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CHEMICAL PROTECTION OF PHEROMONES CONTAINING AN INTERNAL CONJUGATED DIENE SYSTEM FROM ISOMERIZATION AND OXIDATION

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Abstract—Conjugated diene systems are common in natural products, including pheromones. The systems are sensitive to heat, light, and oxygen, among other things. They can be protected by antioxidants and UV absorbers, which slow down *cis–trans* isomerization and oxidation. Three sex pheromones (one as an analog) containing *Z,E*, *E,Z*, and *E,E* units were studied: (*Z,E*)-9,11-C_{14}OAc, (*E,Z*)-7,9-C_{12}OAc, and (*E,E*)-10,12-C_{16}OAc. The UV absorber 2-hydroxy-4-methoxybenzophenone and the antioxidants BHT and BHA were found to be effective in solution. The protective effect of the UV absorber against photoisomerization on paper carriers was not as good as that in solution. Preliminary studies on the utilization of formulations containing these compounds and (*Z,E*)-9,11-C_{14}OAc in the mass trapping of Egyptian cotton leafworm male in cotton fields showed the new combinations to be as good as a previously used formulation with UOP 688, a compound which is unpleasant to handle.

Key Words—*Lobesia botrana*, *Spodoptera littoralis*, *Earias insulana*, conjugated dienes, sex pheromone, photoisomerization, UV absorbers, antioxidants, protection of pheromones.

INTRODUCTION

As integrated pest management (IPM) becomes more sophisticated, the main role played by pheromones will be that of monitoring and disruption of communication (confusion) via controlled release of the active ingredients in the field. The longer the desired field life of the pheromones, the greater the quantity of pheromones that will be degraded by chemical and physical processes. Evaporation is known to be a major cause of the loss of material in short-lived

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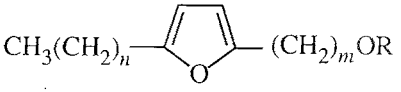
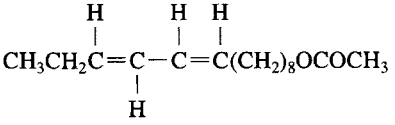
devices, but not much is known about chemical degradation under field and/or laboratory conditions. The few studies that have been performed have dealt mainly with the oxidation and isomerization of double bonds (Goto et al., 1974; Bruce and Lum, 1976, 1981; Fujiwara et al., 1977; Shani and Klug, 1980a, b; Ideses et al., 1982b, c; Shani et al., 1982; Vaintraub et al., 1983; Davis et al., 1984; Vylegzhanina et al. 1984; Guerin et al., 1984; Nesterova, 1985; Nesterova et al., 1985; Chisholm et al., 1985; Brown and McDonough, 1986; Sychev et al., 1987), with transformations of aldehydes (Weatherston et al., 1981; Shaver and Ivie, 1982; Dunkelblum et al., 1984), and with hydrolysis of acetates in the field (Shani and Klug, 1980b).

Our group (Shani and Klug, 1980a, b; Shani et al., 1982; Ideses et al., 1982b, c) has already shown that the conjugated diene systems in several sex pheromones of moths are isomerized into a mixture of the four possible geometric isomers and oxidized in the field (or under simulated field conditions in the laboratory) to a furan system (Scheme 1, structure I), via a peroxide.

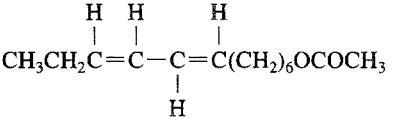


I

Ia: $m = 6, 8, 9$; $n = 1, 2$; R = Ac
Ib: $m = 7$; $n = 0$; R = H



II



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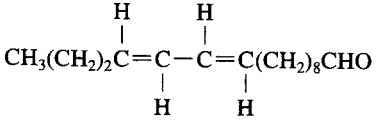
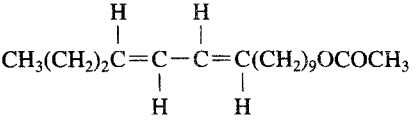


IV



V

Scheme 1.

With the aim of finding means of protecting these sensitive chemicals and prolonging their biologically active period in the field, we studied the effect of antioxidants and UV absorbers on pheromone stability both in the laboratory and under field conditions. Three internal conjugated diene systems known to be present in moth sex pheromones were studied: *Z,E* dienes as found in (*Z,E*)-9,11-tetradecadien-1-yl acetate (TDDA) (II), the main component of the sex pheromone of the female Egyptian cotton leafworm (*Spodoptera littoralis*) (Nesbitt et al., 1973; Tamaki et al., 1973); *E,Z* dienes as found in (*E,Z*)-7,9-dodecadien-1-yl acetate (DDA) (III), the sex pheromone of the female European grapevine moth (*Lobesia botrana*) (Roelofs et al., 1973; Buser et al., 1974); and *E,E* dienes, as found in (*E,E*)-*10,12*-hexadecadienal (HDAL) (IV) [studied as the corresponding ester (*E,E*)-10,12-hexadecadien-1-yl acetate (HDDA) (V)], the sex pheromone of the female spiny bollworm (*Earias insulana*) (Hall et al., 1980).

We report here the results of these studies and a preliminary study of the efficiency of protected pheromone carriers in cotton fields in Israel in mass trapping of Egyptian cotton leafworm males.

METHODS AND MATERIALS

Chemicals. The purity of the pheromones and the pheromone analog was determined by GLC: (*Z,E*)-9,11-C_{14}OAc 98%, 2% *E,E*-isomer; (*E,Z*)-7,9-C_{12}OAc 92%, 8% *E, E*-isomer; (*E,E*)-10,12-C_{16}OAc 100%. Antioxidants 3(2)-*tert*-butyl-4-hydroxyanoisole (BHA) and 2,6-di-*tert*-butyl-4-methylphenol [butylated hydroxytoluene (BHT)] were purchased from Sigma. UV absorbers 2-hydroxy-4-methoxybenzophenone [$\lambda_{max}^{C_6H_{12}}$ 288, 360 nm (ϵ = 14,770, 9,090); $\lambda_{max}^{t\text{-BuOH}}$ 286, 340 nm (12,860, 7,750)] (trade name Eusolex 4360), and a eutectic mixture of 4-isopropyldibenzoylmethane and 3-(4-methylbenzylidene)camphor [$\lambda_{max}^{C_6H_{12}}$ 312, 342 nm (ϵ = 15,790, 18,420); $\lambda_{max}^{t\text{-BuOH}}$ 299, 350 (22,470, 19,720)] (trade name Eusolex 8021) were purchased from Merck. UV spectra were determined with a Bausch & Lomb Spectronic 2000 in spectroscopic grade cyclohexane or in *tert*-butanol.

GLC analyses were performed on a Packard GLC model 417 fitted with a flame ionization detector and with either a fused silica capillary column of SP 2340 30 m × 0.25 mm, flow rate (He) 0.4 ml/min at 130–160°C or a WCOT Silar 9 25 m × 0.5 mm, flow rate (He) 2.7 ml/min at 130–160°C, depending on the pheromone studied.

All solutions contained 100 mg of a pheromone in 5 ml cyclohexane or *tert*-butanol in a corked Pyrex flask, and 50 μl were withdrawn and diluted to 0.5 ml with cyclohexane and then injected twice ($\pm$1%) into the GLC (1–2 μl).

Flasks were refilled to 5 ml every day to compensate for evaporation. Solid carriers (two replicates of each sample) were extracted with hexane (2 × 2 ml), evaporated and then diluted to 1 ml and injected into the GLC. All formulations (solutions or solids carriers) were subjected to diffused sunlight on the roof of the building for the greater part of the experiment, although for some of the time they were placed in direct sunlight. (Details of the light regime are given in the tables or in the text.) Samples were usually withdrawn every two to four days until no pheromone (or its isomers) could be detected by GLC; this period usually lasted five to six weeks. Thus, samples analyzed up to the third or fourth week contained enough material for detection (in general 20–40% of the starting material and isomers were present). In the absence of antioxidant, the pheromone decomposed much faster, and the last sample that contained measurable amounts is documented in the Tables.

RESULTS AND DISCUSSION

It has already been established that heat (50°C in the laboratory hood) causes thermal oxidation via $^3O_2$ and that the process can be slowed down by antioxidants such as BHA or BHT (Shani et al., 1982).

The effect of light seems to be more complicated. In the field, both direct and scattered sunlight may be present, a situation that may affect both pheromone carriers in traps and slow-release devices that are covered by leaves and other objects in the field. Moreover, the excitation of the diene system could be through direct absorption of light by its end absorption (Shani and Klug, 1980b; Shani et al., 1982) or via energy transfer from a sensitizer. In addition, in tropical or subtropical regions, exposure during the summer means that the pheromones are subjected to a combination of high-intensity sunlight and temperatures of 40°C or more. We have already found (Shani and Klug, 1980b) that the rate of direct photoisomerization in sunlight is two to three times faster in summer than in winter. These results are in keeping with the summer and winter figures for total solar energy in Be'er-Sheva (5500–6900 vs. 2300–3500 kcal/m^2/day)[1]. Therefore, in all the experiments described below, the pheromones were, in fact, exposed to a combination of heat, light, and oxygen. Thus, the protective effect of the antioxidant is crucial. The set of experiments performed by us was designed, therefore, to include all possible factors that also play a role in any study on the effect of light on isomerization of pheromones.

Effect of Antioxidants. When pheromones are subjected to heat and light, two competing chemical processes take place—thermal decomposition (oxida-

[1]We thank A. I. Kudish, Department of Chemical Engineering, Ben-Gurion University for the data.

tion) and photoisomerization. Heating alone (in the hood) caused decomposition of the pheromone within a few days (Shani et al., 1982), as was the situation in this experiment with pheromones exposed to sunlight and not protected by an antioxidant. In this case, very little isomerization took place (entries 1, 4, and 7 in Table 1). Pheromones protected by an antioxidant and hence exposed to longer periods of sunlight underwent more extensive isomerization, almost reaching the equilibrium composition, which was found to be 68–75% of the *E,E* isomer, 12–16% of each of the *Z,E* and *E,Z* isomers, and 1–3% of the *Z,Z* isomer (Shani et al., 1982; Ideses and Shaní, 1986). In an earlier study (Shani and Klug, 1980b), we observed that the rate of photoisomerization is somewhat slower in the presence of the antioxidant, as compared to the process in its absence. After 11 days of sunlight, 17% of (*E,E*)-9,11-TDDA was found when

TABLE 1. PHOTOISOMERIZATION OF (*Z,E*)-9,11-C_{14}OAc (TDDA), (*E,Z*)-7,9-C_{12}OAc (DDA) AND (*E,E*)-10,12-C_{16}OAc (HDDA) EXPOSED TO SUNLIGHT IN PRESENCE OF UV ABSORBERS[a]

		Without BHA						With BHA					
				Composition (%)						Composition (%)			
Entry	Pheromone	UV absorber	Period (days)[b]	*Z,E*	*E,Z*	*Z,Z*	*E,E*	UV absorber	Period (days)	*Z,E*	*E,Z*	*Z,Z*	*E,E*
1.	TDDA		7	75	5		20		6	80	8		12
									25[c]	25	15		60
2.	TDDA	E-4360	11	82	7		11	E-4360	11	90	5		5
								E-4360	23[c]	86	7		7
3.	TDDA	E-8021	11	58	20		22	E-8021	11	73	13		14
			14	50	24		26	E-8021	14	66	16		18
								E-8021	27[c]	47	23		30
4.	DDA		3		87		13		3		85		15
									30[c]	20	36	2	42
5.	DDA	E-4360	10		90		10	E-4360	10		89		11
								E-4360	30[c]		85		15
6.	DDA	E-8021	10		85		15	E-8021	10	5	74		21
								E-8021	32[c]	9	63	1	27
7.	HDDA		10	5	5		90		10	7	8		85
									25[c]	10	10		80
8.	HDDA	E-4360	10	2	2		96	E-4360	10	2	2		96
								E-4360	30[c]	3	3		94
9.	HDDA	E-8021	10	6	6		88	E-8021	10	6	6		88
								E-8021	20[c]	9	9		82

[a] Each sample contained 100 mg of pheromone, 100 mg of antioxidant, and 100 mg of UV absorber (when mentioned) in 5 ml cyclohexane.

[b] Due to fast decomposition, the last sample withdrawn which gave measurable results is presented. Without antioxidant, the oxidation product I was formed in some cases (Ideses et al., 1982c).

[c] Last sample withdrawn when some 20–40% of starting material and isomers were still present in solution.

BHT was added to the pheromone solution as opposed to 30% of the *E,E* isomer when it was not present. After 16 days of sunlight exposure, both solutions contained 35% of the *E,E* isomer. That study was performed during May 1979, when the total sunlight energy is very high (6000–6900 kcal/m^2/day), but temperatures in Be'er-Sheva are still moderate.[2] This might explain why we could still detect the isomers of TDDA after 16 days in sunlight while in the current study, which was performed in August 1985, decomposition was much faster, being complete within seven days (Table 1, entry 1). The first experiment with (*E,Z*)-7,9-C_{12}OAc (entry 4) was done in July 1981 and repeated in July–August 1985.

Effect of UV Absorbers. We studied the effect of two UV absorbers that have their main absorption bands in the region of 300 nm (see Methods and Materials). The photoisomerization of the three diene systems was followed in solution, and the results are summarized in Table 1.

The effect of the antioxidant is again demonstrated in that less pheromone is decomposed in the solution, and exposure period to sunlight is thus lengthened. The effect of the UV absorber is dramatic, as can be seen by comparing the composition in entries 2, 3, 5, 6, 8, and 9 with entries 1, 4, and 7 of Table 1. Exposure to sunlight for three to four weeks brings the isomeric mixture closer to equilibrium (see above), except in the presence of UV absorbers which slow down this process, allowing very little isomerization to take place (entries 2, 5, and 8 of Table 1). The difference between E-4360 and E-8021 (entries, 2, 5, 8 and 3, 6, 9 in Table 1) is clear. We attribute the protective effect to the intense absorption of E-4360 at 288 nm, which exactly covers the end absorption of the conjugated diene system (Shani and Klug, 1980a, b, Shani et al., 1982). The other UV absorbers (E-8021) is less effective, as its main absorption bands are at longer wavelengths, which do not mask the diene absorption. We may also assume that E-8021 does not act as a photosensitizer, since its components have essentially the same chromophor system as that of E-4360. As aromatic ketones, these chemicals probably possess a very high quantum yield for intersystem crossing in solution ($S_1 \rightarrow T_1$) (ΦISC 0.9–1.0) and, when excited, contain about the same triplet energy (ca. 70 kcal/mol) (Calvert and Pitts, 1966).

In order to learn more about the efficacy of both the antioxidant and the UV absorber on the photoisomerization process, we prepared solutions with different amounts of these two essential additives, as shown in Table 2. It is clear that a pheromone solution containing 10% of the antioxidant and 10% of the UV absorber is well protected from both thermal oxidation and photo-

[2] The average daily maximum temperatures (°C) in Be'er-Sheva during different periods of study were as follows: 1979, May 28.7, December 17.0; 1981, July 33.1; 1985, July 32.9, August 34.0. We thank Dov Mills of the Regional Meteorological Station in Be'er Sheva for the data.

TABLE 2. EFFECT OF DIFFERENT AMOUNTS OF UV ABSORBER AND ANTIOXIDANT ON PHOTOISOMERIZATION AND OXIDATION OF TDDA[a]

Entry	Pheromone (mg)	BHA (mg)	E-4360 (mg)	Period in sunlight (days)	Composition (%)				Oxidation product
					Z,E	*E,Z*	*Z,Z*	*E,E*	
1	100	100		16	55	15		30	none
2	100	100	100	16	94	3		3	none
3	100	100	10	17	90	6		4	none
4	100	10	10	17	92	2		6	none
5	100	10		17	47	16		37	none

[a] All samples were solutions in 5 ml cyclohexane.

isomerization of the internal conjugated diene system under sunlight (compare entries 2 and 4 in Table 2).

Effect of Photosensitizer. In the presence of a photosensitizer (in our case rose bengal) the photoisomerization is very fast, yielding an equilibrium mixture, and the process can be accomplished within 90 min (Shani et al., 1982) as compared with direct illumination for several weeks in sunlight without photosensitizer. The question whether the UV absorber could slow down this energy transfer and excitation was investigated, and the results are summarized in Table 3.

The effect of E-4360 in slowing down the sensitized photoisomerization is impressive, as compared with that of E-8021, the latter compound being completely ineffective (compare entries 3 and 4 in Table 3). These results are in keeping with the findings for these two UV absorbers in direct sunlight (Table 1). The photosensitizer (rose bengal) probably transfers its energy to E-4360,

TABLE 3. EFFECT OF UV ABSORBER ON PHOTOISOMERIZATION OF TDDA IN PRESENCE OF PHOTOSENSITIZER[a]

Entry	UV absorber	Exposure time (min)	Composition (%)			
			Z,E	*E,Z*	*Z,Z*	*E,E*
1		45	16	13	1	70
2		75	15	12	1	72
3	E-4360	60	65	10		25
4	E-8021	60	13	16	3	68

[a] Each sample contained 100 mg of (*Z,E*)-9,11-C_{14}OAc, 10 mg of rose bengal, and 100 mg of UV absorber in 5 ml *tert*-butanol.

which, having absorption bands at 288 and 360 nm, does not take part in energy transfer to the diene system. We thus may consider E-4360 as a good "filter."

It was interesting that the antioxidant (BHA) was also effective in slowing down the sensitized photoisomerization. As noted above (entries 1 and 2 in Table 3) and as has already been published (Shani et al., 1982), sensitized photoisomerization towards equilibration of the four isomers is fast, being accomplished in 30–100 min. However, when a solution of 100 mg of pheromone (TDDA or DDA) containing 10 mg of rose bengal and 100 mg of BHA was left in the sunlight, the rate of isomerization was much slower, and more than 50% of the starting isomer was detected in the tested solution after 4 hr. When the UV spectrum of an admixture of rose bengal and BHA was studied, two separate and unchanged spectra of the components were clearly observed. Still, energy transfer from rose bengal to BHA can take place since the absorption band of BHA is wide and intense at this concentration (100 mg in 5 ml solution) even beyond the 300 nm. Another explanation could be that the phenoxy radical reacts with the photosensitizer and thus decreased its efficacy as a photosensitizer. More experiments should be undertaken in order to determine the preferred mechanism.

The effect of radicals (I_2, C_6H_5SH) on the isomerization was also studied, and we found that the process with I_2, but not with the thiophenol, is slowed down by antioxidants as radical scavengers. The reaction is temperature dependent and can be considered as a catalytic process in 5–10% of iodine in solution (Ideses and Shani, in preparation).

Simulated and Real Field Conditions. The effect of the binary mixture of the antioxidants and the UV absorber was also checked in pheromone carriers, which are usually applied in the field in traps. We selected to study (*Z,E*)-9,11-$C_{14}OAc$, since this compound is used extensively in mass trapping of males of the Egyptian cotton leafworm in cotton fields in Israel. The pheromone is usually applied into the carrier as a solution of the active ingredients (the solvent evaporates in a short time and then the carriers are stored in a refrigerator until used). These carriers are installed into traps under a "cover" that protects them from direct sunlight. We thus investigated these carriers on the roof of our building in diffused sunlight. The results are shown in Table 4.

We found that the photoisomerization of pheromones in solution takes place at a slower rate than that in pheromones impregnated on a carrier. This phenomenon may be explained in terms of the observation that upon application of solution, "paper chromatography" took place and two or three zones appeared on the carrier. We cannot determine how much of overlapping of the components is effective, but it is interesting that the UV absorber is not as effective on the carrier as it is in solution, especially on the cigarette filter (entries 2 and 6 in Table 4). In fact, it seems that the antioxidant alone is almost as good as the binary mixture of antioxidant and UV absorber. This finding could be

TABLE 4. PHOTOISOMERIZATION OF (*Z*,*E*)-9,11-C_{14}OAc LOADED ON CARRIERS IN PRESENCE OF ANTIOXIDANT (BHA) AND UV ABSORBER (E-4360)[a]

Entry	Carrier	Relative amount (%)			Exposure time (days)[b]	Composition (%)			
		Pheromone[a]	BHA	E-4360		*Z*,*E*	*E*,*Z*	*Z*,*Z*	*E*,*E*
1	Solution	100	10		17[c]	47	16		37
2	Solution	100	10	10	17	92	2		6
					21	84	6		10
3	Cardboard	100	10		18	69	12		19
					25	60	16		24
4	Cardboard	100	10	10	17	81	8		11
					24	78	10		12
5	Cigarette filter	100	10		18	64	14		22
					21	55	20		25
6	Cigarette filter	100	10	10	18	61	19		20
					21	59	20		21

[a] Each carrier was loaded with cyclohexane solution containing 2 mg of pheromone, 0.2 mg of BHA, and 0.2 mg of E-4360 (when mentioned). The solution contained 100 mg of pheromone in 5 ml cyclohexane. The carriers (two of each sample) were kept in a Pyrex dish, covered with a watch glass. All samples were kept on the roof of the building in diffused sunlight.

[b] The amount of the starting isomer was 20–40% of its original quantity. For technical reasons, analyses of samples were performed on different days.

[c] The flask was broken.

explained by the protective effect of the solid support of the carrier, which may furnish better masking from sunlight than is available in a clear solution. It is also possible that some additives in the paper act as either UV absorbers or quenchers, as the antioxidant acts in the presence of a photosensitizer (see above). Such a phenomenon was found in carriers made of rubber septa (Fujiwara et al., 1977; Brown and McDonough, 1986; Teich and Shani, unpublished results). It is important to remember that without an antioxidant, the pheromone decomposed on the carriers in a few days and could not be detected on the GLC.

The real test of the biological activity of the pheromone carriers loaded with the binary protecting mixture was conducted in kibbutz cotton fields. The usual pheromone carrier on a cigarette filter was loaded with 2 mg of (*Z*,*E*)-9,11-C_{14}OAc and 8 mg of UOP 688 (*N*-phenyl-*N'*-(1-methylheptyl)-*p*-phenylenediamine). The latter compound is a dark, viscous, and unpleasant material that may act as a protecting "solvent" for the pheromone and also for slowing down evaporation. Preliminary results of catching efficacy of different preparations are summarized in Table 5. No significant difference ($P = 0.05$, Student's *t* test) was found between each of the five experimental preparations and the standard (UOP), or among the five compounds themselves, except for two

TABLE 5. MASS TRAPPING OF EGYPTIAN COTTON LEAFWORM MALES BY DIFFERENT PHEROMONE PREPARATIONS IN COTTON FIELDS IN 1986

		Average No. of males caught in a trap per night[b]			
		Kibbutz Mefalsim			
		1st experiment		2nd experiment	Kibbutz Reshafim
Entry	Pheromone formulation[a]	Jun 22–Jul 24	Jul 24–Aug 28	Jul 24–Aug 28	Jul 4–Aug 2
1	BHA + E-4360	0.3	6.4	12.2	13.8[c]
2	E-4360	0.4	10.4	11.2	10.8
3	BHA	0.7	7.2	8.7	10.7
4	BHT	1.1	10.3	11.9	14.7[c]
5	BHT + E-4360	3.1	10.9	12.5	12.7
6	UOP 688 (standard)	0.2	6.7	9.3	6.2

[a] Each carrier was loaded with a cyclohexane solution of 2 mg of (*Z*,*E*)-9,11-C_{14}OAc, 0.2 mg of BAH or BHT, and 0.2 mg of E-4360 (when mentioned). With UOP 688, 8 mg of the material was loaded on each carrier with 2 mg of pheromone.

[b] Dry traps with long sleeves were erected at random, 50 m apart, six replicates of each sample. Catches were monitored twice a week.

[c] Significantly different from UOP 688 at $P = 0.10$ (Student's t test).

formulations (entries 1 and 4 in Table 5) in the experiment carried out at Kibbutz Reshafim, which were significantly different from UOP 688 (entry 6) ($P = 0.10$, Student's t test). These results strengthen previous observations (Teich, Shani, and Klug, unpublished results) made during the 1981–1982 seasons, which showed not only that BHA and BHT were better protecting chemicals for (*Z*,*E*)-9,11-C_{14}OAc than UOP 688, but also that they increased catching efficacy. Therefore, it should be desirable to replace UOP 688 as an antioxidant in pheromone protections with BHA and BHT, at least for technical and handling reasons.

It is interesting that both the UV absorber and the antioxidant as a single additive prolonged the trapping efficacy of the pheromone. This fact may be in keeping with our earlier findings (see Table 4) that the behavior of the solid carriers was very much like that of one (antioxidant) or two additives and not to the positive effect observed for the UV absorber in solution (Tables 1, 2, and 4). The exact quantity of the pheromone and the relative composition of its geometrical isomers remaining on the solid carriers in the field can indicate the

correlation between the chemical processes and the biological activity (Shani and Klug, 1980b). At this stage we should remember that, when analyzing the results from the field study and comparing them with the chemical transformations of the pheromone, either in solution or on solid carriers, we are comparing two different processes and results. It could be, and we indeed found earlier in two cases, that not much of the real pheromone is needed for attraction, and the other geometric isomers do not interfere with trapping (Shani and Klug, 1980b; Ideses et al., 1982a). Therefore, the chemical results obtained in the laboratory do not necessarily reflect the biological findings in the field and vice versa. As long as enough active pheromone is present on the carrier and the other isomers are inactive and do not interfere, there may be high activity in the field despite the fact that isomerization and/or oxidation has destroyed much of the pheromone. In solutions studies, the pheromones and their isomers could be detected by GLC for up to six weeks afer the start of the experiment, while in the field the carriers attracted the Egyptian cotton leafworm for up to two months. The results in Table 5 show that, in the first experiment at Kibbutz Mefalsim, trapping in the second month (24.7–28.8) was almost as high as that in the first month of the second experiment.

We may summarize the results as follows:

Thermal Decomposition–Oxidation. Addition of an antioxidant prolonged the life-span of the diene system both in solution and in the carrier from several days to 2 weeks to six to eight weeks (Shani and Klug, 1980b; Ideses et al., 1982b; this work).

Isomerization. Addition of a UV absorber effectively slowed down isomerization in the diene system in solution and was less effective on the solid carrier. Both additives are crucial in solution, but the effect of the UV absorber becomes less important on the solid carriers.

Biological Activity. We have found that (*Z*,*E*)-9,11-C_{14}OAc attracts the Egyptian cotton leafworm in the field up to two months. The (*E*,*Z*)-7,9-C_{12}OAc isomer was found to attract the European grapevine moth in the field for up to seven weeks (Ideses et al., 1982a), which time is in the range of the chemical stability. The (*E*,*E*)-10,12-C_{16}Ald isomer is active in catching the spiny bollworm for four to five weeks (Kehat et al., 1981). The chemical behavior of this isomer was studied on the corresponding acetate, as the sensitive group is the aldehyde. The isomerization was very slow as the *E*,*E* isomer is the most stable one in the mixture.

Israeli entomologists and farmers usually change the carriers in traps for all three once in four to six weeks, although from scattered observations in the fields, some traps were found to be active for two months or more.

All these findings lead to the conclusion that results of laboratory studies and experimentation cannot necessarily be extrapolated to the real-life situation

in the field: the ultimate test of pheromone efficacy is the biological activity on the field, when all factors come into full expression and the weighted system is the governing power.

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