed with water and the water is allowed to evaporate off, some of the compound will pass off with the water even though the compound itself does not show any significant amount of volatility. This possibility was checked with the tricyclohexyltin hydroxide by placing a small aliquot of a methanol solution of the miticide in scintillation vials, adding water, and allowing the water to slowly evaporate off. Once the sample was dry, it could be counted and the loss of the tricyclohexyltin hydroxide determined.

RESULTS AND DISCUSSION

The rate of decomposition of tricyclohexyltin hydroxide by light is indicated in Figures 2 and 3. Figure 2 shows the results obtained when the miticide was placed directly on the glass slide. The results are given in terms of the numbers of hours of irradiation. A 1-h irradiation would correspond roughly to 1 day of irradiation in a sunny climate.

It is apparent from Figure 2 that the tricyclohexyltin hydroxide was being broken down via the dicyclohexyltin oxide and cyclohexylstannoic acid to inorganic tin. The dicyclohexyltin oxide appeared to be accumulating during the first 8–10 h of the irradiation. By this time the majority of the tricyclohexyltin hydroxide (65%) has disappeared. The quantity of the dicyclohexyltin derivative then decreased until a constant level was obtained between 20 and 30 h of irradiation. The cyclohexylstannoic acid increased during the first 10 h and then remained constant throughout the observation period. The tetracyclohexyltin was present as an impurity in the original compound.

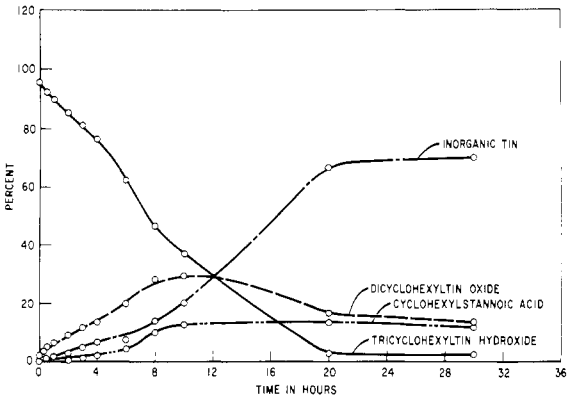

Figure 2. Decomposition of tricyclohexyltin hydroxide by uv light. Glass slides.

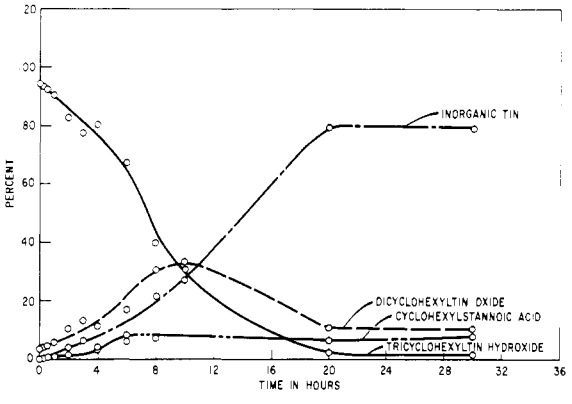

Figure 3. Decomposition of tricyclohexyltin hydroxide by uv light. Glass slides with apple wax coating.

The presence of apple wax on the slide did not have any significant effects on the breakdown of the tricyclohexyltin hydroxide (Figure 3).

The results obtained indicate that the tricyclohexyltin hydroxide undergoes photodecomposition, the main breakdown product being inorganic tin (80%) with trace quantities of the dicyclohexyltin oxide (10%) and the cyclohexylstannoic acid (5%). There were still traces of the tricyclohexyltin hydroxide (4%) and the tetracyclohexyltin (1%) which was present as an impurity in the original sample.

The results obtained from the field with apples indicated a similar pattern of decomposition. The tricyclohexyltin hydroxide slowly decomposes with the formation of inorganic tin, the dicyclohexyltin oxide and cyclohexylstannoic acid derivatives. The amount of tricyclohexyltin hydroxide decomposed will depend on the intensity of the light and the length of the irradiation. In the laboratory this can be demonstrated by changing the height of the light source. The intensity of the light decreased as the square of the distance from the light to the slide. The rate of breakdown of the tin compounds showed a similar relationship. The lower the light intensity the slower the rate of decomposition. The longer the irradiation the more

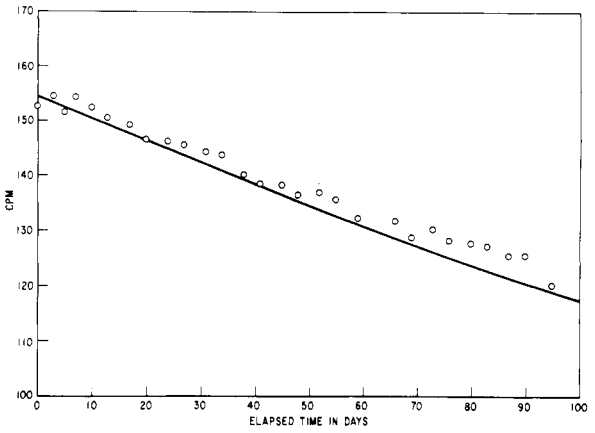

Figure 4. Volatility of tricyclohexyltin-^{119}Sn hydroxide.

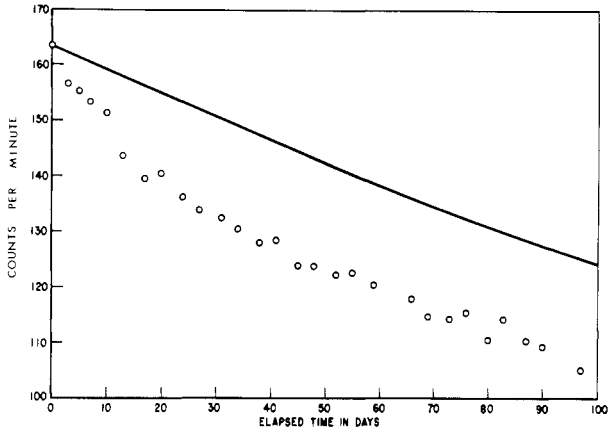

Figure 5. Volatility of dicyclohexyltin-^{119}Sn oxide.

tricyclohexyltin hydroxide decomposed.

The effects of light intensity were also observed in the field. Apples obtained from Midland, Mich. showed about half as much decomposition of the miticide on the surface of the apples as was observed with apples obtained from California. The days in Michigan were generally overcast with low light intensity while the California apples were exposed to long days of intense sunlight.

The volatility of the organic tin compounds was determined by means of the Meseran instrument.

The results obtained with the tricyclohexyltin hydroxide and the dicyclohexyltin oxide are shown in Figures 4 and 5. Since these studies were conducted with ^{119}Sn-labeled compounds, there will be a gradual decrease in observed count due to radioactive decay. The ^{119}Sn isotope has a radiochemical half-life of 275 days. In Figures 4 and 5, the theoretical decay of the isotope is indicated by the solid line while the observed count is given as individual points. It can be seen that the decay curve is essentially the same as the curve which could be drawn through the observed counts for the tricyclohexyltin-^{119}Sn hydroxide. This indicates that there was no significant loss of the tin compound by volatility over the observation period of 100 days (Figure 4).

With the dicyclohexyltin-^{119}Sn oxide, the curve obtained from counting the sample dropped below the theoretical decay curve, indicating some loss of the compound due to volatilization. The loss in count indicates about a 10% loss of the dicyclohexyltin oxide due to volatilization (Figure 5). In volatilization studies with the Meseran instrument, it has been observed that there is an initial drop in the counting rate during the first part of the exposure. The curve then tends to approach the same slope as the theoretical curve. This change in slope has been shown to be

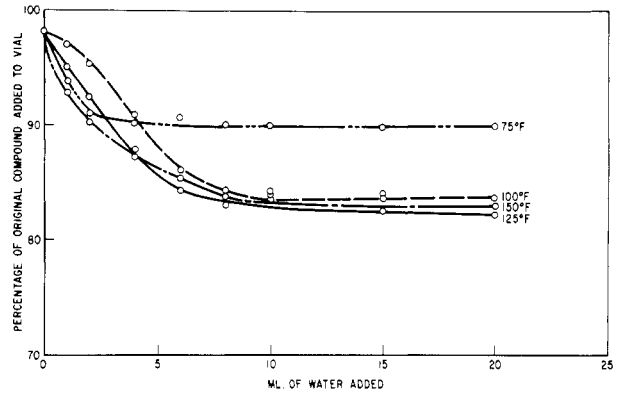

Figure 6. Co-distillation of tricyclohexyltin hydroxide with water.

due to the adsorption of the compound onto the glass slide. This was checked with each determination by identifying the material remaining on the slide and by determining the total amount of radioactivity before and after the exposure. With the tricyclohexyltin hydroxide, there were no breakdown products and the decrease in radioactivity could be accounted for by decay.

In the case of the dicyclohexyltin-^{119}Sn oxide only the parent compound was found on the slide. When a large quantity of the dicyclohexyltin oxide was placed on the slide, approximately 50% of the compound was lost in 16 days indicating a loss by volatilization.

With monocyclohexylstannoic-^{119}Sn acid, the results obtained were similar to those obtained with the tricyclohexyltin hydroxide and indicated no significant loss of the compound due to volatilization.

It has been known for many years that compounds which have low volatility can be co-distilled with other solvents (Audus, 1964; Fang et al., 1961; Hollingsworth and Ennis, 1953). Since this tin miticide will be applied to fruit trees as a water suspension, some of the miticide will undoubtedly fall on the soil. Under such conditions some of the miticide on soil particles might be transferred to bodies of water by environmental factors such as erosion. It was therefore desirable to determine if the tricyclohexyltin hydroxide would co-distill with water. The extent of co-distillation was determined by placing known amounts of the tricyclohexyltin hydroxide in scintillation vials and adding various amounts of water. The samples were then taken to dryness in an oven at various temperatures. The results of these studies are shown in Figure 6. There was loss of tricyclohexyltin-^{119}Sn hydroxide which was influenced both by temperature and quantity of water. As the quantity of water was increased from 0 to 10 ml, there was an increase in the amount of compound lost. Similarly, as the temperature was increased from 75 to 100 °F there was an increase in the amount of compound lost. Temperatures above 100 °F did not appear to have any effects.

Thin-layer chromatographic analyses of the material remaining in the vial showed the presence of dicyclohexyltin oxide and monocyclohexylstannoic acid. The presence of these latter two compounds indicates that there has been some decomposition of the parent compound.

From these exploratory studies it appears that there are at least two ways that the tricyclohexyltin hydroxide might be lost from a water solution. The compound could be lost by co-distillation with part of the compound being broken down, or the tricyclohexyltin hydroxide may be breaking down and the breakdown products lost by co-distillation. The water coming off the solution was trapped and analyzed for tin compounds; the tricyclohexyltin hydroxide and the dicyclohexyltin oxide were found in the vapors.

Thus, both the parent compound and at least one of its breakdown products can be lost by co-distillation.

The leveling off of the radioactivity in the vials after the water had been removed (see Figure 6) can be explained on the basis of adsorption of the compounds on the surface of the glass and the formation of dry water insoluble decomposition products.

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Degradation and Metabolism of Drepamon in Rice and Barnyard Grass

Romano Santi and Franco Gozzo*

The fate of $C_6H_5{}^{14}CH_2SCON\text{-}(sec\text{-}C_4H_9)_2$ ([^{14}C]Drepamon), applied in preemergence to overspreading water, was investigated in a system including soil, water, and rice plants. A product of microbiological oxidation was isolated from both water and plants and identified as $HOOC^{14}CH_2SCON\text{-}(sec\text{-}C_4H_9)_2$, whose formation was strictly related to the presence of soil. Among the metabolites of [^{14}C]Drepamon two compounds were identified by cochromatography with its chemical oxidation products as $C_6H_5{}^{14}CH_2S(O)CON\text{-}(sec\text{-}C_4H_9)_2$ and $C_6H_5{}^{14}CH_2S(O)_2CON\text{-}(sec\text{-}C_4H_9)_2$. The former showed unspecific herbicidal activity when applied to demineralized water as the only growing medium for both rice and barnyard grass. The selective action of Drepamon appeared to be unrelated to the level of this metabolite in the plant as a whole and is better explained in terms of different absorption and metabolism of the herbicide in the crop with respect to the weed.

S-Benzyl *N*,*N*-di-*sec*-butylthiolcarbamate (Drepamon) is a new herbicide developed for the selective control of barnyard grasses (*Echinochloa crusgalli* (L.) Beauv. and *Echinochloa colonum*) in rice (*Oryza sativa* L.). Although its recommended dosage in both pre- and postemergence treatments is 4 kg/ha, it appeared not to adversely affect most varieties of rice even at 15 kg/ha, under laboratory conditions (Arsura, 1972).

The present work was undertaken to investigate its fate in each of the components of the ternary system water–soil–crop, under conditions simulating a flooded paddy field. The finding that a metabolite of Drepamon had high, although unspecific, herbicidal activity prompted us to extend part of the work to a differential study in barnyard grass and rice, under various conditions, and contributed to the discovery of a new class of herbicides (Santi et al., 1974; Gozzo et al., 1975). Similar approaches and advances were at the same time independently followed by Stauffer researchers and Casida et al. (1974).

Soil degradation and plant metabolism of thiolcarbamates have received moderate attention, so far. All the works published point out a hydrolytic cleavage of the sulfur–carbamoyl bond as the main pathway together or after N-dealkylation (Kearney and Kaufman, 1969). The last reported study with *S*-(4-chlorobenzyl)-*N*,*N*-diethylthiocarbamate (Benthiocarb) did not add anything to change this picture (Ishikawa et al., 1973).

However, when the present work had already been concluded, Casida et al. anticipated evidence in favor of sulfoxidation of thiolcarbamate herbicides as an intermediate step of their metabolism both in the liver of mice (Casida et al., 1975) and in plants (Lay et al., 1975). Their attempts to show the presence of the corresponding sulfoxide in the liver of Benthiocarb-treated mice failed.

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MATERIALS AND METHODS

$C_6H_5{}^{14}CH_2SCON\text{-}(sec\text{-}C_4H_9)_2$ ([^{14}C]Drepamon) had a specific activity of 45 μCi/mg with a radiochemical purity higher than 98%. It was always applied as a 70% liquid formulation. Authentic samples of the following compounds were used to identify the degradation products of Drepamon: *N*,*N*-di-*sec*-butylcarbamoylthiolglycolic acid (compound A), obtained as described later; benzyl *N*,*N*-di-*sec*-butylcarbamoyl sulfoxide (B) and benzyl *N*,*N*-di-*sec*-butylcarbamoyl sulfone (C), prepared by oxidation of Drepamon according to a method previously described (Santi et al., 1974); dibenzyl disulfide (D), a commercial sample.

Preparation of A. Sodium hydroxide (24 g, 0.6 mol) in water (20 ml) was added to a solution of thiolglycolic acid (27.6 g, 0.3 mol) in benzene (300 ml) and the water was removed by azeotropic distillation. To the vigorously stirred boiling slurry di-*sec*-butylcarbamoyl chloride (57.5 g, 0.3 mol) was added dropwise and the mixture was kept under reflux for 4 h and then cooled and treated with water (300 ml). The aqueous layer was separated, acidified with 5 N hydrochloric acid, and extracted with dichloromethane (2 × 100 ml). The combined extracts were washed with water (300 ml), dried (Na_2SO_4), and evaporated under reduced pressure to give a yellowish oil (23.0 g). This was then dissolved in 1 N sodium hydroxide (450 ml), the resulting solution was extracted with 1-butanol (450 ml), and on evaporation of the latter a solid was obtained that was taken up with an excess of 1% hydrochloric acid. The mixture was extracted with diethyl ether (70 ml), the solvent was evaporated, the residue was dissolved in