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Photodecomposition of an Acaricide, Fenazaquin, in Aqueous Alcoholic Solution

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Fenazaquin (**I**) is a new acaricide of the quinazoline class. The photodecomposition of **I** was studied in aqueous methanolic and 2-propanolic solution under UV light (30 h) and sunlight (70 h) separately. The photolytic half-lives in aqueous methanolic solution were found to be 17.1 h (UV) and 38.1 h (sunlight), whereas these were 12.9 h (UV) and 29.2 h (sunlight) for aqueous 2-propanolic solution; all followed a first-order reaction kinetics. Six photoproducts were obtained: β-phenyl (*p-tert*-butyl) ethyl alcohol (**II**), 4-hydroxyquinazoline (**III**), *p-tert*-butyl vinyl benzene (**IV**), 2,4-dihydroxyquinazoline (**V**), phenyl (*p-tert*-butyl) acetic acid (**VI**), and 2-methyl-2-[4′-(2″-hydroxyethyl)phenyl]propanoic acid (**VII**). Compounds **VI** and **VII** could be isolated only from aqueous 2-propanolic solution under sunlight irradiation. The major degradation products are formed as a result of cleavage of the ether bridge linking the quinazoline and phenyl ring systems of the molecule, oxidation of the *tert*-butyl substituent, and oxidation of the heterocyclic portion of the quinazoline ring. A probable mechanism of formation of the photoproducts is also suggested.

KEYWORDS: Fenazaquin; photometabolite; methanol; 2-propanol; UV; sunlight

INTRODUCTION

The quinazolines offer a unique chemical configuration, consisting only of one acaricide, fenazaquin (4-*tert*-butylphenethylquinazolin-4-yl ether, **I**). It is used for control of mites (*Eutetranychus, Panonychus*, and *Tetranychus* spp.) on cotton, stone and pome fruits, citrus, grapes, and ornamentals (*1*, *2*). It is a contact and stomach acaricide. It has ovicidal activity, gives rapid knockdown, and controls all stages of mites. It has a novel mode of action and is being used as an ideal mite management tool. Fenazaquin inhibits mitochondrial electron transport at site I of the mitochondrial respiratory chain (*3*, *4*). It is a lipophilic compound and hence is immobile in soils and is not translocated in plants. Studies on the field dissipation suggest that the half-life in soil ranges between 26 and 71 days (*5*). From our recent study on the residues and dissipation in chili, it was found that the half-life values ranged from 4.3 to 6.02 days and followed a first-order reaction kinetics (*6*). To study the environmental degradation and dissipation of this acaricide after its application in the field, experiments have been done on the photodecomposition of **I** under sunlight and UV irradiation in aqueous methanolic and 2-propanolic solution. The primary objectives of this study were to characterize the photodegradation products and to determine their probable mechanism of formation.

MATERIALS AND METHODS

Chemicals. Fenazaquin 10% EC and analytical standard (99.8%) were obtained from M/S De-Nocil Crop Protection Pvt. Ltd. (Mumbai, India). **I** was isolated in bulk from the formulation by column chromatography and subsequently purified by repeated crystallization from hexane, mp 81 °C (99.5% pure). All of the solvents used were of analytical reagent grade and were redistilled before use. Water used was double glass distilled.

Apparatus and Chromatography. The purity of **I** and quantification of results were carried out with HPLC, model 1050 Hewlett-Packard (HP), equipped with an HP 1050 UV detector set at λ_{max} = 214 nm and coupled to an HP model 3392 A integrator. The column used was reversed-phase Hypersil (ODS) of Shandon HPLC, U.K. (μ Bondapak C_{18}); the mobile phase was acetonitrile (100%) at a flow rate of 0.6 mL/min; volume injected was 20 μL; and retention time (RT) was 5.50 min. Mass spectra (electron impact, 70 eV, direct insertion) were recorded on a JEOL JMSD X 300 mass spectrometer. NMR spectra were recorded on a Bruker DRX-300 spectrometer (300 MHz) using TMS as an internal standard. IR spectra were taken of KBr pellets by using a Perkin-Elmer model 1310 spectrophotometer. GC-MS spectra were obtained on a Shimadzu QP 2000 instrument (70 eV). The GC conditions were as follows: an ULBON HR-1 equivalent to OV-1; fused silica capillary (0.24 mm × 12.5 m) with film thickness = 0.25 μm; temperature program, 100 °C for 6 min increased at 10 °C/min to 250 °C.

TLC was performed on 20 × 20 cm glass plates coated with 0.5 mm silica gel G using iodine as chromogenic reagent. Column chromatography was conducted using glass columns of various sizes packed with a slurry of silica gel (60−120 mesh) in hexane (bp 69.5 °C). All melting points are uncorrected.

Irradiation Experiment. I (250 mg, 250 ppm) was dissolved in methanol−water (4:1 v/v, 1 L) and 2-propanol−water (4:1 v/v, 1 L) separately and mixed thoroughly. The above two mixtures were separately irradiated for 30 h in a photoreactor made of borosilicate glass (capacity = 1 L) with a high-pressure mercury lamp (HPK, 125

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Table 1. Extraction Scheme for Fenazaquin Photodecomposition Products

irradiated solution	fraction	compound	
		UV	sunlight
methanol–water (4:1)	hexane–benzene (1:1)	**II**	**II**
	benzene	**I**	**I**
	benzene–ethyl acetate (7:3)	**III**	**III**
2-propanol–water (4:1)	hexane–benzene (1:1)	**II** + **IV**	**II** + **IV** + **VI**
	benzene	**I**	**I**
	benzene–ethyl acetate (7:3)	**III** + **V**	**III** + **V** + **VII**

Table 2. Relative Amount (Percent) of Fenazaquin Photodecomposition Products

photoproduct	relative amount (%)			
	UV		sunlight	
	methanol–water (4:1)	2-propanol–water (4:1)	methanol–water (4:1)	2-propanol–water (4:1)
fenazaquin	30.00	20.00	28.00	17.00
II	17.15	19.30	18.05	21.40
III	15.6	18.35	17.30	20.95
IV		4.75		5.75
V		2.35		3.75
VI				2.35
VII				1.85
unidentified	37.25	35.25	36.65	26.95

W, Philips) jacketed with a water-cooled quartz filter to achieve maximum intensity of UV light at $\lambda \geq 250$ nm under continuous stirring by a magnetic stirrer. The temperature of the photolysis solution did not exceed 25 °C. Similarly, the same amount was irradiated for 70 h under natural sunlight (at Kalyani, 22° 57′ N latitude, 7.8 m altitude, India), in methanol−water (4:1 v/v, 1 L) and 2-propanol−water (4:1 v/v, 1 L) separately in borosilicate flasks. The mouths of the flasks were tightly covered with a polythene sheet to prevent contamination. Samples were removed at intervals and analyzed by HPLC to monitor the rate of photolysis of **I.** To obtain enough of the photoproducts for structure elucidation, the solutions obtained from irradiation of eight batches each of aqueous methanol and aqueous 2-propanol solution (250 mg of **I** in 1 L in each case) were pooled separately from irradiated (UV and sunlight) solutions.

Isolation of Photoproducts. The combined methanolic and 2-propanolic solutions of **I** under UV and sunlight irradiation were extracted separately with dichloromethane and concentrated by rotary vacuum evaporator (∼40 °C) and were subjected to column chromatography over silica gel as summarazied in **Table 1**. The relative amounts of the different photoproducts are shown in **Table 2**.

RESULTS AND DISCUSSION

Identification of Photoproducts. Elution with hexane−benzene (1:1 v/v) of UV/sunlight-irradiated methanolic and 2-propanolic solutions afforded a yellowish liquid (**II**), bp 143−145 °C. Upon mass analysis, the compound gave a molecular ion peak at *m*/*e* 178 (the major mass fragments are recorded in **Table 3**). The IR spectrum of **II** indicated the presence of primary alcoholic groups at 1270 and 1050 cm^{-1} in addition to 3320 cm^{-1} (O−H stretching), 1460 and 1400 cm^{-1} (C−C stretching within the ring), and 1110 cm^{-1} (C−O stretching). The NMR spectrum of **II** disclosed the presence of four aromatic protons at δ 7−9. Two benzylic protons at δ 2.83 and two

Table 3. HPLC Retention Time and Mass Spectral Data of Photometabolites of **I**

product	retention time, min	mass found	% abundance	structure
II	11.41	178	31.8	M^+
		163	100.0	$M^+ - CH_3^\bullet$
		147	26.3	$M^+ - CH_3^\bullet - OH^\bullet + H^\bullet$
		105	36.2	$M^+ - CH_3^\bullet - OH^\bullet + H^\bullet - (CH_3)_2C^\bullet$
		91	47.2	$M^+ - CH_3^\bullet - OH^\bullet + H^\bullet - (CH_3)_2C^\bullet - CH_3^\bullet + H^\bullet$
III	3.11	146	18.4	M^+
		145	100.0	$M^+ - 1$
		129	29.2	$M^+ - OH^\bullet$
		91	20.0	tropylium ion
IV	28.53	160	44.5	M^+
		145	100.0	$M^+ - CH_3^\bullet$
		131	9.7	$M^+ - CH_3^\bullet - CH_3^\bullet + H^\bullet$
		117	13.0	$M^+ - CH_3^\bullet - CH_3^\bullet + H^\bullet - CH_3^\bullet + H^\bullet$
		91	8.6	$M^+ - CH_3^\bullet - CH_3^\bullet + H^\bullet - CH_3^\bullet + H^\bullet - C_2H_3^\bullet + H^\bullet$
V	29.90	162	27.1	M^+
		161	7.6	$M^+ - 1$
		145	100.0	$M^+ - OH^\bullet$
		129	14.1	$M^+ - OH^\bullet - OH^\bullet + H^\bullet$
		91	10.8	tropylium ion
VI	12.26	192	4.3	M^+
		191	20.6	$M^+ - 1$
		148	77.1	$M^+ - 1 - CO_2 + H^\bullet$
		135	100.0	$M^+ - 1 - CO_2 + H^\bullet - CH_3^\bullet$
		121	63.0	$M^+ - 1 - CO_2 + H^\bullet - CH_3^\bullet - CH_3^\bullet + H^\bullet$
		107	90.2	$M^+ - 1 - CO_2 + H^\bullet - CH_3^\bullet - CH_3^\bullet + H^\bullet - CH_3^\bullet + H^\bullet$
		91	13.0	$M^+ - 1 - CO_2 + H^\bullet - CH_3^\bullet - CH_3^\bullet + H^\bullet - CH_3^\bullet + H^\bullet - CH_3^\bullet + H^\bullet$
VII	32.36	208	13.9	M^+
		206	46.2	$M^+ - 2H^\bullet$
		188	100.0	$M^+ - 2H^\bullet - OH^\bullet - H^\bullet$
		160	53.7	$M^+ - 2H^\bullet - OH^\bullet - H^\bullet - CO$
		132	23.6	$M^+ - 2H^\bullet - OH^\bullet - H^\bullet - CO - CO$
		91	22.5	$M^+ - 2H^\bullet - OH^\bullet - H^\bullet - CO - CO - (CH_3)_2C^\bullet + H^\bullet$

alcoholic protons at δ 3.84 appeared as a triplet. The appearance of a singlet at δ 1.31 showed the presence of a *tert*-butyl group. On the basis of MS, NMR, and IR data, the structure of **II** could be assigned as β-phenyl (*p-tert*-butyl) ethyl alcohol.

Further elution with benzene−ethyl acetate (7:3, v/v) yielded an off-white amorphous solid (**III**), mp 222−224 °C, showing a molecular ion peak at *m*/*e* 146, which was 160 mass units less than **I** (*m*/*e* 306) corresponding to the loss of β-phenyl (*p-tert*-butyl) ethyl side chain. The remaining mass fragments are shown in **Table 3**. Consequently, **III** could be assigned as 4-hydroxyquinazoline. The NMR spectrum of **III** indicated the presence of five aromatic protons [δ 7.26 (lH, s), 7.54 (1H, m), 7.79 (1H, m), 8.09 (1H, s), and 8.31 (1H, t)] and one OH group at δ 3.49, which disappeared on D_2O exchange, and a new peak appeared at δ4.75. Furthermore, the IR spectrum of **III** also supported the presence of a hydroxyl group (3120 cm^{-1}).

The fractions that were subjected to GC-MS analysis gave indications of the compound having molecular ion peaks at *m*/*e* 160, 162, 192, and 208, and on the basis of the MS data (**Table 3**) the compounds were identified as *p-tert*-butyl vinyl benzene (**IV**), 2,4-dihydroxyquinazoline (**V**), phenyl (*p-tert*-butyl) acetic acid (**VI**), and 2-methyl-2-[4′-(2″-hydroxyethyl)phenyl]propanoic acid (**VII**), respectively.

As fenazaquin (**I**) is insoluble in water, the photolysis reaction was carried out in methanol−water (4:1 v/v) and 2-propanol−water (4:1 v/v) under UV irradiation at $\lambda \geq 250$ nm and sunlight. Kinetics study showed that 50% of **I** degrades in 15 and 50 h in the case of UV and sunlight, respectively. The photolytic half-lives in aqueous methanolic solution were found to be 17.1 h (UV) and 38.1 h (sunlight), whereas those in 2-propanolic solution were 12.9 h (UV) and 29.2 h (sunlight); the half-lives followed a first-order reaction kinetics. A dark control was kept, and no reaction was observed during the entire UV and sunlight irradiation period. The aqueous 2-propanolic solution showed faster photodecomposition than the methanolic solution, irrespective of UV and sunlight irradiation (**Figure 1**) The higher rate of degradation in 2-propanol is probably due to rapid transformation of **I** involving hydrogen atom abstraction, which is more facile from 2-propanol than from methanol. This is because of the much greater stability of the component radical species generated from 2-propanol than from methanol (*7*).

The major degradation products are formed as a result of breakage of the ether bridge linking the quinazoline and phenyl ring system of the molecule, and this leads to the formation of two common photolysis products, **II** and **III**, from which the formation of all other products could be rationalized. Compound **II**, on dehydration, oxidation of the primary alcoholic group, and oxidation of one of the methyl groups in the *tert*-butyl group, leads to the formation of **IV**, **VI**, and **VII**, respectively. The presence of water and oxygen in the medium facilitates the conversion of **III** to **V**, involving abstraction of a hydroxyl radical by the compound **III**, which seems to arise by a mechanism shown in

$$\mathbf{I} \rightarrow \mathbf{I}^{\bullet} \quad (1)$$

$$\mathbf{I}^{\bullet} + O_2 \rightarrow O_2^{\bullet} + \mathbf{I} \quad (2)$$

$$H_2O + O_2 \rightarrow OH^{\bullet} + O_2{}^{\bullet}H \quad (3)$$

Compounds **VI** and **VII** were isolated only from sunlight-irradiated 2-propanol solution of **I**. This variation in the distribution of photoproducts might possibly be due to variation in wavelength and time of irradiation. On the basis of photoproducts identified, a plausible mechanism of the formation of these photoproducts from **I** is presented in **Figure 2**.

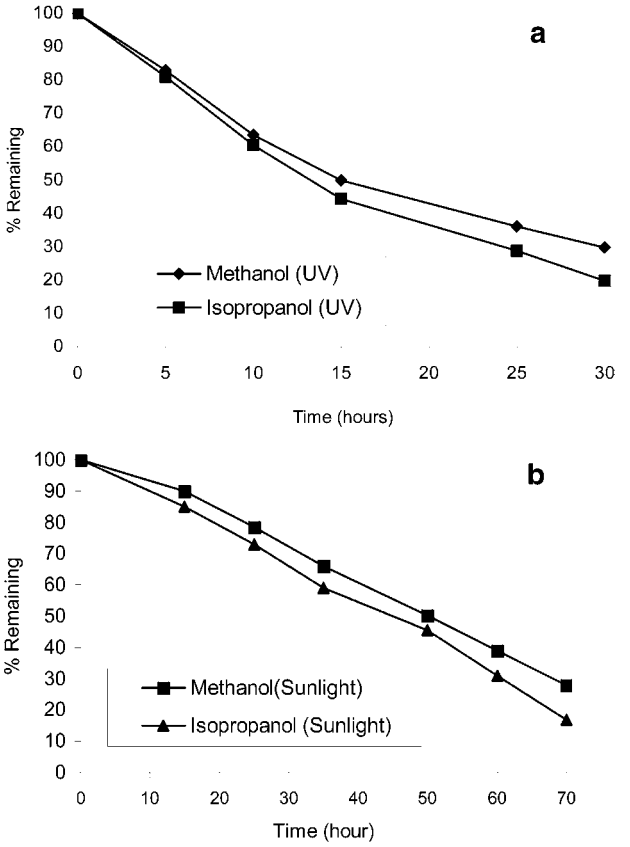

Figure 1. Photokinetics of fenazaquin in aqueous solution under (a) UV irradiation and (b) sunlight irradiation.

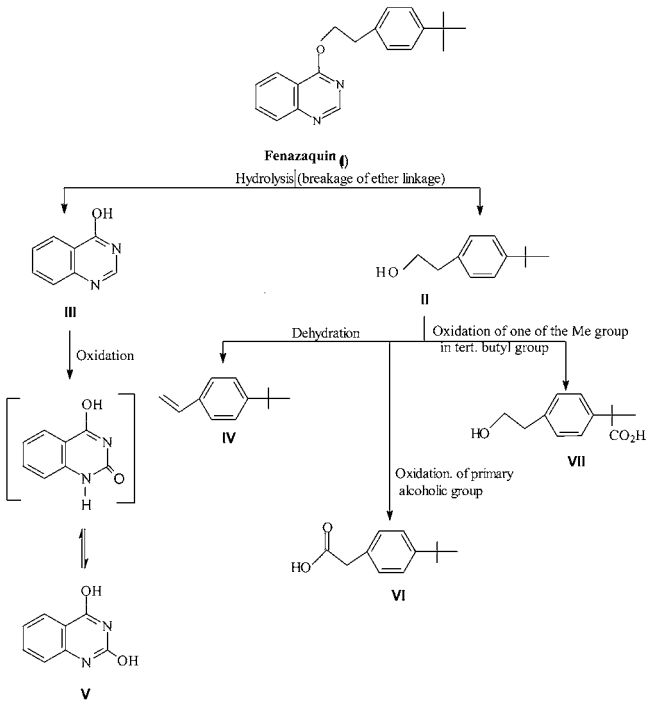

Figure 2. Plausible photometabolic pathways of fenazaquin in aqueous methanol and 2-propanol solution under UV and sunlight irradiation.

Pesticides suffer photodegradation by hydroxyl radicals (*8*) that have been shown to be present in sunlight-irradiated natural waters (*9*). Accordingly, the reactivity of **I** toward hydroxyl radicals and the nature of the products formed would be the

same to what may be expected in natural waters. Thus, it seems that a potential exists for the application of photolysis in the removal of traces of quinazoline acaricide. Moreover, the present study indicates that the main phototransformation pathway of **I** involves hydrolysis, oxidation, and dehydration.

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