Aqueous Photolysis of Napropamide

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Photolysis of napropamide [*N*,*N*-diethyl-2-(1-naphthalenyloxy)propanamide] has been examined at 25 °C in aqueous solution buffered at pH 7 by using radiation from a xenon arc lamp. The pseudo-first-order photolysis half-life and rate constant were 5.7 min and 1.2×10^{-1} min^{-1}, respectively. Three major photodegradation products were produced in yields up to 20%, 27%, and 9%. The three photodegradation products were isolated by HPLC and their structures identified by NMR and mass spectrometry.

INTRODUCTION

Napropamide [*N*,*N*-diethyl-2-(1-naphthalenyloxy)propanamide, **1**] is the active ingredient in Devrinol, used as a preemergence herbicide controlling weeds in certain fruit and nut crops. The synthesis of **1** was reported by Baker et al. (1969) and Tseng et al. (1973). The herbicidal activities of its optical isomers were described by Chan et al. (1975). Considerable interest has been demonstrated on the photodecomposition of formulated napropamide in soil (Hurle, 1978, 1981; Gerstl and Yaron, 1983; Stanger and Vargas, 1984; Walker et al., 1985). The first-order half-lives for photodegradation on nine soils incubated at 20 °C varied from 72 to 150 days (Walker et al., 1985). However, no information was provided on the identities of the degradation products. No photodegradation study of napropamide in water has been reported in the literature. The purpose of this study was to determine the photolysis rate of napropamide in water and to identify and quantify the degradation products formed. The results obtained from this study will be of value in assessing the environmental impact posed by the use of napropamide.

EXPERIMENTAL PROCEDURES

Napropamide. Both nonlabeled and labeled napropamide were used. The nonlabeled material, purity 99.7%, was an Analytical Reference Standard provided by ICI Americas Inc., Richmond, CA. The radiolabeled [*naphthalene*-1-^{14}C]napropamide in benzene solution was purchased from Pathfinder Laboratories (now a division of Sigma Chemical Co.). The radiopurity of this material, as determined by HPLC, was 99.3%. The specific activity was 13.5 mCi/mmol. The structures of the labeled and nonlabeled napropamide were confirmed by NMR and mass spectrometry.

Buffer. The buffer solution used during the photolysis rate study to maintain a constant pH of 7 (±0.05) was prepared according to the system established by Clark and Lubs (Lange, 1961). A buffer concentration of 0.0025 M was used. Napropamide had previously been shown to be stable toward hydrolysis over the pH range 5–9.

Other Reagents. The water used in all procedures was deionized and distilled in a Corning Mega-Pure system, Model MP-12A. This water meets the requirements of ASTM Type II water (ASTM, 1984). All other solvents used in experiments (acetonitrile, *n*-hexane, and trifluoroacetic acid) were Fisher Certified ACS grade. The "cocktail" used for liquid scintillation counting (LSC) was Scint-A obtained from Packard.

Light Source. A Heraeus Suntest xenon arc lamp served as the light source. The spectral distribution of the output of the xenon lamp was determined with a LI-COR Model LI-1800/12 portable UV–visible spectroradiometer. The local (Richmond, CA) solar spectral distribution was similarly measured for comparison. The two distributions were shown to correspond well. Comparisons of spectral distributions are shown in Figure 1; this particular xenon lamp produced, at some wavelengths, radiation more intense than present in sunlight. For the tests reported here, the average light flux in the wavelength range 300–420 nm was used for intensity comparisons. The average light flux over this spectral region for the xenon lamp was measured to be 100.8 W/m^2. The solar light flux in the same region, measured over 3 consecutive days in June 1988, is shown in Figure 2. As can be seen in Figure 2, the maximum intensity, occurring at approximately 1:02 pm, was 85.6 W/m^2. Therefore, 1 min of exposure to the xenon lamp is equivalent to 1.2 min of irradiation under the summer noon sun at Richmond, CA (latitude 37° 56′ N).

Photolysis Reactor. Two types of photolysis trials were carried out. The first, carried out on a small scale with radiolabeled napropamide, was designed to monitor the concentrations of napropamide remaining and various degradation products formed. Preliminary studies indicated that no volatile products formed during the photolysis of napropamide. Therefore, a closed system, consisting of a 10-mL quartz test tube (10 mm i.d.) equipped with a tapered, ground joint and a PTFE stopper, was used as the photoreactor. The temperature of the sample was controlled by immersing the test tube in a constant-temperature bath thermostated at 24 °C prior to each irradiation. At the end of each irradiation, the temperature of the test solution, measured with a thermocouple, was below 26 °C. In this manner, the temperature of the photolysis solution was controlled at 25 ± 1 °C. Trials of the second type were conducted to generate products in sufficient quantity for spectroscopic characterization. The photoreactor was a stainless steel chamber (30 × 15 × 5 cm) closed with a quartz window (34.5 × 19.4 × 0.64 cm) at the top and equipped with a cooling system so that the test solution was maintained at 25 ± 1 °C at all times.

Gas Chromatograph–Mass Spectrometry (GC–MS). Gas chromatograph–mass spectrometric (GC–MS) analysis was conducted with a Finnigan-Mat Model 4021 mass spectrometer equipped with a 15 m × 0.25 mm i.d. DB-5 (1.0 μm film thickness) fused silica capillary column. The column oven temperature was initially held at 40 °C for 3 min, programmed to 230 °C at 30 °C/min and then to 280 °C at 8 °C/min, and finally held at 280 °C for 30 min. Helium carrier gas was used at a head pressure of 5 psig. Sample was injected in the splitless mode. The MS was operated in the electron-impact (EI) mode. Direct exposure probe (DEP) MS analysis was performed with a VG Model 7070 EHF mass spectrometer operated in the EI mode. The maximum probe temperature was 600 °C.

Nuclear Magnetic Resonance (NMR) Spectrometry. NMR spectra were obtained on Varian Model XL-400 and General Electric Model QE-300 multinuclear spectrometers. Both spectrometers were fitted with carbon–proton switchable probes. Two-dimensional homonuclear (COSY) shift-correlated experiments were performed by using the conventional COSY pulse sequence (Bax et al., 1981). The spectral widths were 812 Hz in both the F_2 and F_1 dimensions. The number of data points were 512 in F_2 with 128 increments recorded. Before Fourier transformation, the data were multiplied with a pseudo-echo function (Bax et al., 1981) to obtain a clean Gaussian line shape in the

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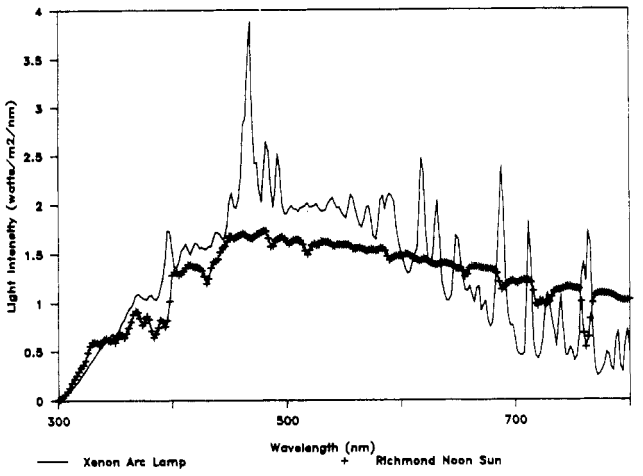

Figure 1. Comparison of xenon arc and solar spectral distributions.

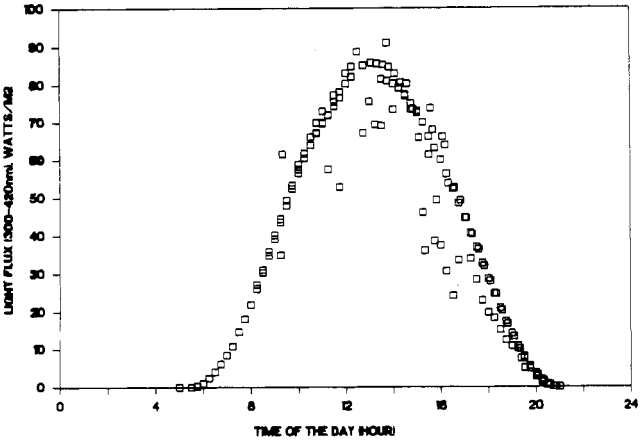

Figure 2. Time profile of summer Richmond sun, June 21–23, 1988.

absolute-value mode. After 2 dummy scans, 64 transients were collected for each t_1 increment. The recycle time was 1 s. Proton chemical shifts recorded in $CDCl_3$ were referenced to tetramethylsilane. Carbon chemical shifts were referenced to solvent peak $CDCl_3$ (76.90 ppm).

Liquid Chromatograph. High-performance liquid chromatographic analyses were conducted with a Perkin-Elmer Series 410 unit equipped with a Rheodyne Model 7125S injector and a Perkin-Elmer Model LC-95 UV–vis spectrophotometric detector set at 280 nm. A Radiomatic Flow-One-Beta Model IC radioactive flow monitor (RAM) was connected to the exit port of the UV–vis detector for the detection and quantitation of radiolabeled compounds. The combined system is abbreviated as HPLC/UV/RAM. A ChemcoPak Ultra-High column, 15 cm × 4.5 mm (i.d.) with 5 μm 30% carbon ODS, was used for all analyses. The mobile phase, flowing at 1 mL/min, was a mixture of 1:1 (v/v) acetonitrile and 0.1% trifluoroacetic acid in water for the first 5 min, programmed to 98:2 (v/v) over the next 10 min, and finally held at that composition for another 10 min. Under these conditions, the retention time of napropamide was 14.6 min.

Liquid Scintillation Counter. All radioactivities due to ^{14}C were measured with a Packard Model 460C liquid scintillation counter (LSC).

Photolysis Kinetics. A buffered aqueous solution (pH 7) of radiolabeled napropamide was prepared and exposed to xenon light of known intensity and spectral characteristics. At various time intervals, levels of napropamide and various products were monitored in duplicate with the HPLC/UV/RAM technique. The labeled napropamide test solution was prepared by pipetting 162.5 μL of labeled stock solution into a quartz test tube. After removal of the benzene solvent via a stream of dried nitrogen, a 10.5-mL portion of buffer solution (pH 7, 0.0025 M) was then added. The resulting solution had an activity of 83215 dpm/50 μL and an approximate napropamide content of 15 mg/L. A 1-mL portion of this solution was transferred into a vial wrapped in aluminum foil to serve as dark control. The test tube containing the balance of the test solution was then irradiated. Two 125-μL aliquots were removed after 0, 0.5, 1.0, 1.5, 2.0, 3.0,

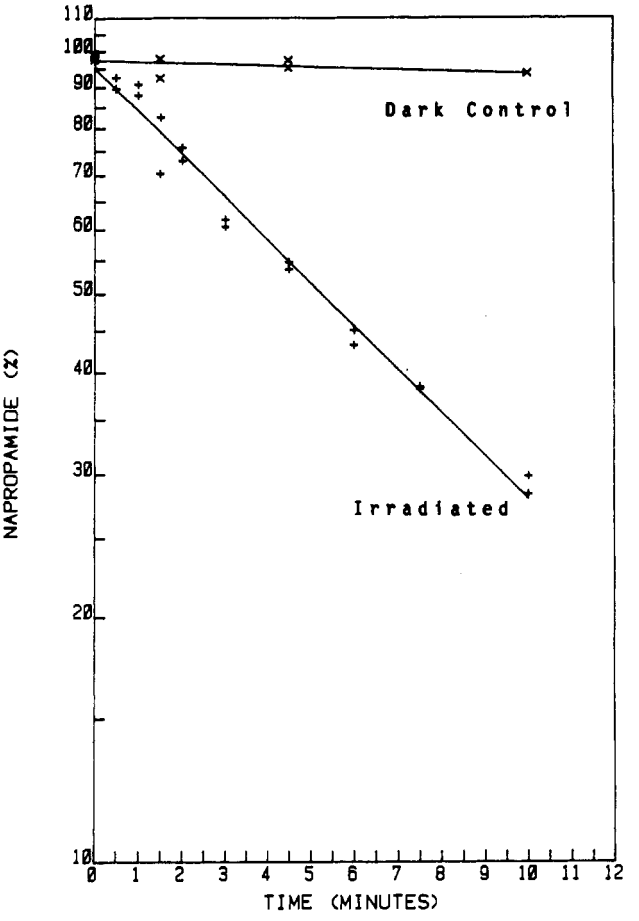

Figure 3. Photolysis rate plot of napropamide at pH 7 at 25 °C.

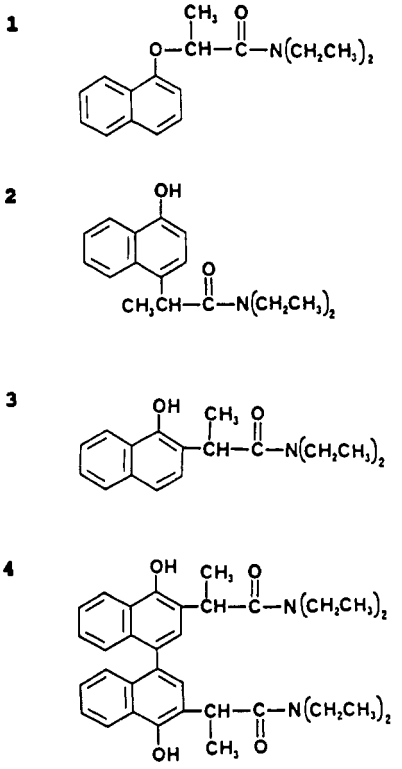

Figure 4. Structures of napropamide and photolysis products.

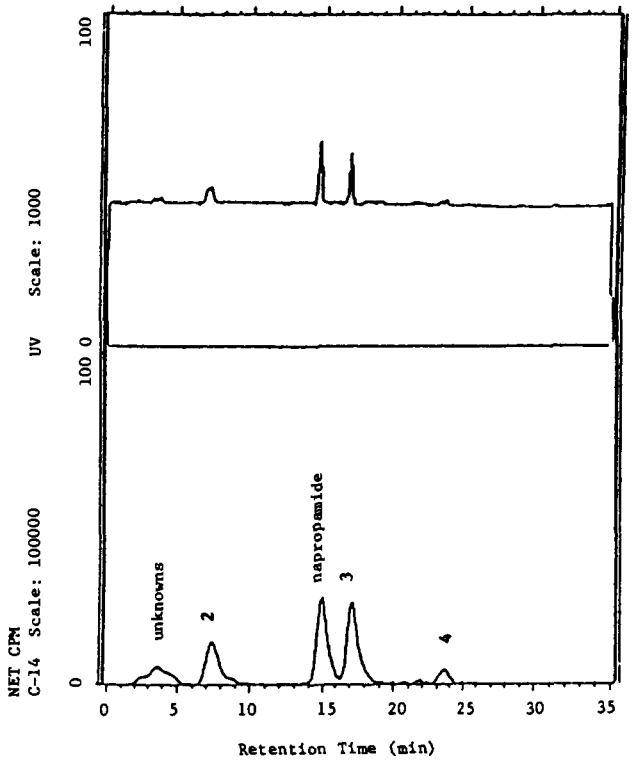

Figure 5. HPLC/UV/RAM chromatogram of a typical photolyzed sample. (Top) UV output; (bottom) RAM output.

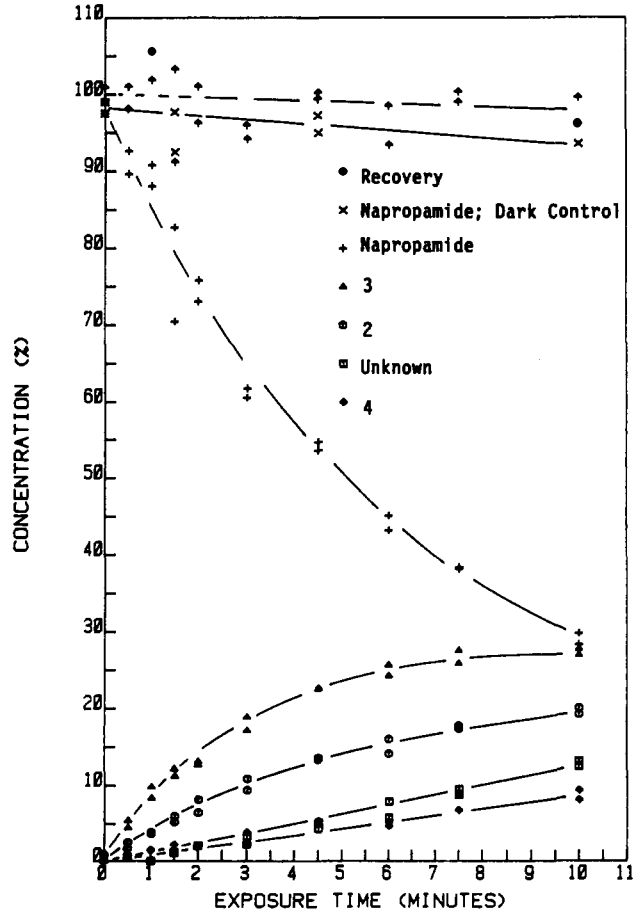

Figure 6. Time profile of napropamide and various products. 4.5, 6.0, 7.5, and 10.0 min of irradiation. Portions of dark control solution were similarly removed at 1.5, 4.5, and 10 min. Each aliquot was diluted with an equal volume of acetonitrile. A 100-μL aliquot of each dilute solution was analyzed by the HPLC/UV/RAM method.

Product Preparation. The solution used to generate a larger quantity of photolysis products was prepared by dissolving 120 mg of nonlabeled napropamide in 2 L of 0.013 M, pH 7, buffer. The resulting solution was photolyzed in four 500-mL batches for 10 min each in the stainless steel photolysis reactor so that the light path (1 cm) was approximately the same as that in the rate study. The photolyzed solutions were combined and evaporated to dryness under reduced pressure at 40 °C on a rotary evaporator. The residue was extracted with 10 mL of methylene chloride, which was then reduced in volume under a stream of dry nitrogen gas to approximately 1 mL, to which was added 1 mL of acetonitrile. Preparative HPLC of the acetonitrile solution using UV–visible detection separated unreacted 1, retention time (T_r) at 14.1 min, and three degradation products, 2 (T_r = 8.5), 3 (T_r = 15.8), and 4 (T_r = 20.2).

RESULTS AND DISCUSSION

Kinetic Data. Figure 3 shows that napropamide, although stable in the dark, degraded rapidly upon irradiation with simulated sunlight. The percent concentration of napropamide, plotted against time on a semilogarithmic scale, resulted in a straight line, suggesting pseudo-first-order kinetics. The photolysis half-life and the rate constant, in actual experiment time, were 5.7 min and 1.2×10^{-1} min^{-1}, respectively. Since 1 min of exposure is equivalent to 1.2 min of irradiation under the summer noon sun at Richmond, CA, the half-life and the rate constant, when expressed in equivalent natural sunlight, become 6.8 solar min and 1.0×10^{-1} solar min^{-1}, respectively. Photodegradation of napropamide is significantly faster in water than on soil.

Product Identification. The NMR and mass spectral data of napropamide and its degradation products are listed in Table I. The mass spectral data suggested 2 and 3 are isomers of napropamide, all having a molecular weight of 271. Compound 4 has a molecular weight of 540, indicating coupling of two molecules of napropamide.

The assignment of structures for these products was made from the NMR spectra. Proton NMR chemical shifts of napropamide have been reported by Tseng et al. (1975). However, no assignment has been made for the individual aromatic protons. Using two-dimensional (2-D) COSY data and the chemical shifts of 1-naphthalenol (Emsley et al., 1970) as a model, the individual aromatic protons of napropamide were assigned as shown in Table I. These assignments were necessary for establishing the exact substitution patterns for the photodegradation products.

The methine proton of 2 was observed at 4.44 ppm, a 0.66 ppm upfield shift from that in napropamide (5.10 ppm). The shift suggests that the propanamidyl group has migrated from the naphthalenol oxygen to an aromatic ring carbon. This structural change was further confirmed by the presence of a singlet at 6.03 ppm for a phenolic OH and reduction of the number of aromatic protons from six to five. A doublet at 6.77 ppm (H-2) indicated no change in the aromatic proton ortho to a hydroxyl group. The proton (H-3) at 7.21 ppm changed from a triplet to a doublet, indicating that H-4 was replaced by the propanamidyl group. Product 2 is therefore assigned to be *N*,*N*-diethyl-4-hydroxy-α-methyl-1-naphthaleneacetamide.

The proton NMR spectrum of 3 showed that, relative to napropamide, the upfield proton (about 6.8 ppm) corresponding to H-2 was absent and H-3 became a doublet at 7.07 ppm, due to coupling to H-4 at 7.27 ppm. These data indicate that the propanamidyl group had migrated to the 2-position of 1-naphthalenol. The carbon-13 NMR spectrum of 3 also indicated the methine carbon shifted upfield to 43.18 from 74.39 ppm observed for napropamide. The ring C-2 resonance shifted downfield to 117.60 from 105.78 ppm observed for napropamide. Therefore,

Table I. Spectral Data of Napropamide and Photolysis Products

compound	NMR chemical shift, ppm		mass data[c]
	proton[a]	carbon[b]	m/z
napropamide	0.97 (t, CH_3); 1.09 (t, CH_3); 1.71 (d, CH_3); 3.36–3.56 (m, 2 CH_2N); 5.10 (q, CH); 6.81 (d, H-2); 7.31 (t, H-3); 7.42 (d, H-4); 7.46 (m, H-6, H-7); 7.77 (dd, H-5); 8.28 (dd, H-8)	12.59, 14.07, 17.94, 40.32, 41.03, 74.39, 105.78, 120.93, 122.04, 125.29, 125.74, 126.42, 127.44, 134.61, 153.21, 170.15	271 (50) 171 (20) 128 (80) 100 (30) 72 (100) 57 (18)
2	0.87 (6, CH_3); 1.10 (t, CH_3); 1.50 (d, CH_3); 2.89, 3.10, 3.20, 3.59 (4 m, 2 CH_2N); 4.44 (q, CH); 6.05 (s, OH); 6.77 (d, H-2); 7.21 (d, H-3); 7.49, 7.56 (2 dt, H-6, H-7); 8.01 (d, H-5); 8.28 (dd, H-8)		271 (50) 171 (100) 128 (25) 100 (70) 72 (53)
3	1.11 (t, CH_3); 1.26 (t, CH_3); 1.62 (d, CH_3); 3.42–3.52 (m, 2 CH_2N); 4.00 (q, CH); 7.07 (d, H-3); 7.27 (d, H-4); 7.42 (m, H-6, H-7); 7.71 (m, H-5); 8.36 (m, H-8); 11.55 (s, OH)	12.80, 14.85, 17.35, 41.60, 42.73, 43.18, 117.60, 118.80, 122.80, 124.85, 126.05, 126.63, 126.79, 128.45, 133.90, 152.99, 176.37	271 (41) 198 (88) 170 (100) 152 (12) 141 (15) 128 (12) 100 (15) 74 (27) 58 (34)
4	1.15–1.23 (m, 4 CH_3); 1.68 (m, 2 CH_3); 3.38–3.52 (m, 4 CH_2N); 3.98 (2 q, CH); 4.01, 4.02 (2 q, CH); 7.05, 7.06, 7.13 (3 s, 2 H-3); 7.23; 7.30, 7.45 (3 m, 2 H-5, 2 H-6, 2 H-7); 8.48 (m, 2 H-8); 11.54, 11.62, 11.70, 11.77 (4 s, 2 OH)		540 (20) 467 (13) 394 (100) 366 (28) 338 (32) 313 (34) 100 (15) 84 (96) 75 (100) 58 (43)

[a] H NMR spectra obtained in $CDCl_3$ and referenced to tetramethylsilane; s, d, t, q, and m signify singlet, doublet, triplet, quartet, and multiplet, respectively. [b] C NMR spectra obtained in $CDCl_3$ and referenced to $CDCl_3$ (76.90 ppm). [c] Mass spectra obtained by EI at 70 eV or by DEP-EI; relative intensities in parentheses after m/z values.

3 is assigned as *N,N*-diethyl-1-hydroxy-α-methyl-2-naphthaleneacetamide.

The results of proton NMR and 2-D NMR analyses of **4** indicated that napropamide first formed **3**, which then coupled with a second molecule of **3** at the 4-position. The spectrum was complex due to nonplanarity of the two naphthalene rings and presence of two chiral carbons. A total of four isomers could be distinguished. Four sets of quartets were resolved for the methine proton centered about 4.00 ppm. In the aromatic region, resonances at 7.05, 7.06, and 7.13 ppm with relative intensities of 1:1:2 were confirmed to be three singlets by the 2-D COSY experiment. The range of the singlets coincides closely with H-3 in **3**. These data supported the coupling of **3** at the 4-position. Coupling of **2** was ruled out because the methine protons of the coupling product appeared at approximately 4.0 ppm, identical with the methine proton chemical shift of **3**. On the other hand, the methine proton chemical shift of **2** appeared at 4.44 ppm. Therefore, **4** is assigned as *N,N,N',N'*-tetraethyl-4,4'-dihydroxy-α,α'-dimethyl[1,1'-binaphthalene]-3,3'-diacetamide. The structures of napropamide and its photolysis products are shown in Figure 4.

Examination of the structures of the photodegradation products suggests that aqueous photolysis of napropamide involves an initial rearrangement of the propanamidyl group to the 2-position (**3**) or to the 4-position (**2**) of the naphthalenyloxy ring. Coupling occurred at the 4-position of **3** to yield product **4**. Coupling involving **2** was not observed, presumably due to effects of steric hindrance.

Product Distribution and Mass Balance. The product distribution and mass balance data were obtained from the experiment using radiolabeled napropamide. A typical HPLC/UV/RAM chromatogram of napropamide after it was photolyzed for 10 min is given in Figure 5. Five peaks eluted at retention times of 3.7, 7.4, 15.0, 17.2, and 23.7 min. The unknown peak, which eluted at around 3.7 min, actually consisted of three components, in approximately equal amounts, with a total content of 13% at the end of photolysis. Due to poor response to the UV detection system, the unknown peak could not be isolated for identification. The peaks with retention times of 7.4, 15.0, 17.2, and 23.7 min, corresponding to **2**, napropamide, **3**, and **4**, amount to 20%, 29%, 27%, and 9%, respectively. Figure 6 shows time course plots of degradation products, remaining napropamide, and the total recovery. Also included in Figure 6 is the time course plot of napropamide content in the dark control. Average recoveries are 98.6% and 95.8%, respectively, for irradiated materials and dark controls.

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