EXAMINATION OF THE CONVERSION PRODUCTS OF PYRETHRINS AND ALLETHRIN FORMULATIONS EXPOSED TO SUNLIGHT BY GAS CHROMATOGRAPHY AND MASS SPECTROMETRY*

YOSHIHIKO KAWANO* and KARL YANAGIHARA

Department of Agricultural Biochemistry, College of Tropical Agriculture and Human Resources, University of Hawaii, Honolulu, HI (U.S.A.)

and

TORU MIYAMOTO and IZURU YAMAMOTO

Department of Agricultural Chemistry, Tokyo University of Agriculture, Setagaya, Tokyo (Japan)

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SUMMARY

Natural and synthetic pyrethrins in kerosene solution similar to commercial formulations were stored in clear soft-glass bottles and exposed to sunlight through clear window glass. Transition photoproducts were observed by gas chromatography (GC) for cinerin I and II, and jasmolin I and II, which revealed slightly shorter retention times than the pyrethrins. No photoproducts for pyrethrin I and II were observed, which may have polymerized or been converted into products of higher polarity. Critical studies on the photoproduct from jasmolin I indicated the isomerization of (Z)-pent-2-enyl side-chain of the rethrolone moiety to the (E)-isomer. Other circumstantial evidence indicated that a similar change occurred with jasmolin II and cinerin I and II. Allethrin, under similar conditions, had a photoproduct with a longer retention time, which was identified as an isomer with a cyclopropyl side-chain, the *d,l*-cyclopropylrethronyl *d-trans*-crysanthemate.

INTRODUCTION

The presence of "false" pyrethrins in pyrethrin extracts was reported by Brown and co-workers[1-4]. Brown *et al.*[4], utilizing the modified sulfur color test[5], examined the heated extracts and identified two isomers, isopyrethrin I and isopyrethrin II. The conversion products were noted when pyrethrin extracts were examined by gas chromatography with flame-ionization detection by Head *et al.*[6]; however, the products were not identified. The acid moiety of the photodegradation products of pyrethrins from the exposure of extracts to UV light was identified by thin-layer chromatography (TLC)[7]. Abe *et al.*[8] observed an unknown component of a pyrethrin film, irradiated with a 500-W incandescent lamp, by gas–liquid chromatography.

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Bullivant and Pattenden[9] applied direct photolysis to the major constituents of pyrethrins by exposing the material to a 100-W medium-pressure mercury-arc quartz-filtered light and monitored the reaction by gas chromatography (GC). Elliott[10] noted that new isomers were formed when *cis*-pyrethrolone and related compounds were heated, and he confirmed the tentative findings of Brown *et al.*[4] that isopyrethrin I and isopyrethrin II were found in heat-treated pyrethrin extracts. Recently, the formation of isopyrethrin I and isopyrethrin II were confirmed by gas chromatography–mass spectrometry (GC–MS) of the pyrethrin extracts in heat-treated sealed tubes[11].

In this study, extracts of pyrethrins and allethrin exposed to sunlight through clear window glass were examined by GC and GC–MS. Supporting data was obtained by GC, NMR and solid probe mass spectrometric analyses of isolated photoproducts of jasmolin I and allethrin which had been exposed to a 100-W mercury lamp.

EXPERIMENTAL

Chemicals

Refined natural pyrethrin extracts from Kenya, Tanzania and Ecuador were supplied by Dr. Dean Kassera of McLaughlin Gormley King Co., U.S.A.; the sample of Fumakilla Brand pyrethrin extract was received from T. Takano, Japan Pyrethrin Institute, Kyoto, Japan; and the World Standard pyrethrin extracts were supplied by V. M. Shah, Pyrethrum Marketing Board, Nakura, Kenya.

Two grams of each refined extract (20% pyrethrins) were weighed into a 50-ml volumetric flask and diluted to 50 ml with kerosene. Equal parts of the solution were transferred into an 8-oz Owens clear glass bottle and a 50-ml brown bottle.

Jasmolin I was isolated from a pyrethrum extract (66.5%, Dainippon Jotyugiku, Osaka, Japan).

Allethrin, 0.1 g (purity 90%, supplied by Sumitomo Chemical, Osaka, Japan), was weighed into a 50-ml volumetric flask and diluted to 50 ml with kerosene. The solution was divided in the same manner as described above.

Bioallethrin, *d-trans*-chrysanthemate of *d,l*-allethrolone (>93%), was supplied by Maruwaka Kagaku, Osaka, Japan.

Chromatography and analytical procedure

TLC of the mercury lamp-exposed jasmolin and allethrin was performed on 0.25-mm pre-coated silica gel 60F$_{254}$ glass plates (Merck, Darmstadt, G.F.R.). The plates were developed with *n*-hexane–ethyl acetate (4:1). Detection was accomplished by spraying the plates with saturated ethanolic molybdophosphoric acid solution and heating at 110°C for 3–4 min. Dark blue spots were observed under 253.6-nm UV light.

Pure jasmolin I was isolated by column chromatography through two columns. The first column, 50 cm × 43 mm I.D., was slurry packed with 36.5 cm of 100–200-mesh silica gel (Kanto Chemical, Japan) in *n*-hexane. The Dainippon extract (6 g) was then added and eluted with 800 ml of 95:5 and 1200 ml of 90:10 *n*-hexane–ethyl acetate. Fractions of 7.8 g were collected and monitored by TLC for jasmolin I. Approximately 430 mg of crude jasmolin I were collected in fractions 22–28. The crude jasmolin I was purified on a second column, 100 cm × 20 mm I.D.,

prepared in the same manner as the first column except that 61.5 cm of silica gel was added. The same solvent mixtures were used with reduced volumes of 300 and 400 ml, respectively. The purified jasmolin I (100 mg) was collected in fractions 12–15. Isolation of the unknown allethrin photoproduct from 1 g of the Maruwaka allethrin formulation exposed to the mercury lamp was accomplished through a single column chromatographic step. The same column chromatographic procedure as used for the initial isolation of the crude jasmolin I isolated 290 mg of pure allethrin photoproduct in fractions 13–17.

Infrared (IR) spectra of carbon disulfide solutions of allethrin and its photoproduct were determined with a Shimadzu 27S grating infrared spectrophotometer.

Proton nuclear magnetic resonance (PMR) spectra of jasmolin I (J_1), allethrin and their corresponding photoproducts were obtained in deuterochloroform solution on a JEOL JNM-PMX60 NMR spectrometer.

Electron-impact mass spectra (MS) were obtained with a JEOL JMS-D400 mass spectrometer. The operating conditions were as follows: accelerating voltage, 3 kV; scan speed, 10 sec; multiplier, 1.3 kV; ionizing voltage, 75 eV; ionizing current, 300 μA; solid probe sample temperature settings, for J_1 70°C and for the photoproduct of allethrin 45°C.

The Hitachi 063 gas chromatograph was equipped with a 1 m × 3 mm I.D. stainless-steel column packed with 10% SE-30 on Chromosorb W (100–120 mesh), with an oven temperature of 210°C. The flow-rate of the carrier gas (nitrogen) was 40 ml/min.

The Shimadzu GC-6A gas chromatograph was equipped with a 2 m × 3 mm I.D. glass column packed with 10% SE-30 on Chromosorb W (100–120 mesh), with an oven temperature of 245°C.

The F & M Model 810 gas chromatograph was equipped with a flame-ionization detector (FID). A 60 cm × 3.2 mm I.D. glass column was packed with 2.5% XE-60 on Chromosorb W, acid washed, DMCS treated (60–100 mesh) [a mixture of equal parts of 3% XE-60 on Chromosorb W (80–100 mesh) and 2% XE-60 on Chromosorb W (60–80 mesh)] (see details in ref. 12). The operating conditions were as follows: injection port temperature, 190°C; column temperature, matrix temperature programming from 150 to 205°C; detector temperature, 225°C. The matrix temperature programming for the pyrethrin study was as follows. The initial temperature was set at 150°C and held there for 5 min starting from the initial rise of the solvent peak. The temperature was then programmed at 20°C/min to 175°C and held there until 2.25 min past the apex of the Py_1 peak. The oven temperature was then further increased at 20°C/min to 205°C and held there until the elution of the Py_2 group.

A matrix temperature program was used for the allethrin study. The initial temperature was set at 150°C and held there for 5 min after the initial rise of the solvent peak. The oven temperature was programmed at 20°C/min to 170°C and held there until the elution of allethrin and its photoproduct.

A Finnigan Model 3000 mass spectrometer was used with a sensitivity setting of 10^{-6} A/V, electron multiplier high voltage −2.00 kV and electron energy 69.5 V. The mass spectrum was taken at the apex of each peak. A glass column, 45 cm × 2 mm I.D., was packed with 2.5% XE-60 on Chromosorb W (60–100 mesh). The helium flow-rate was 20 ml/min and the system was matrix programmed as described above for the F & M 810.

Exposure to sunlight under mild conditions

The control solutions in the 50-ml brown bottles were stored in the dark. The solutions in the clear glass bottles were placed on a platform 3 in. away from a clear glass window for the exposure study. The entire bottle was exposed to sunlight for about 3 h each morning through a clear glass window facing the east side of the building. During the remainder of each day, no direct sunlight struck the bottles. The samples were exposed to sunlight for 121 days (period between June and September). The temperature of the liquid in the bottles ranged from 30 to 58°C on exposure to direct sunlight and decreased to 23 to 27°C during the shaded period of the day.

Photochemical reaction

The irradiations were performed with a 100-W high-pressure mercury vapor lamp made by Riko Kagaku Sanyo (Chiba, Japan). Before irradiation, the reaction solutions were purged with dry nitrogen for 1 h. The photochemical reactions were monitored by removing samples at intervals followed by GC analysis with an FID. Photolysis was continued until photoequilibrium was established. After the removal of the solvent by distillation *in vacuo*, the photoproducts were isolated and purified by chromatography.

RESULTS AND DISCUSSION

Six insecticidally active esters were identified in pyrethrin extracts: cinerin I (C_I), jasmolin I (J_I), pyrethrin I (Py_I), cinerin II (C_{II}), jasmolin II (J_{II}) and pyrethrin II (Py_{II}). The first three esters are grouped together as Py_1; the other three are grouped together as Py_2 (see Fig. 1).
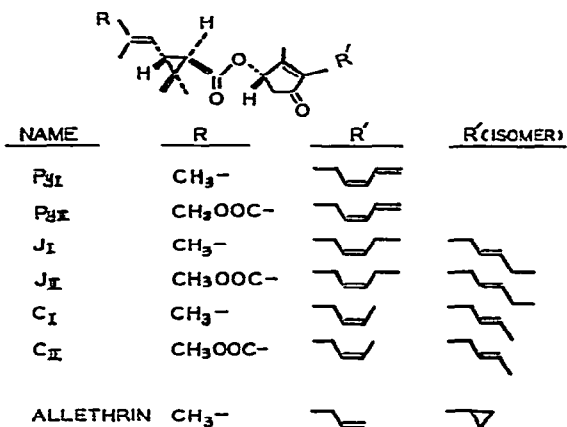

Fig. 1. Structures of the six insecticidally active esters of pyrethrins, the synthetic pyrethroid allethrin and their sunlight products (J_I', J_{II}', C_I', C_{II}' and allethrin).

The chromatogram of the unexposed extract from Kenya (Fig. 2A) revealed the six major constituents C_I, J_I, Py_I, C_{II}, J_{II} and Py_{II}. The chromatogram of the extract from Kenya exposed to sunlight (Fig. 2) revealed decreasing peak areas of C_I, J_I, Py_I, C_{II}, J_{II} and Py_{II}. Simultaneously, unknown peaks labeled C_I', J_I', C_{II}'
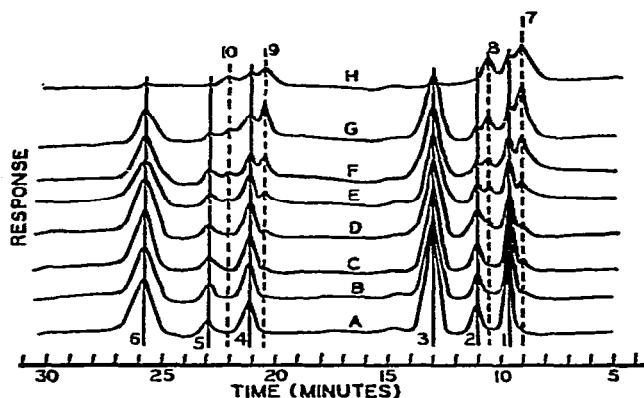
Fig. 2. Comparison of gas chromatograms of a pyrethrin formulation made with an extract from Kenya exposed to sunlight 0 (A), 8 (B), 29 (C), 39 (D), 52 (E), 56 (F), 63 (G) and 121 (H) days. Peaks: $1 = C_I$; $2 = J_I$; $3 = Py_I$; $4 = C_{II}$; $5 = J_{II}$; $6 = Py_{II}$; $7 =$ unknown C_I'; $8 =$ unknown J_I'; $9 =$ unknown C_{II}'; $10 =$ unknown J_{II}'.

and J_{II}' increased in area with increasing exposure to sunlight. Similar chromatograms were observed in sunlight-exposed extracts of Ecuador (Fig. 3), Fumakilla (Fig. 4) and Tanzania (Fig. 5).
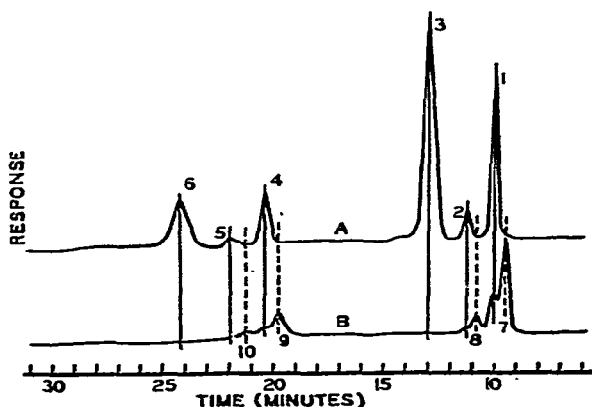
Fig. 3. Comparison of gas chromatograms of a pyrethrin formulation made with an Ecuador extract exposed to sunlight for 0 (A) and 100 days (B). Peaks as in Fig. 2.

Apparently, the sum of the areas of the reduced C_I, C_{II}, J_I and J_{II} and their conversion products are approximately equal to that of the original pyrethrin esters. When the sunlight exposure time was increased, the sum of the area calculation did not hold as it did initially. The area calculation was attempted on chromatograms of Tanzania extract used for the sunlight exposure study (see Fig. 6). Peak areas of C_I, C_I', C_{II} and C_{II}' were measured using a planimeter. The areas of J_I, J_I', J_{II} and J_{II}' were not taken as the resolutions of the peaks were poor.

Fig. 4. Comparison of gas chromatograms of a pyrethrin formulation made with a Fumakilla Brand extract from Japan exposed to sunlight for 0 (A) and 100 days (B). Peaks as in Fig. 2.
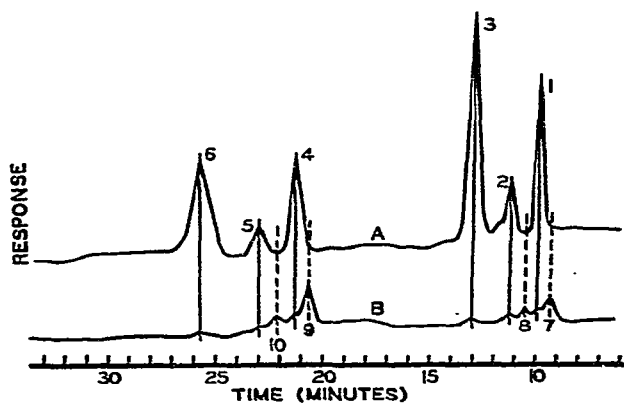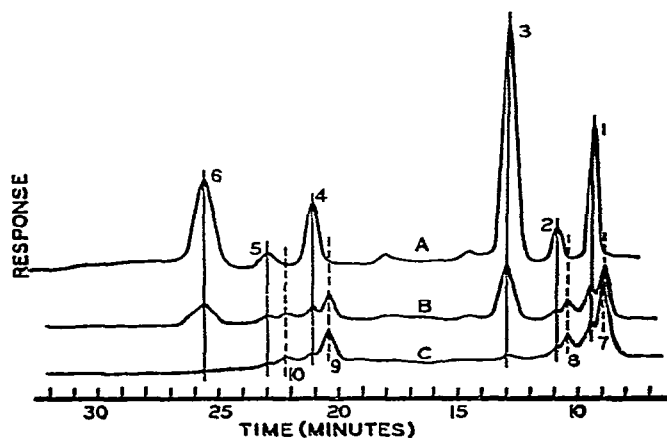
Fig. 5. Comparison of gas chromatograms of a pyrethrin formulation made with an extract from Tanzania exposed to sunlight for 0 (A), 28 (B) and 45 (C) days. Peaks as in Fig. 2.
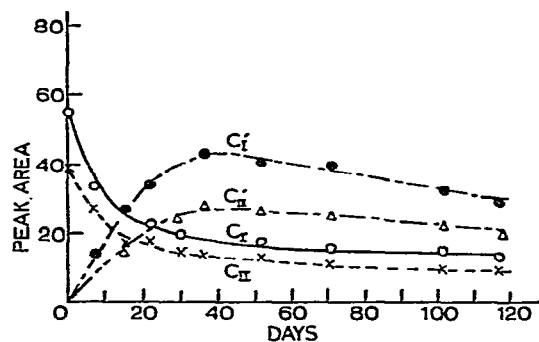
Fig. 6. Changes in concentration of C_I, C_I', C_{II} and C_{II}' with increasing sunlight exposure in a Tanzanian extract formulation. Arbitrary area units are used to express concentration.

The unknown peak areas reached their maximum between 35 and 50 days and thereafter decreased, and it may be assumed that sunlight products C_I' and C_{II}' were further converted into other products not detected by the GC parameters.

Miskus and Andrews[13] reported that window glass (usually soft glass) transmitted radiation above 300 nm, whereas borosilicate glass (Pyrex) was effective at 290 nm. They noted that pyrethrins were destroyed within the UV range 290–320 nm. The more effective range of radiation, 290–300 nm, was excluded by soft glass; thus any changes in the pyrethrin or allethrin properties would be expected to be milder. If the unknown compounds C_I' C_{II}', J_I' and J_{II}' were oxidation products, they would be polar in nature and would not be chromatographed at the indicated retention time positions.

The gas chromatogram of the pyrethrin extract from Tanzania (Fig. 5A) showed peaks 1–6, identified as C_I, J_I, Py_I, C_{II}, J_{II} and Py_{II}, respectively. When exposed to sunlight, the extract showed a different chromatogram (Fig. 5B and C). GC–MS revealed spectra (see Table I) very similar to those of compounds C_I, C_{II}, J_I and J_{II} for peaks corresponding to compounds C_I', C_{II}', J_I' and J_{II}'. Molecular ions were observed for C_I', J_I', C_{II}' but not for J_{II}'. The molecular ion for J_{II}' was not observed owing to its relatively lower concentration. With the GC–MS system used, it was very difficult to observe the molecular ions of the Py_2 group because of their low intensities of less than 0.1 % relative. However, Py_I and Py_{II} were not observed; the former almost disappeared and the latter completely disappeared from the chromatogram after exposure for 45 days. The major peaks 7 and 9 had shorter retention times relative to C_I and C_{II}, respectively.

The GC–MS spectra indicate that the molecular weights of unknown compounds C_I', J_I', C_{II}' and J_{II}' were identical with those of the starting materials. Similarly, the acid moiety and ester bond of the unknown compounds showed no change compared with those of the starting materials. Therefore, it is presumed that the unknown compounds were the isomers of the starting material which was modified in the alcohol moiety. However, Py_I and Py_{II} photoproducts were not chromatographed. They may be converted into substances of higher polarity or polymerized and not detected by GC.

For example, 150 mg of jasmolin I in 200 ml of *n*-hexane were irradiated with a high-pressure mercury vapor lamp for 1 h to obtain a 2:1 mixture of the photoproduct and the starting material. The GC elution order of jasmolin I and its mercury lamp-induced photoproduct coincided with its sunlight-exposure product. Isolation of the photoproduct was accomplished by collection of the product as it eluted from the Hitachi 063 gas chromatograph. The IR and mass spectra of the photoproduct almost agreed with those of jasmolin I (See Table I, J''). However, the PMR spectrum of the photoproduct differed slightly from that of jasmolin I in several shift positions. The PMR spectrum of the photoproduct in $C^2H_2Cl_3$ indicated $\delta = 0.94$ ppm (3H, t, $J = 7.3$ Hz, CH_2CH_3), $\delta = 1.14$ ppm (3H, s, CH_3), $\delta = 1.26$ ppm (3H, s, CH_3), $\delta = 1.41$ ppm (1H, d, $J = 5.4$ Hz, CHCO), $\delta = 1.72$ ppm (6H, s, $(CH_3)_2C =$). $\delta = 2.03$ ppm (3H, s, $CH_3C =$), $\delta = ca.$ 2.0 ppm (obscured, 2H, CH_2, CH_3), $\delta = ca.$ 2.0 ppm (obscured, 1H, $(CH_3)_2C = CH-CH$), $\delta = ca.$ 2.2 ppm (obscured, 1H, dd, $CHHCO$), $\delta = 2.89$ ppm (1H, dd, $J = 6.0$ and 18.4 Hz, $CHHCO$), $\delta = 2.91$ ppm (1H, d, $J = 4.3$ Hz, $= C-CH_2-C=$), $\delta = 4.90$ ppm (1H, dm, $J = ca.$ 8 Hz, $Me_2C = CH$), $\delta = 5.26$–5.54 ppm (2H, CH = CH), $\delta = 5.66$ ppm (1H, dm, CH–0).

TABLE I

INTENSITIES OF FRAGMENT IONS IN THE MASS SPECTRA OF A SUNLIGHT-EXPOSED FORMULATION MADE WITH TANZANIA EXTRACTS

Values are expressed as a percentage of the base peak.

m/e	C_I'	C_I	J_I'	$J_I'^*$	J_I	C_{II}'	C_{II}	J_{II}'	J_{II}
360						0.07	0.08		
344								0.5	0.3
343								0.5	0.7
331			0.2	1.7	0.1	0.1			
330			0.4	3.6	0.2	0.2	0.1		
329						0.4	0.4		
318	0.04								
317	0.1	0.1							
316	0.35	0.33							
212						1.2	1.3	1.6	1.4
211						1.4	1.2	1.7	1.3
169	0.6	0.8	0.5		0.4	0.7	0.8	3.2	1.2
168	2.8	2.9	3.1	5.3	2.9	3.3	3.4	5.0	4.7
167	0.8	0.8	1.0		0.6	25.0	25.5	27.8	29.6
166								2.3	1.3
165			1.9	2.9	2.1			3.6	2.7
164			15.7	19.8	15.4			9.6	14.6
163			8.9	9.6	3.0	1.2		27.3	34.3
162			4.5	5.3	2.5	1.5		5.9	8.2
161			4.1			1.1		2.3	2.6
160								0.4	0.3
153	2.5	2.2	3.4	4.6	2.4	1.6	1.4	4.5	1.9
152	0.4	0.3					0.8	1.8	0.9
151	2.9	3.6				2.6	2.3	3.6	1.4
150	21.4	19.2				17.2	15.2		
149	10.5	5.8		9.6		53.8	28.8		
148	5.5	4.2				12.6	6.9	6.4	1.4
147	1.2	0.7				2.5	1.5	4.1	3.7
146								1.4	1.5
145								4.1	5.9
136				4.6					
135	1.5	1.0	12.0	17.8	9.8	8.8	7.4	34.0	40.1
134			1.6	3.1	1.0		2.8	5.5	4.4
133	5.2	4.9	11.0	4.8	6.0	13.7	8.2	13.7	14.6
132			0.5				2.3	2.3	1.1
131			1.1			4.4	2.3	4.5	1.6
125	3.0	2.4	4.6		2.6	3.0	4.7	7.3	6.1
124	10.3	10.0	10.8	11.1	10.9	1.0		2.7	1.6
123	100.0	100.0	100.0	100.0	100.0	4.2	3.4	18.3	6.1
122	3.9	3.9	3.6	3.1	2.3	8.0	6.2	6.4	6.1
121	25.7	23.5	22.3	12.0	13.4	72.0	57.6	56.9	41.8
120							1.4	4.1	3.9
119		1.8		2.4		4.6	3.4	6.9	5.7
109	4.7	2.8	9.4	7.0	7.7	6.0	6.1	9.1	12.6
108	7.0	7.5	6.4	4.6	5.9	13.7	12.5	12.3	15.0
107	15.2	16.6	16.4	10.8	14.3	100.0	100.0	100.0	100.0
106	2.5	2.3	1.8		1.5	4.7	3.9	6.8	3.6
105	11.3	11.0	8.9	6.7	7.0	22.0	17.0	22.8	17.5

TABLE I (continued)

m/e	C_I'	C_I	J_I'	$J_I'^*$	J_I	C_{II}'	C_{II}	J_{II}'	J_{II}
104					0.7			3.6	1.3
103	1.9	2.2			1.5		2.7	5.0	3.0
97	1.6	0.8		2.4	2.7			4.5	3.6
96	1.8	0.8		2.2	2.4			3.6	2.4
95	8.7	14.2	8.9	5.8	7.4		3.2	6.8	6.0
94	4.0	3.6	3.6	3.9	3.9		6.4	4.7	7.4
93	36.6	37.5	30.8	17.8	28.8	81.0	67.8	70.5	68.9
92	3.4	3.4	4.1	3.9	3.1	7.2	6.0	9.3	6.9
91	12.4	23.7	23.1	14.2	19.8	50.0	57.3	45.5	47.1
85	2.0	1.1	11.3	2.4	2.9		1.0	15.6	2.2
84	0.6	1.3	4.8	2.4	1.2		0.2	7.3	1.2
83	4.4	4.1	18.9	4.1	6.0	5.0	4.1	14.0	8.2
82	1.3	3.9	5.1	2.4	4.2	2.0	1.8	7.0	3.5
81	40.6	42.0	41.2	19.3	41.4	8.5	6.7	16.2	16.5
80	4.0	4.1	4.8	3.1	5.1	5.6	4.6	11.6	8.2
79	24.0	25.4	26.0	11.1	24.0	40.3	33.4	49.0	42.2
78	4.4	4.8	4.8	2.9	4.1	8.4	5.9	7.0	6.4
77	21.0	22.4	22.0	11.3	17.4	36.6	30.2	37.2	32.4
73	1.8	1.1	38.4		8.1			3.7	2.2
72		1.5			0.6			3.3	0.5
71	2.2	2.8	16.6	2.4	5.4				
70		1.1	4.9	2.4	2.3				
69	16.8	13.3	30.2	9.6	19.4	18.5	8.9	28.0	21.4
68	1.8	1.9	2.9	2.4	2.9	1.5	1.5	1.4	4.0
67	14.8	16.0	21.6	8.7	16.7	13.5	10.9	21.0	19.4
66	2.7	3.2		2.4	3.0	4.7	4.1	3.7	5.5
65	7.6	8.8	8.5	5.1	7.8	13.5	11.4	16.3	14.8
59					1.7	14.8	11.9	16.3	15.5
57	9.3	13.8	44.3	7.2	17.2	1.2	0.5	37.2	23.3
56	2.1	2.5	9.0	4.3	4.2	2.3	1.6	4.7	4.4
55	30.0	38.0	64.0	17.3	47.9	43.0	33.6	60.5	79.6
54				2.4					
53	5.5	17.0	14.8	7.0	13.7	18.5	15.3	25.6	19.1
52		2.9		2.4	1.9	2.5	2.8		
51	3.6	5.1		3.6	3.3	6.5	4.6		
45				2.4					
44				2.7					
43	44.5	63.5	87.0	16.6	58.5	34.6	29.9	91.0	70.9
42				2.2					
41	37.0	44.0	75.0	22.9	54.3	32.0	27.8	70.0	65.0
40				2.4					
39	14.0	22.0	18.0	6.0	13.4	19.0	16.5	28.0	21.4
29	18.0	24.8	39.4		18.3	31.0	27.9	46.5	26.2
27	8.9	17.4	13.1		11.0	12.4	9.5	18.6	15.0

* Photoproduct of jasmolin I exposed to a 100-W mercury lamp. Electron impact spectra were obtained from a solid probe analysis of the isolated photoproduct using a JOEL JMS-D100 mass spectrometer.

That is, the shift positions of methyl, 1-methylene and 4-methylene protons on the pent-2-enyl group in the photoproduct were downfield 0.05–0.08 ppm from those of the corresponding protons in jasmolin I. Pent-2-enyl group CH=CH protons

in the photoproduct also absorbed from $\delta = 5.26$ to 5.54 ppm; these protons in jasmolin I absorbed from $\delta = 5.08$ to 5.53 ppm.

The photoproduct was the (E)-isomer of jasmolin I. Bullivant and Pattenden[14] also reported the formation of an (E)-olefin of jasmolin I on irradiation with a high-pressure mercury vapor lamp.

A similar type of sunlight exposure study was conducted with the synthetic pyrethroid allethrin. Sunlight-exposed and unexposed samples were examined by GC. The chromatograms are shown in Fig. 7. The retention time of the unknown peak in exposed allethrin was longer than that of the starting material, in contrast to the conversion products C_I', J_I', C_{II}' and J_{II}'.
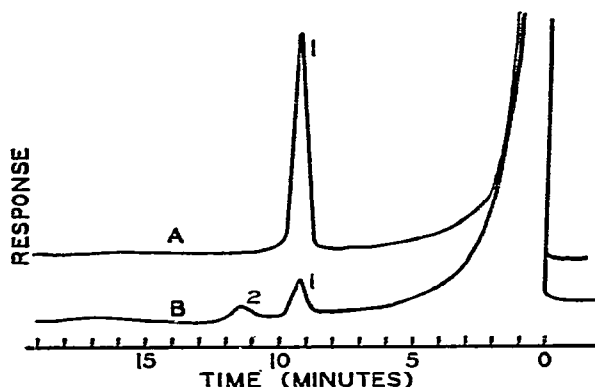

Fig. 7. Comparison of gas chromatograms of a *d-trans*-allethrin formulation exposed to sunlight for 0 (A) and 30 days (B). 1 = *d-trans*-allethrin; 2 = unknown product of *d-trans*-allethrin.

The peak area of the unknown of allethrin increased with time until a plateau was observed after 3 weeks with a corresponding decrease in the allethrin conversion products thereafter (see Fig. 8). The GC–MS study of the unknown material isolated from sunlight-exposed allethrin revealed (see Table II) that it had a fragmentation pattern, including the same apparent molecular ion (*m/e* 302), similar to that of the
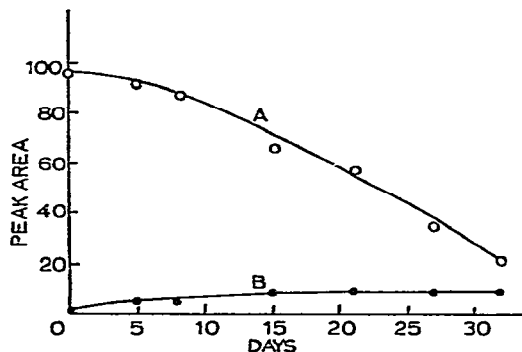

Fig. 8. Comparison of the relative concentration changes of allethrin (A) and photoproduct (B) with increasing exposure to sunlight.

TABLE II

INTENSITIES OF FRAGMENT IONS IN THE MASS SPECTRA OF SUNLIGHT-EXPOSED (A) AND UNEXPOSED (B) ALLETHRIN

Values are expressed as a percentage of the base peak.

(A) Exposed						(B) Unexposed					
m/e	%	m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
303	0.3	115	1.4	69	30.1	303	0.12	106	1.3	57	7.1
302	1.2	111	3.2	68	3.1	302	0.6	105	5.9	56	1.3
285	0.04	110	1.2	67	22.0	169	0.4	104	0.3	55	18.5
284	0.36	109	6.9	66	4.1	168	3.3	103	1.0	54	1.6
169	1.1	108	9.6	65	15.3	167	1.0	97	1.0	53	13.3
168	5.7	107	56.6	64	1.0	154	0.2	96	1.0	52	2.3
167	1.0	106	2.0	63	1.9	153	2.5	95	7.1	51	3.7
153	2.2	105	9.3	59	1.6	152	0.2	94	2.6	50	0.9
152	0.74	104	0.7	58	1.6	151	0.5	93	22.0	45	0.44
151	2.2	103	2.0	57	22.0	150	0.2	92	4.7	44	2.1
150	3.1	99	0.9	56	3.3	149	0.6	91	28.7	43	40.6
149	1.1	98	0.9	55	37.7	139	0.7	85	1.0	42	2.8
145	1.1	97	3.0	54	3.0	138	0.2	84	0.3	41	46.0
139	1.1	96	2.0	53	21.1	137	2.3	83	3.5	40	3.1
138	0.5	95	13.3	52	4.7	136	20.0	82	3.4	39	17.1
137	4.0	94	5.0	51	7.4	135	2.8	81	40.6	29	29.0
136	30.6	93	44.8	50	1.9	134	1.1	80	4.7	28	5.3
135	30.0	92	8.4	45	1.4	133	1.0	79	45.6	27	13.9
134	11.6	91	50.0	44	5.3	125	2.5	78	3.5	15	0.7
133	3.2	85	2.7	43	68.1	124	10.5	77	14.0		
131	1.1	84	1.1	42	4.3	123	100.0	71	1.5		
125	2.7	83	7.5	41	69.0	122	2.0	70	0.7		
124	11.2	82	4.9	40	5.7	121	4.4	69	10.0		
123	100.0	81	56.1	39	25.4	119	1.0	68	1.5		
122	4.9	80	7.4	29	44.3	111	0.8	67	13.6		
121	6.4	79	74.6	28	8.2	110	0.6	66	2.7		
119	3.1	78	6.7	27	23.2	109	3.1	65	10.0		
118	0.4	77	25.3	15	3.1	108	5.5	63	1.1		
117	2.2	71	3.9			107	43.3	59	0.6		

unexposed allethrin standard. The relative intensities of the various peaks differed with a general increase in intensity of the fragment ions below m/e 123, compared with the allethrin standard. In both instances m/e 123 is the base peak, and there appears to be no change in the acid moiety and the ester bond. Only the relatively low intensity fragment ions m/e 284 and 285 of the photoproduct were not observed in the allethrin spectrum.

One gram of bioallethrin in 200 ml of n-hexane was irradiated with a high-pressure mercury vapor lamp for 24 h to obtain a 15:2 mixture of the photoproduct and the starting material. The photoproduct was isolated from the allethrin formulation by elution through a silica gel column. GC performed on the Hitachi GC-063 instrument using a 10% SE-30 column revealed the same elution order of the photoproduct generated by the mercury lamp.

The PMR spectrum of the photoproduct of allethrin in CDCl$_3$ indicated $\delta = 0.55$–0.93 ppm (2H, m, cyclopropyl group), $\delta = 1.14$ ppm (3H, s, CH$_3$), $\delta =$

0.93–1.54 ppm (3H, m, cyclopropyl group), $\delta = 1.25$, 1.28 ppm (3H, s, CH_3), $\delta = 1.39$ ppm (1H, d, $J = 1.39$ Hz, CHCO), $\delta = 1.71$ ppm (6H, s, $(CH_3)_2C =$), $\delta = 2.07$ ppm (3H, s, $CH_3C =$), $\delta = ca.$ 2.1 ppm (obscured, 1H, $(CH_3)_2C = CH–CH$), $\delta = ca.$ 2.2 ppm (obscured, 1H, dd, $CHHCO$), $\delta = 2.81$ ppm (1H, dd, $J = 6.0$ and 18.2 Hz, $CHHCO$), $\delta = 4.90$ ppm (1H, dm, $J = 7.2$ Hz, $(CH_3)_2C = CH$), $\delta = 5.63$ ppm (1H, broad, CHO).

The mass spectrum of the mercury lamp-induced photoproduct had the same fragmentation pattern as that of the sunlight photoproduct of allethrin including the fragment ions m/e 284 and 285. The m/e 284 and 285 ions were not observed in the mass spectrum of the original standard allethrin. The photoproduct was identified as d,l-cyclopropylrethronyl d-trans-chrysanthemate, which has been previously observed in photodecomposition studies of allethrin in petroleum solutions[9,14–16]. A di-π-methane rearrangement involving hydrogen migration of the central $-CH_2-$ grouping of the prop-2-enyl side-chain has been proposed as the mechanism in the rearrangement of the alcohol moiety's prop-2-enyl side-chain to a cyclopropyl ring[9,16,17].

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