in herbicide-pretreated *Scenedesmus* cells. Chlorophyll photooxidation strongly depends on the environment, and lipids can protect chlorophyll against being photooxidized (Stillwell and Tien, 1977). Therefore, degradation of the protective lipids will cause irreversible photooxidation of unprotected pigments. Further, toxic decomposition products of lipid hydroperoxides may also be responsible for pigment degradation either by cooxidation of the pigment (Holden, 1965; Schobert and Elstner, 1980) or by inactivation of enzymes necessary for chlorophyll biosynthesis (Gardner, 1979).

Summarizing, lipid peroxidation is the dominant toxic reaction in oxyfluorfen-treated *Scenedesmus* cells. The peroxidation process is directly related to severe light-dependent consequences such as pigment damage. Cell death is finally caused by the sum of all toxic events. Among them, peroxidative membrane damage seems to be the most potent reaction. Simultaneous treatment of cells with both oxyfluorfen and antioxidants such as ethoxyquin or α-tocopherol, which are powerful protectors against lipid peroxidation and pigment destruction, strongly diminishes herbicide toxicity.

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Registry No. Oxyfluorfen, 42874-03-3; ethoxyguin, 91-53-2; *dl*-α-tocopherol, 10191-41-0; DPPD, 74-31-7; BHT, 128-37-0; ascorbic acid, 50-81-7; mannitol, 69-65-8.

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Photochemistry and Volatility of Drepamon in Water

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The aquatic environmental chemistry of the herbicide Drepamon (*S*-benzyl *N*,*N*-di-*sec*-butylthiocarbamate) was investigated in laboratory studies of photochemical reactivity and volatilization. In distilled water Drepamon photooxidized slowly to *N*-[(benzylsulfinyl)carbonyl]-*N*,*N*-di-*sec*-butylamine (Drepamon sulfoxide), an intermediate that underwent further direct photochemical conversion to benzaldehyde. Traces of hydrogen peroxide greatly accelerated the photodecomposition of Drepamon and altered the distribution of photoproducts so that phenols predominated. Peroxide-initiated free radical photooxidation included sulfur oxidation and N-dealkylation as well. Drepamon, its phenolic products, benzaldehyde, and *sec*-butylamine were analyzed by gas–liquid chromatography. The thermally unstable sulfoxide and sulfone were determined by high-pressure liquid chromatography. Drepamon volatilized from aqueous solutions more rapidly than the structurally related herbicides molinate and thiobencarb.

Drepamon or tiocarbazil (proposed common name) is an effective herbicide for the selective control of barnyardgrass (*Echinochloa* spp.) in submerged rice fields. Control of this weed increases yields, shortens the growing season, and is of major economic importance in paddy rice culture. The structurally related herbicides molinate and thiobencarb are currently used for grass control in flooded California rice fields. Previous studies in this laboratory (Soderquist et al., 1977) and others have shown that volatilization is a major route of dissipation for the thiolcarbamates under field-use conditions. Molinate and thiobencarb also are degraded photochemically in sunlight in both direct and indirect photolysis processes (Soderquist

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et al., 1977; Draper and Crosby, 1981; Ishikawa et al., 1977).

As part of an overall program to maintain air and water quality in California's Sacramento Basin and to evaluate alternate herbicides for use in rice culture, laboratory studies of the photochemistry and volatility of Drepamon were conducted. The objectives of this investigation were to define the major routes for transformation and dissipation of Drepamon in water and to develop analytical procedures for potential environmental residues.

MATERIALS AND METHODS

Chemicals. Drepamon (I) was purified by Florisil column separation from a 70% emulsifiable concentrate formulation (Drepamon SE70) provided by Montedison S.p.A. (Milano, Italy); Drepamon is a registered trademark of this firm. The clear, viscous oil was homogeneous to thin-layer chromatography (TLC) and was greater than 99% pure by temperature-programmed gas–liquid chromatography (GLC): mass spectrum (GLC–MS, 70 eV) m/e (rel intensity) 57 (base, C_4H_9), 91 (88, C_7H_7), 100 (71, $C_5H_{10}NO$), 156 (35, $C_9H_{18}NO$), no M^+; MS (solid probe, 20 eV) m/e (rel intensity) 56 (base, C_4H_8O), 70 (71), 91 (57), 55 (54, C_4H_7), 122 (46, C_7H_6S), 156 (45%), no M^+; Infrared spectrum (IR) 3070, 2980, 1660 (CO), 1245 cm^{-1}; nuclear magnetic resonance (NMR) spectrum δ (chloroform-*d*) 7.25 (s, 5, phenyl), 4.2 (s, 2, $-SCH_2-$), 2.0–1.0 [complex, 12, $-CH(CH_3)CH_2-$], 0.85 (t, 6.2, CH_2CH_3).

N-[(*Benzylsulfinyl*)*carbonyl*]-*N*,*N*-*di*-*sec*-*butylamine* (*II*). II was synthesized by oxidation of I with 1 equiv of 3-chloroperoxybenzoic acid in chloroform followed by purification on a Florisil column (Casida et al., 1975). The oil obtained slowly crystallized, yielding one of the geometric isomers as white needles; mp 62–65 °C; MS (solid probe, 70 eV) m/e (rel intensity) 57 (base, C_4H_9), 91 (48, C_7H_7), 100 (40, $C_5H_{10}NO$), 156 (16, $C_9H_{18}NO$), no M^+; MS (solid probe, 20 eV) m/e (rel intensity) 70 (base, C_4H_8N), 91 (99), 100 (84), 55 (72, C_4H_7), 122 (44, C_7H_6S), 77 (57, C_6H_5), no M^+; IR 3080, 2980, 1680 (CO), 1460, 1245, 1035 (SO) cm^{-1}; NMR δ (chloroform-*d*) 7.32 (s, phenyl), 4.2 [s, $-S(O)CH_2-$], 2.2–1.0 (complex). The isolated product was free of I and III as determined by high-pressure liquid chromatography (HPLC) or TLC.

N-[(*Benzylsulfonyl*)*carbonyl*]-*N*,*N*-*di*-*sec*-*butylamine* (*III*). III was synthesized with the procedure described for II except that a 5-fold molar excess of peroxyacid was used: white plates; mp 64–67 °C [lit. mp 73.5–74 °C; Santi and Gozzo (1976)]. MS (solid probe, 70 eV) m/e (rel intensity) 57 (base, C_4H_9), 100 (43, $C_5H_{10}NO$), 91 (26, C_7H_7), 156 (25, $C_9H_{18}NO$), no M^+; MS (solid probe, 20 eV) m/e (rel intensity) 100 (base), 91 (72), 70 (76, C_4H_8N), 56 (68, C_4H_8), 77 (47, C_6H_5), 121 (45, C_7H_5S), no M^+; IR 3080, 2980, 1690 (CO), 1125 (SO_2) cm^{-1}; NMR δ (chloroform-*d*) 7.38 (s, phenyl), 4.6 [s, $-S(O_2)CH_2-$], 2.2–0.75 (complex). The synthetic material was not contaminated with I or II.

N-[2,6-*Dinitro*-4-(*trifluoromethyl*)*phenyl*]-*N*,*N*-*di*-*sec*-*butylamine*. The (trifluoromethyl)dinitrotoluene (DNT) derivative of dibutylamine was synthesized by reaction of di-*sec*-butylamine (1.3 g, 10 mmol) with 4-chloro-3,5-dinitro-α,α,α-trifluorotoluene (2.0 g, 7.5 mmol) for 10 min in 50 mL of acetone (Crosby and Bowers, 1968). An oily layer separated upon addition of 150 mL of water, and this material was washed with water and recrystallized twice from ethanol, yielding yellow crystals, mp 54.5–56 °C.

N-[2,6-*Dinitro*-4-(*trifluoromethyl*)*phenyl*]-*N*-*sec*-*butylamine*. The DNT derivative of the primary amine was prepared in an identical manner except that *sec*-butylamine (0.73 g, 10 mmol) was substituted for the secondary amine to provide yellow, flocculent plates, mp 70.5–71.5 °C.

α-*Toluenesulfonic Acid*. Toluenesulfonyl chloride was hydrolyzed in dilute base for 20 min under reflux. The solution was cooled, neutralized, and concentrated to dryness, yielding a white solid, mp >290 °C.

Hydrogen peroxide (30% Mallinckrodt reagent grade) used in these studies contained a stabilizer at trace levels, but no extraneous absorptions were observed in the oxidant's ultraviolet spectrum nor was the material othewise detected. Solvents were pesticide analytical grade or redistilled in glass and other chemicals were reagent grade. Ethereal diazomethane was prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in an appropriate distillation apparatus (Aldrich Chemical Co.), and the reagent obtained was stored at −5 °C.

Apparatus and Chromatography. Drepamon and its photoproducts were determined by GLC using a hydrogen flame ionization detector equipped instrument and operating conditions described previously (Draper and Crosby, 1981). Chromatography columns were 2-mm i.d. (stainless steel or glass) packed with Gas-Chrom Q (60–80 mesh) with 3% OV-17 (1.5 m, column A), 4% OV-17 (4 m, column B), or 1% diethylene glycol adipate (1.5 m, column C) liquid phases; a 1.5-m column packed with the porous polymer Tenax GC (column D) was used for analysis of low molecular weight photoproducts.

An isocratic high-pressure liquid chromatography (HPLC) system fitted with a 254-nm, fixed-wavelength detector was used in the analysis of thermally labile photoproducts, II and III. In separations using a μBondapak C_{18} reverse-phase column the mobile phase was methanol–water (3:1 v/v). A silica gel column (μPorasil) eluted with chloroform was used in normal phase separations. Total solvent flow rates were typically 2 mL/min.

TLC separations utilized precoated silica gel chromatoplates (0.25 mm × 20 × 20 cm silica gel 60 F-254, Scientific Products, Inc.) containing a phosphor. Plates were developed in benzene–methanol (9:1 v/v, solvent A) or butanol–acetic acid–water (4:1:1 v/v/v, solvent B) in tanks without liners. Sorbed materials were detected by quenching of UV light and with a sulfur-specific palladium chloride chromogenic spray reagent or a diazotized amine spray (Pauly's reagent) for phenol detection (Draper and Crosby, 1981).

Spectroscopy. IR spectra were obtained of neat liquid films or pressed potassium bromide disks for solids. Samples were dissolved in deuterated chloroform for 60-MHz NMR spectra, and shift values are reported relative to a tetramethylsilane internal standard. Mass spectra (electron impact, 70 eV) were recorded with a Finnigan Model 3000 quadrupole instrument with sample introduction by solid probe or GLC using column A. A Du Pont 492 mass spectrometer interfaced to a Finnigan Incos data system was used for "soft" ionization (20 eV, solid probe inlet).

Photochemical Studies. Laboratory photochemistry studies were conducted with an F40BL fluorescent black light equipped reactor (Crosby and Wong, 1973) that accurately simulates actinic sunlight. The total radiant energy in the center of the reactor was ~400 $\mu W/cm^2$ and the UV cutoff was 285–290 nm.

Photoproducts of Drepamon were characterized in a preparative-scale photodecomposition. A saturated Drepamon solution was obtained by vigorously stirring a mixture of 6 mg of Drepamon and 3 L of distilled water in a sealed flask for 48 h. The solution thus obtained was filtered (medium-porosity scintered glass), combined with 40 mL of 0.1 M hydrogen peroxide, and irradiated 42 h in a sealed borosilicate flask. The photolysate with 15% of

Table I. Chromatographic Mobility and Chromogenic Reactions of Drepamon and Its Derivatives

compound	TLC[a] R_f	chromogenic reactions		GLC[b] R_t, min	HPLC R_t, min	
		$PdCl_2$	Pauly's		reverse phase	normal phase
I	0.72	yellow	NR[c]	0.75	7.1	1.7
II	0.38, 0.33	peach	NR		2.8	3.9, 4.3
III	0.70	yellow-green	NR		3.9	2.2
IV	0.67	grey	red-brown	1.6, 1.7[d]	4.8, 7.0[d]	2.3
V	0.42	brown	yellow	2.8, 1.9[d]	3.8, 7.0[d]	5.2
VI	0.36	brown	brown	3.0, 2.1[d]	3.8, 7.0[d]	5.4

[a] Benzene–methanol, 9:1 v/v. [b] Column A, 220 °C. [c] No reaction. [d] Methylated derivatives.

the herbicide remaining was extracted with 2 × 300 mL of dichloromethane, and the solvent extract was concentrated to a small volume for fractionation by preparative TLC. The photoproduct bands were characterized by chromogenic spray reagents and eluted with acetone for analysis by GLC–MS. Drepamon and its photoalteration products were subsequently irradiated in distilled water or dilute peroxide to define direct and free radical photodecomposition pathways. Procedures were not different from those described above.

Analysis of Drepamon and Drepamon Photoproducts in Water. Drepamon analysis was routinely accomplished by extraction of 50-mL water samples with 2 × 5 mL of dichloromethane; the organic extract was analyzed by injection on column A with an oven temperature of 180 °C, resulting in a detection limit of 0.1–0.2 mg/L.

Multiresidue analysis of Drepamon and its transformation products, however, required a more involved procedure. Water samples (800 mL) were extracted with 2 × 80 mL of dichloromethane, and the combined organic extract was reduced on a rotary vacuum evaporator to 5.0 mL for analysis of I as described above. For determination of the volatile, low molecular weight products the extract was separated with a porous polymer packing (column D) temperature programmed from 130 to 300 °C at 20 °C/min, resulting in the following elution temperatures: toluene, 172 °C; benzaldehyde, 210 °C; methyl benzoate, 230 °C, bibenzyl, 280 °C. The extract was further concentrated to ~0.1 mL, combined with ~3 mL of ethereal diazomethane, and held at −5 °C for 48 h in a sealed tube. Excess reagent was evaporated and the sample volume adjusted to 1.0 mL with dichloromethane; Drepamon's methylated phenols were resolved with column B at 265 °C. II and III in the methylated extract were determined by reverse-phase HPLC. For increased sensitivity injection volumes of 20 μL (equivalent to 15 mL of water) were required.

The amine fragments of Drepamon were quantitated by using a supplemental electron capture GLC procedure (Crosby and Bowers, 1968; Soderquist et al., 1977). In this procedure amines are isolated by acid–base extraction and converted to highly electron capturing (alkylamino)dinitrotoluenes (DNT). Butylamine–DNT derivatives were separated on a 5% SE30 column at 150 °C (monoamine) or 130 °C (diamine).

Volatilization Studies. Solutions containing ~2 mg/L Drepamon, molinate, and thiobencarb in 1 mM pH 7 or pH 9 phosphate buffer were held at 27.5 °C in a constant-temperature bath. Water depth was monitored during the experiment, and periodically 50-mL samples were removed for analysis. Water samples were extracted with 2 × 5 mL of dichloromethane and herbicides were determined simultaneously in the extract by GLC analysis using column C, which was temperature programmed from 140 to 220 °C at 20 °C/min. The retention times were as follows: molinate, 2.4 min; Drepamon, 5.5 min; thiobencarb, 7.0 min. At the termination of the experiment sealed control samples were analyzed to determine hydrolytic stability.

RESULTS

Transformation Products of Drepamon. The free radical photooxidation photoproducts of Drepamon included Drepamon sulfoxide (II) and three isomeric phenols. The least polar phenol (IV, R_f 0.67, solvent A) gave a butyl isocyanate ion (m/e 100) as the base peak: GLC–MS (70 eV) m/e (rel intensity) 100 (base, $C_5H_{10}NO$), 57 (95, C_4H_9), 107 (53, C_7H_7O), 156 (16, $C_9H_{18}NO$), no M^+. The more polar Drepamon phenols, however, gave butyl cation radicals (m/e 57) as base fragments: (V, R_f 0.42) GLC–MS (70 eV) m/e (rel intensity) 57 (base, C_4H_9), 100 (54, $C_5H_{10}N$), 107 (46, C_7H_7O), 156 (12, $C_9H_{18}NO$), no M^+; (VI, R_f 0.36) GLC–MS (70 eV) m/e (rel intensity) 57 (base, C_4H_9), 100 (70, $C_5H_{10}N$), 107 (70, C_7H_7O), 156 (20, $C_9H_{18}NO$), 70 (20, C_4H_8N), 77 (20, C_6H_5), no M^+. Structural confirmation for each hydroxylated product included the formation of colored complexes with diazotized sulfanilic acid and the sluggish conversion to methoxy derivatives with ethereal diazomethane. The hydroxytropilium ions (m/e 107) of the free phenols were replaced with the expected methoxytropilium fragments (m/e 121, C_8H_9O).

Diagnostic molecular fragments observed for Drepamon and its transformation products included butyl isocyanate and butyl cations mentioned above, dibutyl isocyanate ion (m/e 156, $C_9H_{18}NO$), tropilium (m/e 91, C_7H_7) and hydroxytropilium ions (m/e 107, C_7H_7O), butylamine fragments (m/e 70, C_4H_8N; m/e 72, $C_4H_{10}N$), and ions derived from the aromatic ring (m/e 77, 78, and 79). The fragmentation patterns of I–III were markedly altered by soft ionization, but molecular ions were not detected even in 20-eV spectra.

Attempts to differentiate the phenolic isomers were not successful. For example, the methoxy derivatives were oxidized to the corresponding methoxybenzoates with alkaline permanganate, methylated, and the methyl methoxybenzoate isomers were then resolved by GLC with column B. Although the conversion of Drepamon (12 mg) to methyl benzoate was demonstrated by this procedure, it was ineffective when applied to the low available levels of photoproducts. Insufficient material was available for differentiation by continuous-wave NMR as well.

Analysis of Products. Chromatographic properties of Drepamon and its transformation products are depicted in Table I. Drepamon sulfoxide was resolved, yielding two components on silica gel chromatoplates or a silica gel HPLC column; Santi and Gozzo (1976) report the resolution of a third isomer as well. The multiplicity of products in II result from the three optical centers of the *sec*-butyl and *S*-oxide moieties.

In reverse-phase separations the sulfoxide's geometric isomers coeluted. II and III could not be determined by GLC presumably due to thermal instability. Although I and IV were readily determined by GLC, the polar phenols

Table II. Photodecomposition of Drepamon Sulfoxide[a]

treatment	oxygen	drepamon sulfoxide, mg/L	benzaldehyde, μg/L
light	+	4.4	110
light	-	4.4	160
dark control	+	5.9	15

[a] Solutions of II (6 mg/L) were irradiated 70 h in the laboratory photoreactor. Benzyl alcohol, toluene, bibenzyl, I, and III were not detected in any of the samples.

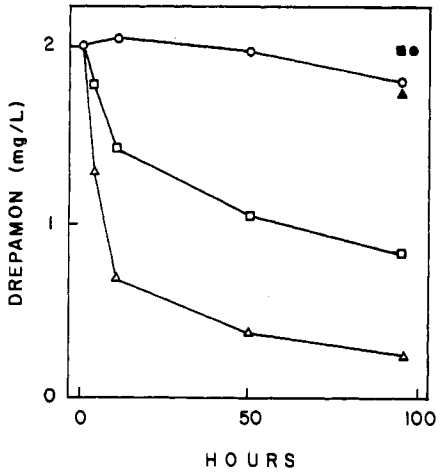

Figure 1. Photodecomposition of Drepamon in water (○) and dilute hydrogen peroxide [10 μM (□); 30 μM (△)]. Filled symbols indicate dark controls.

(V and VI) were not separated prior to methylation. The resolution of the various products was not straightforward by HPLC either with or without methylation. For example, with the C_{18} reverse-phase column III, V, and VI coeluted and in a normal-phase system III cochromatographed with IV and V overlapped VI. The mixed GLC–HPLC method described, however, allowed selective quantitation of the identified products. Interferences were not detected in samples of rice field water. The detection limits for standards by GLC were ~5 ng while 100–150 ng was required as minimum detectable quantities of II and III by 254-nm absorbance detection.

Photodecomposition of Drepamon. *Direct Photolysis.* After 7 days in sunlight (Davis, September) 25–30% of Drepamon was consumed photochemically. The first-order, direct photolysis rate constant, therefore, is approximately 0.046 day^{-1} with a predicted half-life of 15 days. Photoproducts included II and benzaldehyde, which accounted for approximately 15 and 55%, respectively, of the herbicide reacting. Drepamon was stable in solutions held in the dark.

II was converted directly to benzaldehyde in sunlight (Table II), and this photochemical conversion did not require oxygen. Benzyl radicals were not intermediates since irradiation of II did not give toluene and bibenzyl as products under anaerobic conditions (solutions were deoxygenated by triplicate freeze–thaw cycles under nitrogen). The yield of benzaldehyde actually increased under anaerobic conditions. II was considerably more photolabile than I with ~20% conversion after <3 days in the laboratory photoreactor (k = 0.098 day^{-1}, $t_{1/2}$ = 7 days). Photolysis rates in summer sunlight generally exceed those determined in the photoreactor.

Free Radical Photooxidation. Traces of hydrogen peroxide greatly accelerated the photodecomposition of Drepamon (Figure 1). Drepamon photodegradation rates were dependent on peroxide concentrations with the following half-lives: 10 μM oxidant, 60 h; 30 μM, 10 h; 100 μM, ~5 h; 300 μM, ~3 h. The major extractable photooxidation products were phenols (Figure 2) and II but not III. After brief exposure to light (5 h) with <25% photochemical conversion of the parent molecule, ~25% of the herbicide reacting yielded organosoluble products. The polar, unextractable products were not characterized. N-Dealkylation was a minor peroxide-initiated reaction and *sec*-butylamine was detected on irradiation of I or II with oxidant. Monobutyldrepamon was not formed, however, and the low levels of *sec*-butylamine present (<1% of the parent material reacting) indicated that N-dealkylation was not a major reaction. The dialkylamine could not be detected with the method described since the reagent interfered with the di-*sec*-butylamine–DNT derivative.

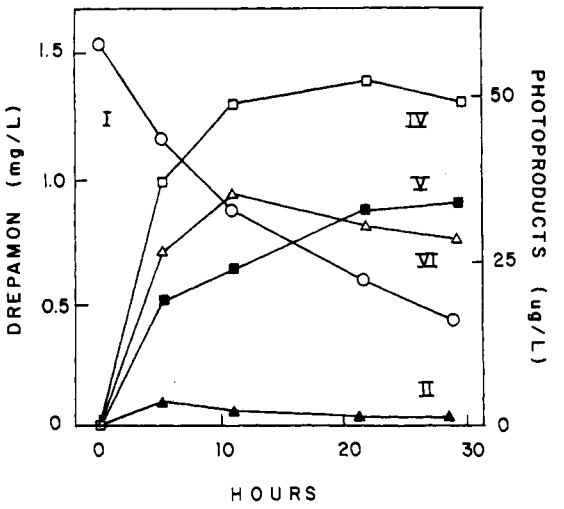

Figure 2. Photooxidation of Drepamon (○) in 30 μM hydrogen peroxide. Organosoluble products included Drepamon phenols (□, △, ■) and drepamon sulfoxide (▲).

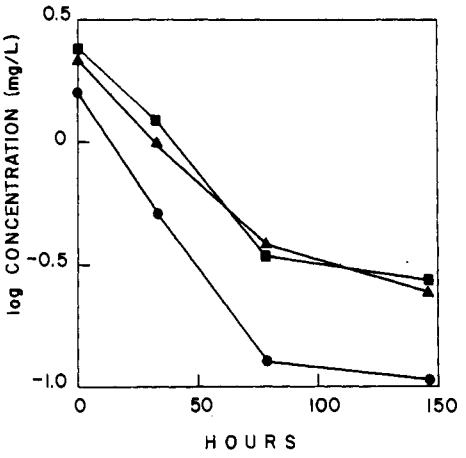

Figure 3. Competitive photooxidation of Drepamon (●), molinate (■), and thiobencarb (▲) in 100 μM hydrogen peroxide (July sunlight, Davis, CA).

The competitive photooxidation of Drepamon and two related thiocarbamate herbicides in dilute hydrogen peroxide indicated equivalent rates of photochemical reaction (Figure 3). The dissipation curves for each compound generated approximately parallel lines in semilog plots. The photodegradation rates were greatly reduced after several days in sunlight due to consumption of the oxidant.

Hydrolysis of Drepamon Sulfone. III rapidly hydrolyzed predominantly to α-toluenesulfonic acid at neutral pH. A methanolic solution of III (3 m/mL) was combined with an equal volume of water, and the formation of α-toluenesulfonic acid was monitored by TLC (solvent B). The sulfonic acid, not detected in methanolic solutions, was a major product within 5 min after addition of water;

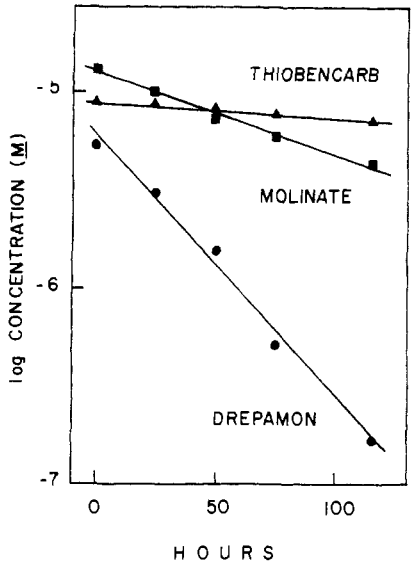

Figure 4. Volatilization of Drepamon (●), molinate (■), and thiobencarb (▲) from pH 7 phosphate buffer at 27.5 °C. The volatility of these herbicides from pH 9 buffer at the same temperature was indistinguishable.

added water also resulted in precipitation of III to a limited extent. Traces of benzaldehyde also may have formed on hydrolysis as a product of similar polarity was detected (solvent A). I and II, in contrast, were relatively stable at pH 7.

Comparative Volatility of Drepamon. At a constant temperature of 27.5 °C, typical of a rice paddy during summer months in the Sacramento Basin, Drepamon volatilized rapidly (Figure 4). First-order volatilization rates varied considerbly, however, for the three thiocarbamates studied and were ranked as follows: Drepamon > molinate > thiobencarb. The volatility in pH 7.0 and pH 9.0 phosphate buffers was identical within experimental error, indicating that the slightly alkaline conditions of local rice paddy water will not alter these relative rates. Losses of the herbicides to the laboratory atmosphere were greater than indicated by Figure 4 since the water itself evaporated at a constant rate of 5 mm/day. The initial water depth was 42 mm.

DISCUSSION

Drepamon undergoes rapid sulfur oxidation in rice plants and barnyardgrass (Santi and Gozzo, 1976). In the aerial parts of treated plants the major residues are II and a thioglycolic acid derivative, the latter metabolite being detected only in systems containing soil microbes. For *S*-ethyl dipropylthiocarbamate (EPTC) applied on soil, however, microbial metabolism appears to be important only when the pesticide is soil incorporated (Danielson et al., 1961). Thiolcarbamate sulfoxides also are formed metabolically in mammalian liver, and in general, these derivatives appear lower in acute mammalian toxicity than the parent herbicides (Casida et al., 1974).

Volatility is a major factor in the losses of thiocarbamate herbicides from soil (Gray, 1965), and sometimes results in poor weed control under moist soil conditions (Kauffmann, 1967). Volatilization rates are lowest in dry soils or when the herbicides are distributed in the soil column (Gray and Weierich, 1965). In a flooded rice field molinate is dissipated primarily by transport to the atmosphere as well (Soderquist et al., 1977).

Photodecomposition also is a factor in the transformation of thiolcarbamates in water. Thiobencarb, for example, undergoes sunlight-induced sulfur oxidation, yielding a sulfoxide derivative and a variety of products resulting

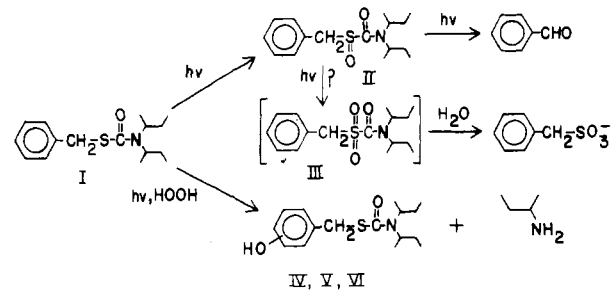

Figure 5. Direct and peroxide-initiated photodecomposition pathways for Drepamon.

from sulfur–carbamoyl bond cleavage (Ross, 1974; Draper and Crosby, 1981). Molinate, which lacks an efficient solar chromophore, undergoes indirect photolysis in flooded rice fields, resulting in the photooxidation of up to 10% of the applied herbicide (Soderquist et al., 1977). Interestingly, tryptophan and the naturally occurring "photosensitizers" promoted similar transformations.

These previous investigations served to focus our studies of Drepamon on the processes of volatilization and photochemistry. Since Drepamon is an aromatic molecule absorbing in the solar near-UV (ϵ_{290} = 110 L mole^{-1} cm^{-1}), direct photodecomposition reactions were possible. Our rationale for studying hydrogen peroxide initiated reactions was based on the demonstration that (1) tryptophan and other chromophores initiate free radical photooxidation reactions by generating this oxidant (Draper and Crosby, 1981) and (2) peroxide is a natural constituent of rice paddy water (Draper and Crosby, 1983).

Direct Photodecomposition of Drepamon. In the present work we find that Drepamon also is converted to its sulfoxide II in sunlight. II, however, does not accumulate in the photolysis mixtures due to its rapid photochemical conversion to benzaldehyde (Figure 5). This photochemical reaction does not involve benzyl radical or thiolcarbamate sulfone intermediates, and the production of benzaldehyde from II is increased under anaerobic conditions. Mechanistic details of the sulfoxide → benzaldehyde photoconversion are not known although the process may involve an intramolecular rearrangement with elimination or an intermolecular process (i.e., hydrolysis of the excited state). An analogous reaction is expected for thiobencarb sulfoxide, and in fact *p*-chlorobenzaldehyde is a thiobencarb photoproduct (Ross, 1974; Ishikawa et al., 1977; Draper and Crosby, 1984).

Free Radical Photooxidation. Hydrogen peroxide at very low concentrations initiated photochemical ring hydroxylation of Drepamon (Figure 5). Aromatic hydroxylation is a typical reaction of hydroxyl free radicals (OH·) and involves hydroxycyclohexadienyl radical intermediates that are oxidized by molecular oxygen to the isolated phenols. *N*-Monobutyldrepamon was not detected as a photooxidation product although free radical N-dealkylation reactions occurred since butylamine was detected on irradiation of I or II.

It is probable that OH· attack at the sulfur atom is a major process as well. The expected sites for OH· attack in Drepamon ar as follows: sulfur > benzylic H ≥ phenyl ring > alkyl groups. These general predictions are based on the vast available knowledge regarding the rates of OH· reactions with organic molecules. In competititve photooxidation studies molinate, Drepamon, and thiobencarb reacted with OH· at very similar rates (Figure 3). Thus, major differences in thiocarbamate substituent groups (i.e., aliphatic vs. aromatic) had little or no effect on the reactivity of herbicides with OH·. The products of OH·

Table III. Experimental Volatilization Rates for Thiocarbamate Herbicides[a]

herbicide	m,[d] day^{-1}	k, day^{-1}	$t_{1/2}$, days 3 cm[b]	$t_{1/2}$, days 15 cm[c]
Drepamon	−0.31	0.71	0.98	4.9
molinate	−0.11	0.25	2.8	14
thiobencarb	−0.013	0.030	23	120

[a] Solutions in pH 7.0 phosphate buffer at 27.5 °C with negligible air and water movement. [b] Average water column with an initial value of 42 mm and a final depth of 18 mm. [c] Estimated from 3-cm data. [d] Slope of the log concentration vs. time plot.

attack at sulfur are not known. A possible reaction of II is carbon–sulfur bond cleavage, which occurs on reaction of alkyl sulfoxides with OH· (Lagercrantz and Forschult, 1969). The importance of direct or indirect photochemical conversion of sulfoxide intermediates to sulfones (and sulfonic acid on hydrolysis, Figure 5) is not established.

Volatilization of Drepamon from Water. Drepamon volatilizes from water even more rapidly than molinate (Figure 4). Thiobencarb evaporated at about the same rate as water in these laboratory experiments, so that with time little change in its concentration was observed. With a typical water depth of 15 cm, application of drepamon at its recommended rate (4 kg/ha) would result in a 1.5-fold excess of the herbicide relative to its solubility limit, i.e., 4.6 mg/L applied vs. 2.5 mg/L solubility. Thus, the solubilization rate of the herbicide may limit its transport to the atmosphere.

Water is usually held in a rice paddy for up to 2 weeks posttreatment for improved weed control and to minimize pesticide residues in runoff water. By extrapolation of these laboratory findings to a hypothetical field situation major differences are predicted in volatilization half-lives (Table III). Experimental conditions in the laboratory reflect rates from single-phase systems (below the solubility limit), still air and water, and a temperature of 27.5 °C. The results extrapolated to a 15 cm deep ond or rice field with the half-life proportional to the water depth predict half-lives of ~5 days for Drepamon and ~14 days for molinate. The flux of herbicides to the atmosphere will be greater and the corresponding half-lives shorter when volatilization of the field water is considered.

Volatilization rates and half-lives calculated based on published vapor pressure data [$\sim 5 \times 10^{-5}$ mmHg at 25 °C (Fabbrini and Galluzzi, 1980)] and water solubility values for Drepamon predict rapid volatilization from shallow water bodies as well. The nondimensional Henry's law constant estimated for Drepamon at 27.5 °C is $\sim 3 \times 10^{-4}$. The estimated overall liquid-phase mass transfer coefficient (K_L) (Mackay and Leinonen, 1975) predicts half-lives of ~10 h in 15 cm of water; this estimate is based on wind and water moving with a velocity of ~2 km/h. In moderately high wind (38 km/h) the predicted half-life drops to <2 h.

CONCLUSION

The major dissipative processes for Drepamon in a rice field under typical field-use conditions will be volatilization ($k > 0.14$ day^{-1}) and photodecomposition ($k > 0.046$ day^{-1}). Drepamon transport to the atmosphere will be most important with predicted half-life values of less than 5 days. At the recommended rate of application, however, insolubility may retard volatilization. Thiobencarb is considerably less volatile than molinate or Drepamon and is expected to remain in the aqueous compartment. In midsummer sunlight Drepamon will undergo direct photodecomposition via the pathway I → II → benzaldehyde. Photochemical oxidants and other naturally occurring substances may significantly accelerate photodecomposition rates, possibly resulting in the formation of hydroxylated products (IV, V, VI), *sec*-butylamine, and sulfur–carbamoyl cleavage products.

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Registry No. I, 36756-79-3; II, 51955-39-6; III, 60002-14-4; H_2O_2, 7722-84-1; H_2O, 7732-18-5; HO-*o*-$C_6H_4CH_2SC(O)N(s\text{-}Bu)_2$, 90321-25-8; HO-*m*-$C_6H_4CH_2SC(O)N(s\text{-}Bu)_2$, 90321-26-9; HO-*p*-$C_6H_4CH_2SC(O)N(s\text{-}Bu)_2$, 90321-27-0; benzaldehyde, 100-52-7; molinate, 2212-67-1; thiobencarb, 28249-77-6; *sec*-butylamine, 13952-84-6; *N*-[2,6-dinitro-4-(trifluoromethyl)phenyl]-*N*,*N*-di-*sec*-butylamine, 10156-71-5; *N*-[2,6-dinitro-4-(trifluoromethyl)-phenyl]-*N*-*sec*-butylamine, 5973-55-7; di-*sec*-butylamine, 626-23-3; 4-chloro-3,5-dinitro-α,α,α-trifluorotoluene, 393-75-9; α-toluenesulfonic acid, 100-87-8; α-toluenesulfonyl chloride, 1939-99-7.

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