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Photolysis of Methyl 2-Benzimidazolecarbamate

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Methyl 2-benzimidazolecarbamate (MBC), as a residue on silica gel G, was exposed to sunlight for 30 h. More than 90% of the compound was recovered. MBC in dilute aqueous solution was exposed to sunlight and to light from UV lamps. Less than 10% of the MBC was lost on exposure to sunlight for 40 h, while greater loss occurred if riboflavin or acetone was added to the solution. Photooxidation of the benzene ring of MBC was the predominant reaction detected. Guanidine, carbomethoxyguanidine, and carbomethoxyurea were detected among the photolysis products. MBC was applied to the leaves of corn plants and the plants exposed to sunlight for 18 h. No photolysis products were detected in extracts of the plants.

The benzimidazole fungicides have been shown to be outstanding agents in disease control. An important member of this group of pesticides is benomyl (methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate). This substance decomposes in aqueous solution (Clemons and Sisler, 1969; Krupka, 1974), soil (Baude et al., 1974; Siegel, 1975), plants (Sims et al., 1969; Peterson and Edgington, 1970; Fuchs et al., 1972; Siegel and Zalbia, 1972; Baude et al., 1973), and animal tissue (Gardiner et al., 1968, 1974) to yield another fungitoxic substance, methyl 2-benzimidazolecarbamate (MBC). The decomposition to MBC is also accelerated by sunlight (Kilgore and White, 1970). Clemons and Sisler (1969) considered MBC to be primarily responsible for the fungitoxicity of benomyl preparations. Another fungicide, thiophanate-methyl (1,2-bis(3-methoxycarbonyl-2-thioureido)benzene) also decomposes rapidly in the environment to form MBC (Selling et al., 1970; Vonk and Kaars Sijpesteijn, 1971; Noguchi, 1971; Soeda et al., 1972a,b; Fuchs et al., 1972; Buchenauer et al., 1973; Fleeker et al., 1974).

The metabolism and persistence of MBC have been studied in plants (Siegel, 1973; Ben-Aziz et al., 1974) and soil (Fleeker et al., 1974). In plant and animal tissue, benomyl and MBC show a resistance to cleavage of the methyl carbamate moiety. The benzimidazole ring and methyl carbamate group are slowly destroyed in soil.

Watkins (1974) has reported data on the photolysis of MBC suspended in methanol and exposed to ultraviolet light. After 4 days of exposure, several photodecomposition products were identified in the photolysate. These were: dimethyl oxalate, guanidine, carbomethoxyguanidine, and dicarbomethoxyguanidine. The data reported here concern the photolysis of MBC in dilute aqueous solutions, on corn plants, and as a residue on silica gel TLC plates.

EXPERIMENTAL SECTION

Chemicals. MBC-2-^{14}C-*methyl*-t_3 was prepared from thiourea-^{14}C and methyl-t_3 chloroformate by the procedures of Loux (1961). Methyl-t_3 chloroformate was prepared from methanol-*t* and phosgene (Soeda et al., 1972c). Radiochemical purity by thin-layer chromatography was greater than 99% and specific activity was 7.21 μCi of ^3H/mg and 0.61 μCi of ^{14}C/mg. Samples of MBC, 2-aminobenzimidazole, 4-hydroxy-MBC, and 5-hydroxy-MBC were provided by E.I. duPont de Nemours and Co., Inc., Biochemicals Department, Wilmington, Dela. Carbomethoxyguanidine and dicarbomethoxyguanidine were prepared by the methods of Junod (1952). Carbomethoxyurea was prepared using the procedure described by Dains and Wertheim (1920).

Equipment. Samples were assayed for ^{14}C and ^3H in a Nuclear-Chicago scintillation counter (Model 6847). Samples expected to show quenching when assayed for radioactivity in this manner were first combusted in a Harvey biological oxidizer. The $^{14}CO_2$ formed on oxidation was collected and assayed in a solution of 500 ml of toluene, 350 ml of methyl Cellosolve, and 150 ml of redistilled ethanolamine containing 5 g/l. PPO (2,5-diphenyloxazole) and 0.5 g/l. dimethyl-POPOP (1,4-bis[2-(5-phenyloxazolyl)]benzene). The ^3H_2O resulting from oxidation was collected and assayed in a solution of one part of Triton X-100 and two parts of toluene containing 5 g/l. PPO and 0.5 g/l. dimethyl-POPOP. A Rayonet Photoreactor, equipped with ten 350-nm lamps, was used in some of the photolysis experiments.

Chromatography. Several solvent systems were used to develop thin-layer chromatograms. For silica gel TLC plates the following solvents were used: *p*-dioxane–formic acid (10:1, v/v), acetone–concentrated NH_3 (97:3, v/v), and ethyl acetate–*p*-dioxane–methanol–concentrated NH_3 (160:20:5:0.5, v/v/v/v). Alumina TLC plates were developed with acetone–concentrated NH_3 (97:3, v/v). Chromatograms of Whatman No. 1 paper were developed (ascending) with 1-butanol–acetic acid–water (120:30:50, v/v/v). At least three of these solvent systems were used in each chromatographic analysis. Radioactivity on chromatograms was detected by cutting the paper or scraping the thin-layer chromatograms in sections and placing the individual sections or scrapings in vials for assay in the scintillation counter. In the chromatography

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of picrates it was advantageous to oxidize the chromatogram strips and collect the ^3H_2O and $^{14}CO_2$ for assay. MBC and 2-aminobenzimidazole were visually detected with UV light on chromatograms containing fluorescent indicator. The urea and guanidine derivatives were visually detected with the diacetyl reagent (Jackson, 1962) or the hypochlorite reagent (Jackson and Moss, 1962).

Photolysis of MBC on TLC Plates. MBC-2-^{14}C-*methyl*-t_3 in acetonitrile was streaked on silica gel TLC plates within an area of 2.0 cm^2. A total of 11.0 μg of the fungicide was placed within this area. The plates were exposed to sunlight 6 h between 0900 and 1500 h on clear or partly cloudy days during July in eastern North Dakota. Plates wrapped in aluminum foil served as dark controls. Loss of radioactivity from the plates was determined by scraping the silica gel containing the fungicide from the plates and measuring the ^{14}C and ^3H in a scintillation vial. Some plates were chromatographed to check for nonvolatile decomposition products.

Photolysis of MBC in Solution. MBC-2-^{14}C-*methyl*-t_3 was dissolved in water to a concentration of 2.0 μg/ml. In each of eight beakers was placed 1500 ml of the MBC solution. In two beakers 7.5 mg of riboflavin was dissolved and in two other beakers 7.5 ml of acetone (redistilled) was added. In the remaining four beakers no further additions were made; however, two of these flasks were wrapped in aluminum foil to serve as dark controls. The flasks were exposed to direct sunlight between 0900 and 1500 h on clear days. When not exposed to sunlight the solutions were kept at 4 °C in the dark. Volumes were maintained by the addition of distilled water. Aliquots (2.0 ml) were removed and evaporated in scintillation counting vials in a forced-air oven at 40 °C. The residue was assayed for radioactivity. Aliquots (20–50 ml) were also removed and concentrated for chromatography.

Sunlight Irradiation of MBC on Corn Plant Leaves. Corn plants (*Zea mays*) were grown in vermiculite in a growth chamber until 10 days old. An 18-h photoperiod was maintained and the temperature was 32 °C during the photoperiod and 28 °C in the dark. Half-strength Hoagland's solution was used to water the plants and supply inorganic nutrients (Hoagland and Arnon, 1938). A solution of MBC-2-^{14}C-*methyl*-t_3 (1.0 mg/ml of 0.01 N HCl in 50% EtOH) was prepared and 10 μl of the solution streaked on the outer half of the second leaf on each plant. Two replicates of 25 plants each were placed in direct sunlight between 0900 and 1500 h for three clear days during July. Two additional replicates served as shaded controls. These were protected from sunlight with a tent of aluminum foil. The plants remained in the dark between exposure periods.

The treated leaves were excised and dipped in diethyl ether for 15 s to remove leaf surface components (Martin and Batt, 1958). The leaves were then frozen and stored at −20 °C until extraction. The untreated leaves, stems, and roots were also frozen and stored until extraction. Aliquots of the ether extract were removed for chromatography and measurement of radioactivity. The remaining solution was taken to dryness and the residue taken up in equal volumes of chloroform and water by vigorous stirring. Essentially all the radioactivity was in the chloroform phase.

The plant tissue was homogenized in 95% ethanol acetone (7:3, v/v) and the homogenate filtered by suction through paper (Whatman No. 1). The filtrate was chromatographed and assayed for ^3H and ^{14}C. Filtrates containing greater than 1% of the radioactivity applied were taken to dryness and the residue was stirred thoroughly with a mixture of water and chloroform (1:1, v/v). Essentially all the radioactivity remained in the chloroform phase.

Detection of Photolysis Products. Aqueous solutions (1600 ml) of MBC-2-^{14}C-*methyl*-t_3 (3.0 μg/ml) and riboflavin (5 mg/ml), in a 2-l. Pyrex beaker, were exposed 12 h to UV lamps (350-nm emission maximum), in the photoreactor. After photolysis, aliquots were removed, taken to dryness, and assayed for ^{14}C and ^3H. Suspected photolysis products in the remaining solutions were estimated by reverse isotope dilution.

A weighed amount (50–100 mg) of the compound to be determined by reverse isotope dilution was dissolved in a portion of the photolysate. These substances were: guanidine carbonate, carbomethoxyguanidine nitrate, dicarbomethoxyguanidine nitrate, and 2-aminobenzimidazole. The solution was concentrated to 30–50 ml by evaporation at 40 °C under reduced pressure. The pH at this stage was adjusted to 6–7, if necessary. The concentrate was then extracted three times with 20-ml portions of chloroform. For the determination of guanidine, carbomethoxyguanidine, and 2-aminobenzimidazole, the aqueous solution was taken to dryness and the residue taken up in about 10 ml of methanol. The methanol solution was centrifuged to remove suspended material and diluted with an equal volume of a saturated solution of picric acid in methanol. The picrate which formed was recrystallized repeatedly from small volumes of boiling water until a constant specific activity was reached. Identity of the picrate was checked by melting point and mixture melting point. Usually three to four recrystallizations resulted in constant specific activity. The picrates were chromatographed by streaking ethanolic solutions of the picrates (dissolved with the aid of a few drops of 2 N HCl) on paper or TLC plates, exposing the spots to ammonia vapor, and then developing with solvent. Chromatography was used to detect radioactive impurities. When MBC appeared to be present in the picrates as a contaminate, the picrate sample was discarded and the analysis carried out again with fresh photolysate until the sample was free of MBC. The chloroform extraction reduced this source of contamination. The use of dual-isotope label in the fungicide aided in the identification of certain radioactive contaminates. Thus, the isolated guanidine picrate could be checked for contamination by the presence of ^3H in the sample.

The determination of dicarbomethoxyguanidine differed from the determination of guanidine and carbomethoxyguanidine in that most of the substance was extracted into the chloroform phase. The chloroform solution was subsequently taken to dryness and the residue recrystallized from small volumes of water (4–8 ml). The compound was identified by melting point, mixture melting point, and IR spectra.

A different isolation procedure was used for estimation of MBC by reverse isotope dilution. A weighed amount of nonradioactive MBC (60–80 mg) was dissolved in 0.1 N HCl and this solution added to a photolysate sample. The resulting solution was concentrated to 10 to 15 ml and adjusted to pH 5–6 with 6 N aqueous NH_3. The resulting MBC precipitate was recrystallized once with acetonitrile, then recrystallized several times by dissolving in dilute HCl and neutralizing the solution with 6 N NH_3. Identity of the product was checked by melting point, mixture melting point, and IR spectra. Radiochemical purity was determined by chromatography.

The detection of $^{14}CO_2$ in the photolysate was also determined by reverse isotope dilution. Immediately after

Table I. Radioactivity Remaining after Exposure of MBC-2-^{14}C-*methyl*-t_3 on Silica Gel G TLC Plates to Sunlight

Expos. time, h	Radioact. remaining		
	^{14}C, dpm	^{3}H, dpm	^{3}H/^{14}C
0	14 800	175 000	11.8
6	14 300	175 000	12.2
12	14 300	175 000	12.2
18	13 900	174 000	12.5
24	14 200	172 000	12.1
30	13 500	166 000	12.3
Dark control	14 800	175 000	11.8

photolysis, 100 mg of $NaHCO_3$ and 5 ml of 0.1 N CO_2-free NaOH were added and dissolved in the photolysate. The resulting solution was concentrated to 40–50 ml by evaporation under reduced pressure. The concentrate was extracted three times with 20-ml portions of chloroform and then diluted with an equal volume of $Ba(OH)_2$ (saturated aqueous solution). The resulting $Ba^{14}CO_3$ precipitate was collected by filtration and washed with water. The $Ba^{14}CO_3$ was converted to $^{14}CO_2$ in a small flask by addition of 6 N HCl and the gas was swept into a $Ba(OH)_2$ collection train with N_2. The $Ba^{14}CO_3$ which was collected in this manner was assayed for radioactivity by the method of Jeffay and Alvarez (1961).

RESULTS AND DISCUSSION

MBC showed resistance to photodecomposition in these studies unless a photoactivator was present. This is illustrated in Table I which shows the results of exposing a layer of MBC-2-^{14}C-*methyl*-t_3 on a TLC plate to sunlight. The ratio of ^{3}H (in the side-chain methyl group) to ^{14}C (in the imidazole ring) changed little during a 30-h exposure to sunlight. Less than 10% of the ^{14}C and ^{3}H was lost from the plates during the exposure period. The radioactivity on the exposed plates chromatographed in a manner similar to MBC (Figure 1). Areas on these chromatograms which contained most of the radioactivity also absorbed ultraviolet light. The silica gel from these areas was scraped from the plates and extracted with 1 N HCl. The ultraviolet spectra of this extract were identical with MBC dissolved in 1 N HCl.

The results of a series of experiments conducted with dilute aqueous solutions of radioisotopically labeled MBC in the presence and absence of photosensitizers are shown in Table II. Little change was found in the ratio of ^{3}H to ^{14}C in solutions of MBC-2-^{14}C-*methyl*-t_3 exposed to sunlight for up to 40 h without photosensitizers. There was no measurable loss of radioactivity in the dark control while less than 10% of the tritium label was lost in the solutions exposed to sunlight.

Solutions of radioactive MBC containing acetone or riboflavin had greater loss of radioactivity, and thus greater photodegradation, than those without these photosensitizers (Table II). The greatest loss of ^{3}H and ^{14}C was in solutions containing riboflavin. In this case 75% of the tritium was lost after 16 h of sunlight. The ^{3}H/^{14}C value also showed a significant drop, suggesting the cleavage of the methyl group from the benzimidazole moiety and loss of the tritium label, perhaps in the form of methanol-*t*.

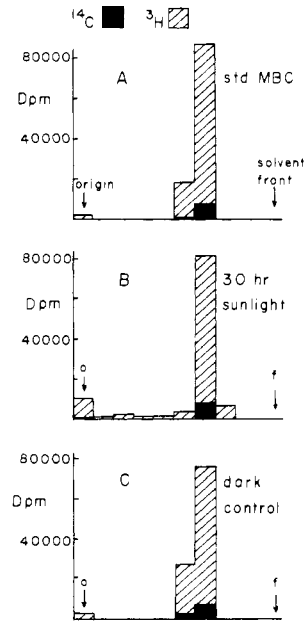

Figure 1. Radiochromatograms of MBC-2-^{14}C-*methyl*-t_3 after exposure of the fungicide to sunlight as a residue on silica gel G: (A) standard MBC-2-^{14}C-*methyl*-t_3; (B) developed after 30 h of exposure to sunlight; (C) dark control; solvent, acetone-concentrated NH_3 (97:3).

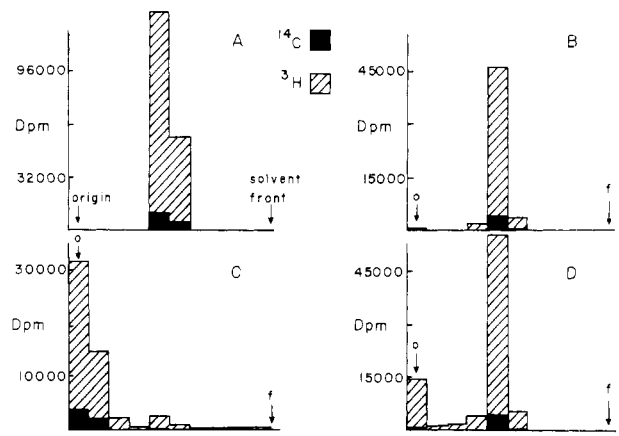

Figure 2. Radiochromatograms on silica gel G of aqueous photolysates of MBC-2-^{14}C-*methyl*-t_3: (A) standard MBC-2-^{14}C-*methyl*-t_3; (B) 40-h exposure to sunlight with no photosensitizer; (C) 16-h exposure with 5 mg/l. riboflavin; (D) 16-h exposure with 5 ml/l. acetone; developing solvent: ethyl acetate-*p*-dioxane-methanol-concentrated NH_3 (160:20:5:0.5).

Little change in the ^{3}H/^{14}C value occurred in MBC solutions containing acetone.

Results from chromatography of the photolysates suggested the formation of polar, nonvolatile photodecomposition products (Figure 2). The chromatograms indicated both radioisotopes were retained in some photodecomposition products. This suggested that the benzene moiety of the benzimidazole structure was undergoing chemical change.

Table II. Nonvolatile ^{3}H and ^{3}H/^{14}C after Exposure of Dilute Aqueous Solutions of MBC-2-^{14}C-*methyl*-t_3 to Sunlight

Photosensitizer	Initial	5 h		16 h		40 h	
	^{3}H/^{14}C	% ^{3}H recovd	^{3}H/^{14}C	% ^{3}H recovd	^{3}H/^{14}C	% ^{3}H recovd	^{3}H/^{14}C
None (dark control)	11.4	100	11.7	100	11.5	100	11.2
None	11.4	100	11.6	98	11.2	93	11.1
Acetone	11.6	96	11.4	90	11.2		
Riboflavin	11.5	28	9.1	25	8.1		

Table III. Distribution of ^{14}C in Compounds Found after Photolysis of MBC-2-^{14}C-*methyl*-t_3[a]

Compound	% of original ^{14}C
MBC	23
Carbomethoxyguanidine	31
Guanidine	2
Carbomethoxyurea	10
Dicarbomethoxyguanidine	<0.05
2-Aminobenzimidazole	<0.05
Carbon-^{14}C dioxide	1
Lost on evaporation of solvent	9
^{14}C in unidentified products	24

[a] Riboflavin served as photosensitizer and the light source emission maximum was 350 nm.

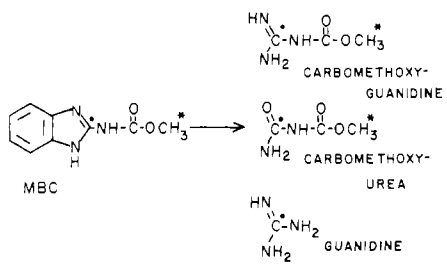

Figure 3. Photolysis products of MBC: (•) position of ^{14}C label; (*) position of ^{3}H label.

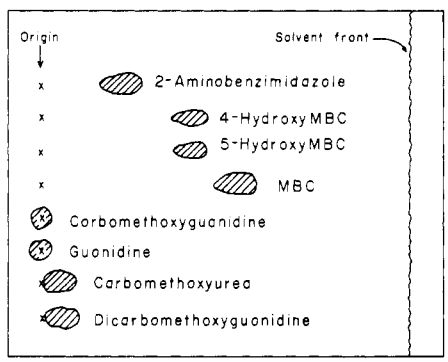

Figure 4. Chromatogram of authentic MBC and suspected photolysis products on silica gel G; developing solvent: ethyl acetate-*p*-dioxane-methanol-concentrated NH_3 (160:20:5:0.5).

Our investigation was aided by the publication of a study which identified several photolysis products of MBC which resulted from the exposure of this substance to UV light while suspended in methanol (Watkins, 1974). The products found were: guanidine, carbomethoxyguanidine, dicarbomethoxyguanidine, and dimethyl oxalate. The identification of these compounds showed that MBC does undergo photooxidation in the carbons of the benzene ring. We estimated the amounts of these substances in dilute aqueous photolysates of MBC by reverse isotope dilution. Certain additional compounds, suspected of being photolysis products and amenable to this technique, were also estimated. For reproducibility, the photolysates were prepared in a photoreaction apparatus.

The results of the analyses are listed in Table III. The major photolysis product found was carbomethoxyguanidine which accounted for 31% of the ^{14}C in the photolysate. The presence of this compound and carbomethoxyurea accounted for over 40% of the radioactivity added to the solution and to a certain extent explains why both isotopes were retained in a nonvolatile form after photolysis (Figure 3). Guanidine and carbon dioxide were the only products estimated that contained only one radioisotope. Urea may also have been present but was not

Table IV. Distribution of Radioactivity Recovered from Corn Plants after Treatment with MBC-2-^{14}C-*methyl*-t_3 and Exposure to Sunlight

Tissue	% of radioact. applied: Dark control	Sunlight
Treated leaves		
Surface	69.5	73.1
Tissue	27.5	24.9
Untreated leaves	<0.01	<0.01
Stems	0.1	0.2
Roots	<0.01	<0.01

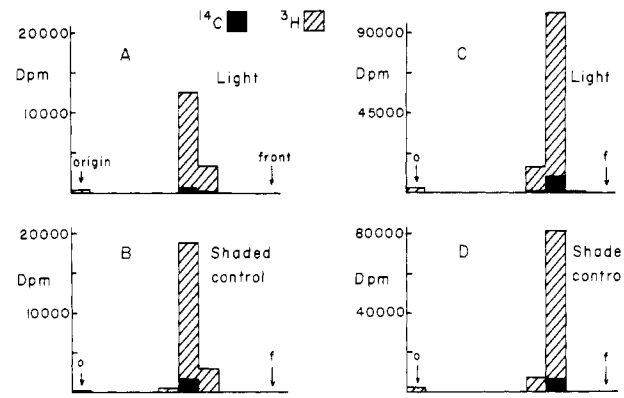

Figure 5. Radiochromatograms of corn plant extracts obtained after foliar application of the plants with MBC-2-^{14}C-*methyl*-t_3 and exposure to sunlight 18 h: (A) extracts of treated leaves after removal of leaf surface components; (B) shaded control of A; (C) radioactivity removed by dipping the treated leaves in ether; (D) shaded control of C; silica gel G; developing solvent: acetone-concentrated NH_3 (97:3).

determined. Nine percent of the ^{14}C radioactivity was lost in a volatile form and this may have been in the form of carbon-^{14}C dioxide or formic acid-^{14}C. A chromatogram of some suspected photolysis products is shown in Figure 4.

Watkins found significant amounts of dicarbomethoxyguanidine; however, we were unable to detect this substance by reverse isotope dilution. The much larger amounts of MBC used by Watkins may have resulted in the formation of large concentrations of carbomethoxyguanidine. Such large concentrations may have brought about a significant rate of an intermolecular transfer of carbomethoxy group to a second molecule of carbomethoxyguanidine to form dicarbomethoxyguanidine and guanidine. The very low concentrations of MBC used in this study would have made the possibility of such an intermolecular reaction very small. The dimethyl oxalate that Watkins observed in the MBC photolysates probably arises from a reaction of methanol with an intermediate degradation product. The oxalate carbons would likely arise from the benzene ring portion of MBC and therefore would not be labeled with ^{14}C in this study.

Table IV shows the results of an experiment with corn plants treated with MBC-2-^{14}C-*methyl*-t_3 and exposed to sunlight for 18 h. A second set of plants was also treated with the fungicide and protected from sunlight. After exposure to light, the MBC remaining on the leaf surface was removed by dipping the treated leaf in ether. The treated leaves were then extracted to solubilize the remaining radioactivity. The distribution of the radioactivity within the plant and the total recovery of radioactivity were essentially the same for the light exposed plants and the controls. Very little of the fungicide was transported to other parts of the plant during the experimental period.

The ether solution and the leaf extract were chromatographed and the results are shown in Figure 5. There was no chromatographic evidence of MBC metabolism or photodegradation in either set of plants. MBC has been reported to undergo metabolic change in plants; however, the fungicide is not rapidly metabolized (Siegel and Zalbia, 1972; Siegel, 1973; Ben-Aziz et al., 1974).

The length of time the plants were exposed to sunlight was kept brief. It is difficult in such an experiment to distinguish between an enzyme-catalyzed reaction of a foreign compound in plant tissue and a photodegradative reaction of the compound, even with a control that does not receive direct sunlight. Alterations in enzyme levels may occur in plants serving as the controls, especially if the length of the experiment is long. Chemical changes of a compound observed in plants exposed to direct sunlight and not observed in the shaded-control plants may actually reflect differences in enzyme levels rather than a photochemical process.

The photolysis of thiabendazole (2-(4-thiazolyl)benzimidazole) has been studied by Jacob et al. (1975). These investigators applied thiabendazole (TBZ), labeled with ^{14}C in the benzene ring carbons, to sugar beet foliage and exposed the plants to sunlight for 14 8-h days. A similar set of plants was placed in a plant growth chamber and served as controls. These workers recovered 78% of the radioactivity applied to the plants that were exposed to sunlight, while 95% of the applied radioactivity was recovered from the plants maintained under artificial light. Essentially no translocation, metabolism, or photodegradation of TBZ occurred with the control plants while 22% of the TBZ was chemically altered in plants exposed to sunlight. Benzimidazole and benzimidazole-2-carboxamide were detected among the photolysis products and constituted 0.8 and 1.2% of the ^{14}C recovered, respectively. These data suggest that TBZ does undergo sunlight-induced alteration. However, because the isotope label was in the benzene-ring carbons of TBZ, it is possible that the loss of radioactivity from plants exposed to sunlight was due to volatility of TBZ-^{14}C or to the loss of $^{14}CO_2$ from the photooxidation of the benzene moiety of the compound, or both. The formation of a guanidine derivative would not have been observed in their studies with TBZ due to the position of the radioisotope label.

The data presented in this study suggest that MBC is moderately stable to photodegradation. The benzene-ring moiety of MBC appears to be the portion of the structure that most readily undergoes photooxidation (Figure 3). These observations are consistent with the chemical properties reported for the benzimidazole structure (Hofmann, 1953). Benzimidazoles are generally resistant to oxidizing agents with the benzene moiety more susceptible to oxidation than the imidazole portion of the molecule.

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