Volatiles from the Foliage of Soybean, *Glycine max*, and Lima Bean, *Phaseolus lunatus*: Their Behavioral Effects on the Insects *Trichoplusia ni* and *Epilachna varivestis*

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Volatiles were isolated by Tenax-GC trapping at ambient temperature (23 ± 1 °C) from the leaves of relatively insect-resistant versus -susceptible soybeans and a preferred host, lima bean. Effects of such volatiles on two insects' (the cabbage looper and the Mexican bean beetle) behavior were investigated. Volatiles from PI 227687 soybean proved repulsive to both insects; those from Davis soybean were attractive, and those from Henderson lima bean were neutral. Such distinct effects apparently involve both qualitative and quantitative differences among the chemical components in the volatiles. Major contributors to the insect repellency of PI 227687 volatiles are 3-tetradecene and 1-dodecene. The attraction of the insects to Davis odors apparently is attributable to the absence of tetradecene and dodecene and the abundance of hexenol acetate, dimethylhexanal, and hexenal. The observed neutrality of the odors from the preferred host, Henderson lima bean, is apparently due to its complex balanced blend of attractants and repellents.

Both morphological and biochemical plant parameters usually influence host acceptance by an insect (Norris and Kogan, 1980). Such selection by phytophagous insects consists of a sequence of behavioral responses to an array of stimuli associated with nonhost and host plants (Visser, 1986). Some insects apparently differentiate among plants based primarily on cues perceived at a distance, whereas others make such distinctions dependent mostly on cues obtained after arrival on the plant (Kennedy, 1977). Some interactions between phytophagous insects and plants involve especially volatile chemical cues that emanate from the plants and evoke specific behavioral responses by the insects (Buttery et al., 1984). Our understanding of the roles of plant "odors" in phytochemical–insect relationships unfortunately is less extensive than that of relatively nonvolatile primary and secondary plant substances (e.g., antifeedants) (Schoonhoven, 1968; Staedler, 1976; Visser et al., 1979; Norris, 1986). One reason for this is that volatiles may constitute only parts per million (ppm), or even parts per billion (ppb), of the plant weight (Buttery and Ling, 1985). Another reason is their dissipative characteristic. Both traits obviously make isolation, measurement, and identification of plant odors more difficult as compared to antifeedants. Specific evidence that volatile phytochemicals play important roles in an insect's rejection or acceptance of a plant includes findings by Gilbert et al. (1967), Gilbert and Norris (1968), Feeny et al. (1970), Jermy (1976), Free and Williams (1978), Kamm and Buttery (1983), and Khan et al. (1987). Volatiles have been reported specifically as attractants of insects to host plants (Hsiao and Fraenkel, 1968; Buttery et al., 1978, 1982a,b, 1985; Visser and Ave, 1978); however, their more important role probably is as insect repellents or deterrents from nonhost plants (Gilbert et al., 1967; Gilbert and Norris, 1968; Saxena and Probha, 1975; Ryan and Guerin, 1982; Salama and Saleh, 1984; Khan et al., 1987). It is quite obvious that the overall functions of volatiles in plant–insect interactions deserve further study.

In any study of volatiles, their isolation from the plant is the first and extremely important step. Several isolation methods have been applied to plant volatiles, e.g., steam distillation, vacuum steam distillation, solvent extraction reaction, cold condensation, absorbent trap, etc. (Gilbert et al., 1967; Weurman, 1969; Visser et al., 1979; Khan and Saxena, 1985; Buttery and Ling, 1985). The most important consideration in designing such a procedure is to maximize recovery of the volatiles from the plant, while minimizing the contaminants. In our study, a relatively gentle method (Tenax-GC trapping) for isolating volatiles from plants, involving only a few steps and chemical agents, was used. This helped to avoid contaminating the volatiles with relatively nonvolatile plant compounds. We used blank controls in parallel analyses to identify and then eliminate contaminants.

METHODS AND MATERIALS

Plants. Volatiles were trapped from freshly detached fully expanded leaves of V8-V10 soybean or lima bean plants. The soybeans were plant introduction (PI) 227687, reported as relatively resistant to the cabbage looper (CL), *Trichoplusia ni* (Hübner) (Leudders and Dickerson, 1977; Khan et al., 1986a,b), and the Mexican bean bettle (MBB), *Epilachna varivestis* Mulsant (Van Duyn et al., 1971; Chiang et al., 1986; Rufener II et al., 1986), and Davis, a commercial cultivar, shown to be more susceptibile than PI 227687 to CL (Khan et al., 1986a,b) and MBB (Chiang et al., 1986) feeding. The lima bean variety was Henderson, one of the more preferred hosts of CL (Shorey et al., 1962) and MBB (Flander, 1984).

Seeds of PI 227687 and Davis soybeans were obtained from Dr. E. E. Hartwig, Delta Branch Experimental Station, Stoneville, MS 38776. Seeds of Henderson lima bean were purchased from L. L. Olds Seed Co., Madison, WI. All seeds were treated with the fungicide Thiram and germinated in flats of moistened vermiculite in a Percival environmental chamber (Liu and Norris, 1988). Seedlings were transplanted, two plants per pot, at the first-leaf (V1) stage. Plants were grown to the V8–V10 stage in 6–8 weeks in the greenhouse or in 3–6 weeks in the U. W. Biotron controlled-environment facility. All fully expanded trifoliolate leaves were then harvested and used immediately for trapping of volatiles.

Chemicals. Thiram was bought from Science Products Co., Inc., Chicago, IL. Tenax-GC was from Alltech Associates, Inc., Applied Science Labs, Deerfield, IL. Hexane (HPLC grade), tetradecene, and dodecene were from Aldrich Chemical Co., Inc., Milwaukee, WI. No. 30 white oil was from American Oil Co., Chicago, IL.

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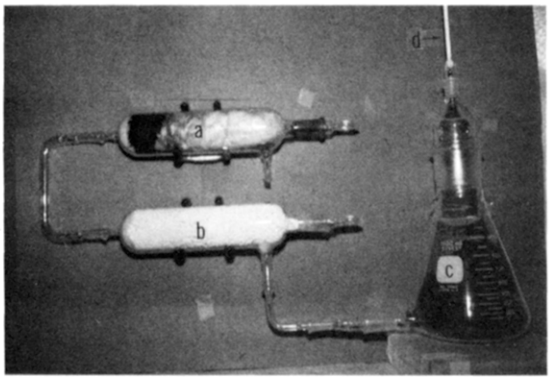

Figure 1. All-glass apparatus for trapping plant volatiles: a, charcoal trap; b, calcium chloride trap; c, leaf-containing chamber; d, Tenax trap.

Insects. The colony of the Mexican bean beetle (MBB), *E. varivestis* Mulsant, was maintained in the greenhouse on snap bean, *Phaseolus vulgaris* L. (Liu et al., 1989); and of the cabbage looper (CL), *T. ni* (Hübner), in the laboratory on a pinto bean based diet (Liu et al., 1988).

Tenax Trapping of Plant Volatiles. Fully expanded trifoliolate leaves (100 g) were removed from soybean or lima bean plants and placed immediately in a modified 1000-mL Pyrex Erlenmeyer flask reservoir (Figure 1). The Tenax trap consisted of a Pyrex tube forming a 0.5-cm diameter by 9-cm length column packed with 0.17 g of Tenax-GC. Using a ground-glass jointed all-glass system, air was first vacuum-filtered through activated charcoal and then desiccated by suction through calcium chloride. It next passed in the system through a side inlet into the bottom of the flask reservoir containing the leaves and then up through the Tenax trap (Figure 1). The metered vacuum air flow through the trap was 2000–2500 mL/min and continued for 24 h at 23 ± 1 °C. Contents of the Tenax trap were placed in a 7-mL screw-capped vial and extracted, using vortexing (2 min) with 3 mL of hexane (HPLC grade). The resultant hexane extract was filtered through Whatman No. 1 paper, weighed in a screw-capped glass vial, and stored at −10 °C.

Bioassays of Plant Volatiles with *T. ni* and *E. varivestis* Female Adults. Behavioral responses of CL and MBB female adults to plant volatiles were assayed in an open-ended horizontal glass tube arena. Each open end was covered uniformly with either a treated or control filter paper disk (Liu et al., 1988). The assay arena was divided into quadrants. Each arena had a centered side wall opening for introduction of the assay insect. A single female adult was thus placed in the center of the assay arena. With a stopwatch, insect orientation and movement were recorded in seconds, according to quadrant.

High-Performance Liquid Chromatography of Soybean and Lima Bean Volatiles. Qualitative and quantitative analyses of the Tenax-trapped plant volatiles were conducted by high-performance liquid chromatography (HPLC) using a column (25-cm length, 4.6-mm diameter) prepacked with 5-μm diameter silica particles (Ultrasphere, Beckman Inc., Berkeley, CA) and a variable UV detector (Hitachi Model 100-40). Previously standardized hexane extractables of the volatiles were concentrated 10 times with pure N_2 before 20 μL was injected per sample for HPLC analysis. Operating conditions for HPLC: temperature, ambient; elution phase, hexane–2-propanol 96:4 for 1 min and then 95:5 for 10 min; flow rate, 1 mL/min; column pressure, 450 psi. The wavelength for detection was 254 nm. Retention time, area, and height of each resolved peak were calculated and recorded by a Spectra Physics Model SP4100 computing integrator (Santa Clara, CA 95051).

Capillary Gas–Liquid Chromatography. Standardized hexane extractables of the volatiles were also analyzed by capillary gas–liquid chromatography with a Hewlett-Packard (HP 5890) GLC, using a capillary column (25 m × 0.25 mm, open tubular wall coated with OV-17). The GLC temperature program for the column was 40 °C for 5 min, to 170 °C at 5 °C/min, at 170 °C for 1 min, and then to 270 °C at 20 °C/min. The inlet pressure was 11.5 psi, and the flow rate was 1.2 cm^3 of He/min. The temperature of the injector was 235 °C; and that of the detector, 275 °C. The split ratio of the injector was 23:1. Standardized hexane extractables (300 μL) were concentrated to 100 μL, and then 1 μL of the latter was used per injection. Retention time, area, and ratio of each peak were calculated and recorded by a HP 3392A computing integrator. An appropriate blank based on the same procedures as used in the Tenax trapping of plant volatiles, except without plant materials present, was run as a control.

Gas Chromatography–Mass Spectrometry Analyses. Gas–liquid chromatography was conducted with a Finnigan-MAT Model 9610 using a DB-5 capillary column (30 m × 0.25 mm, 0.25-μm film thickness) from J & W Scientific, operated in splitless injection mode with helium carrier gas. The GLC was directly connected to the ion source via a fused silica capillary. The GLC was temperature-programmed at 40 °C for 2 min, to 170 °C at 5 °C/min, and next to 270 °C at 20 °C/min. Both the injection port and transfer line were at 250 °C.

A Finnigan-MAT Model 4510 with SuperIncos data system was used for mass spectrometric (MS) identifications. The MS was operated in the electron-ionization (EI) mode under the following conditions: ionization energy, 70 eV; ion source temperature, 100 °C; sensitivity, 10^{-7} A/V; mass range, m/z 34–4000 amu; scan time, 1 s. For the molecular weight information, chemical ionization (CI) with methane was used; and the mass range was 65–400 amu.

Original standardized hexane extractables (500 μL) of volatiles were concentrated to 1 μL for each injection. A blank was used to identify contaminants in each sample.

RESULTS AND DISCUSSION

Biological Activity of Plant Volatiles to CL and MBB Female Adults. Tenax-trapped hexane-extractable volatiles from the relatively insect-resistant PI 227687 soybean were significantly repellent to *T. ni* females ($P < 0.01$, *t*-test) and *E. varivestis* adults ($P < 0.05$, *t*-test) as compared to a solvent (hexane plus white oil) control (Table I). In sharp contrast, such volatiles from the relatively less insect-resistant Davis soybean leaves were highly attractive to the moths ($P < 0.01$, *t*-test) and the beetles ($P < 0.05$, *t*-test) (Table I). Odors from the insect-preferred Henderson lima bean leaves were neutral (neither attractive nor repellent) to the insects ($P < 0.05$, *t*-test); these latter results were similar to those with the solvent and filter paper controls (Table I).

Comparative HPLC and GLC Analyses of Plant Volatiles. All HPLC-resolved peaks in the hexane extractables from the Tenax trappings from PI 227687 and Davis soybeans and Henderson lima bean are listed by retention time in Figure 2. Differences in number, height, and area of peaks among the studied volatiles indicate both qualitative and quantitative distinctions among the involved legumes.

Qualitative and quantitative differences among the volatile extractables from the three studied legumes are even more obvious in the GLC data (Figure 3); e.g., a peak

Table I. Responses of CL and MBB Female Adults to Volatiles from Soybean and Lima Bean Leaves[a]

		CL[c]			MBB[d]		
	treatment[b]	c side	t side	t − c[e]	c side	t side	t − c[e]
I	PI 227687	72.3	27.7	−44.6**	60.9	39.1	−21.8*
II	Davis	21.2	78.8	+57.6**	39.7	60.3	+20.6*
III	Henderson	51.3	48.7	−2.6 NS	49.4	50.6	+1.2 NS
IV	solvent control	50.8	49.2	−1.6 NS	48.9	51.1	+2.2 NS
V	filter paper control	51.8	48.2	−3.6 NS	52.5	47.5	−5.0 NS

[a] Data are the mean times, as percentages, that insects spent in each half (side) (i.e., c = control and t = treated) of the assay arena and averages of 6–18 replications. [b] Treatments consisted of 40 μL of hexane extractables of plant volatiles obtained by Tenax trapping plus 50 μL of white oil (I–III), solvent control was 40 μL of hexane plus 50 μL of white oil (IV), and V was only filter paper. [c] In each replication one female adult *T. ni* was assayed for 300 s (5 min). [d] In each replication one female *E. varivestis* was assayed for 1800 s (30 min). [e] Differences between means followed by a single asterisk are significantly different at $P = 0.05$ level (t-test); double asterisks, $P = 0.01$ level; NS, not significant.

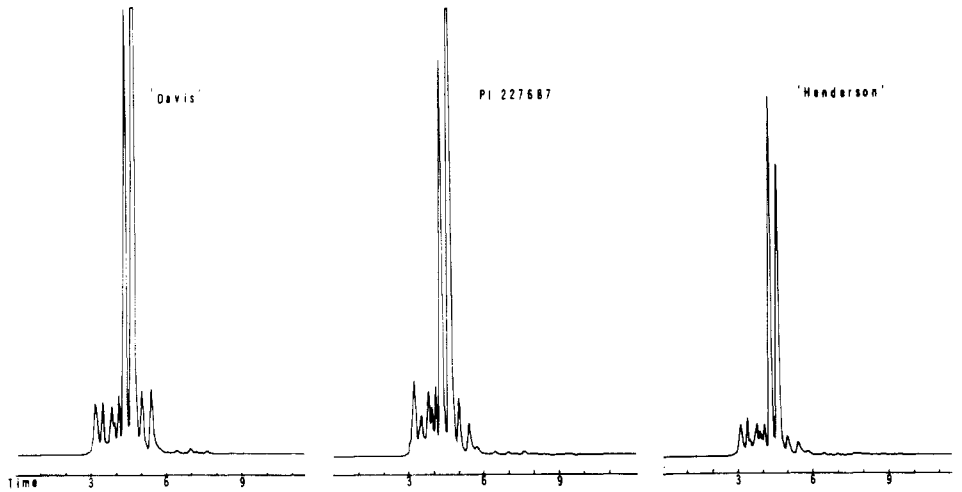

Figure 2. High-performance liquid chromatograms of the volatiles from PI 2276878 or Davis soybean or Henderson lima bean leaves.

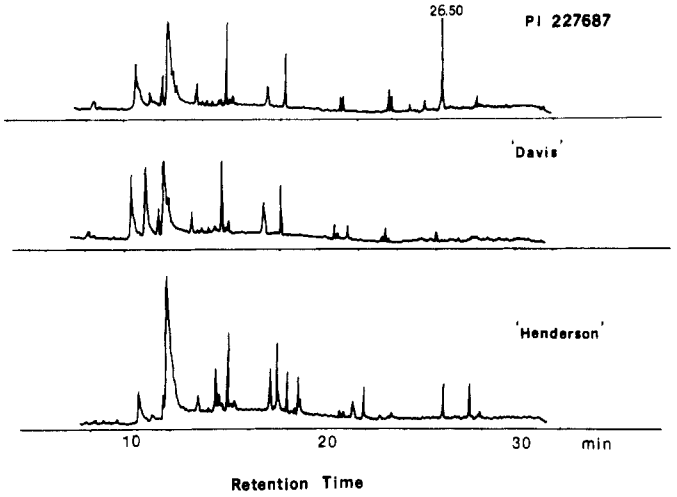

Figure 3. Gas chromatograms of the volatiles from PI 227687, Davis, and Henderson leaves.

(retention time 26.50) is prominent in the PI 227687 volatiles, not in the Davis odors and is very small in area in the Henderson volatiles (Figure 3). It is clear that the odor of Henderson lima bean contains more components than that of either soybean (PI 227687 or Davis).

GC–MS Analyses. Results of GC–MS analyses further confirmed the previous above findings. Compounds and composition ratios were different among the volatiles from PI 227687 and Davis soybeans and Henderson lima beans.

The main components in the volatiles from Davis soybean leaves were 4-hexen-1-ol acetate; 2,2-dimethylhexanal, and 2-hexenal (Table II; Figures 4a and 5); in the volatiles from PI 227687 soybeans, 3-tetradecene, 4-hexen-1-ol acetate, 2,2-dimethylhexanal, and 1-dodecene (Table III; Figures 4b and 5); and in the odors of Henderson lima beans, 4-hexene-1-ol acetate; butanoic acid, 3-hexenyl ester; and 1-nonen-3-ol (Table IV; Figure 4c).

Table II. GC–MS Data for Davis Volatiles

peak no.	scan (1 s)	identification	total, %
1	212	acetic acid	3.1
2	216	unknown	tr
3	222	unknown	tr
4	306	2,4-hexadien-1-ol	2.6
5	364	2-hexenal	2.3
6	369	2-hexenal	5.6
7	375	3-hexenal-1-ol	1.7
8	395	1-hexanol	tr
9	542	7-octen-4-ol	tr
10	547	2,2-dimethylhexanal	1.6
11	578	2,2-dimethylhexanal	9.4
12	590	3-octanone	2.7
13	601	acetic acid, cyclohexyl ester	1.7
14	608	3-octanol	1.5
15	631	4-hexen-1-ol acetate	68.1
16	641	acetic acid, hexyl ester	tr

Our study has confirmed that plant volatiles may have major influences on an insect's orientation regarding plants. Such influences may include repulsion, attraction, or neutrality: i.e., PI 227687 proved repellent, Davis was attractive, and Henderson was neutral to CL and MBB female adults.

From our studies of the three legumes, Henderson lima beans yielded the most volatiles, ca. 19 ppm, whereas Davis soybeans contained about 13 ppm and PI 227687 soybeans contained about 14 ppm. Henderson volatiles contain more components than those of either soybean (Table V). The three plants contain certain common chemicals, but each also has unique ones (Table V). The amounts of

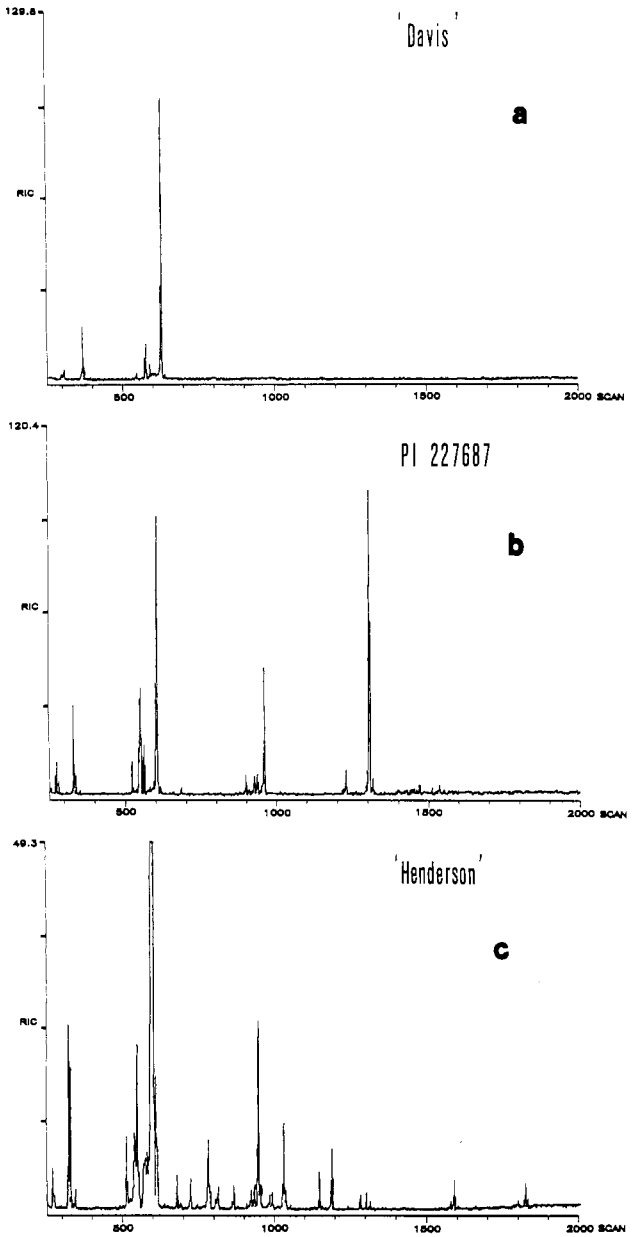

Figure 4. GC–MS analyses: (a) Davis volatiles; (b) PI 227687 volatiles; (c) Henderson volatiles. One scan equals 1 s.

common compounds differ among the three plant cultivars (Tables II–IV); e.g., the attractant 4-hexen-1-ol acetate is 68.1% of all volatiles in Davis, 58.9% in Henderson, but only 29.0% in PI 227687. The main components in the PI 227687 volatiles, 3-tetradecene and 1-dodecene, are absent in Davis. These compounds appear to be major contributors to the insect repellency of PI 227687. Both authentic tetradecene at 0.05% in hexane and dodecene at 0.015% in hexane (these were the concentrations of these components in the hexane extractables of PI 227687 volatiles) showed very strong repellency to cabbage looper female adults (Figures 6 and 7). Tetradecene also was previously isolated from two species of flour beetles, *Tribolium castaneum* Herbst and *Tribolium confusum* Jacquelin DuVel, and was a strong repellent to these same two beetle species (Suzuki et al., 1975).

The attractions of *T. ni* and *E. varivestis* to Davis odors are apparently attributable to the absence of tetradecene and dodecene and the abundance of hexenol acetate, dimethylhexanal, and hexenal. Compared with the relatively wild soybean PI 227687, Davis is a human-altered (-created) commercial cultivar; and its attractive odors for the assayed insects apparently are unintentional (i.e., previously unknown) results of human selection and breeding interventions into the evolution of soybeans. In spite of its being attractive to insects, Davis has retained levels of antifeedant and antibiotic activities to *E. varivestis*, which are comparable to those in PI 227687 (Weiss and Norris, 1989). Thus, plant breeders created with Davis an agronomic "death trap" for *E. varivestis* (i.e., this cultivar attracts adults and subsequently poisons the progeny larvae). Such facts prove that the genetic controls in soybean for volatile defenses are distinct from a major portion of those for antifeedants and antibiotics.

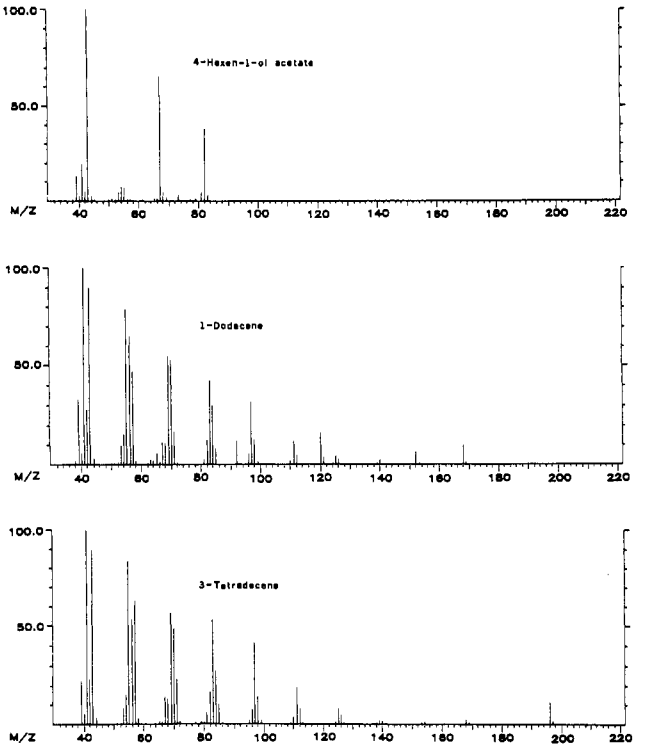

Figure 5. Mass spectra obtained of experimentally isolated compounds: 3-tetradecene, 1-dodecene, and 4-hexen-1-ol acetate.

Table III. GC–MS Data for PI 227687 Volatiles

peak no.	scan (1 s)	identification	total, %
1	221	unknown	tr
2	232	unknown	tr
3	323	2-hexenal	1.0
4	332	2-hexenal	5.0
5	336	3-hexen-1-ol	1.3
6	352	1-hexenol	tr
7	502	unknown	tr
8	523	7-octen-4-ol	2.2
9	528	unknown	tr
10	537	3,5,5-trimethyl-2-hexene	tr
11	545	unknown	tr
12	552	2,2-dimethylhexanal	11.0
13	563	3-octanone	3.6
14	574	unknown	tr
15	581	unknown	tr
16	606	4-hexen-1-ol acetate	29.0
17	616	acetic acid, hexyl ester	tr
18	684	*trans*-ocimene	tr
19	880	unknown	tr
20	916	unknown	tr
21	946	butanoic acid, 3-hexenyl ester	tr
22	961	1-dodecene	9.6
23	1228	unknown	tr
24	1308	3-tetradecene	33.2
25	1421	unknown	tr
26	1551	unknown	tr
27	1576	unknown	tr

Table IV. GC–MS Data for Henderson Volatiles

peak no.	scan (1 s)	identification	total, %
1	227	unknown	tr
2	272	2-methyl-4-pentenal	1.5
3	320	2-hexenal	tr
4	325	2-hexenal	4.1
5	330	3-hexen-1-ol	2.6
6	337	1-hexanol	tr
7	345	1-hexanol	tr
8	414	1-methoxy-3-methylene-2-pentanone	tr
9	421	methoxybenzene	tr
10	515	7-octen-4-ol	1.7
11	521	unknown	tr
12	527	2,2,5,5-tetramethyl-3,4-hexanedione	tr
13	541	2,2-dimethylhexanal	4.8
14	551	1-nonen-3-ol	5.3
15	557	3-octanone	1.1
16	570	unknown	tr
17	576	4-hexen-1-ol acetate	1.0
18	582	3-hexen-1-ol acetate	tr
19	606	4-hexen-1-ol acetate	58.8
20	612	acetic acid, hexyl ester	4.2
21	637	unknown	tr
22	679	*trans*-ocimene	tr
23	689	unknown	tr
24	694	unknown	tr
25	723	unknown	tr
26	745	linalool	tr
27	768	unknown	tr
28	782	unknown	tr
29	814	unknown	tr
30	866	butanoic acid, 3-hexenyl ester	tr
31	918	unknown	tr
32	948	butanoic acid, 3-hexenyl ester	7.0
33	957	unknown	tr
34	1031	unknown	tr
35	1037	unknown	tr
36	1190	unknown	tr
37	1284	hexanoic acid, 3-hexenyl ester	tr
38	1292	2,6-dimethyl-5-heptenal	tr
39	1303	3-tetradecene	tr
40	1429	unknown	tr
41	1590	unknown	tr
42	1660	diphenylmethanone	tr

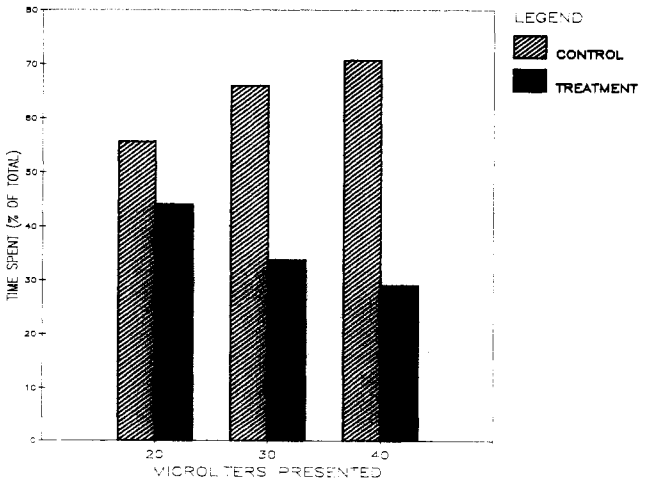

Figure 6. Behavioral effects of different dosages of commercial tetradecene (0.05%) on the cabbage looper female adults: 20 μL, $P = 0.05$ level different (t-test); 30 and 40 μL, $P = 0.01$ level.

The observed behavioral neutrality of the odors from the preferred host, Henderson lima bean, apparently is due to its complex blend of volatile components. In addition to "essential oil", attractive compounds, the Henderson volatiles also contain proven or possibly repellent components such as 3-tetradecene and butanoic acid, 3-hexenyl ester. Our proposed explanation for this overall neutrality

Table V. Chemicals by Class and Their Distribution in Plant Volatiles

chemicals, by class	distribution in Davis	PI 227687	Henderson
aliphatic acids and esters			
acetic acid	+		
4-hexen-1-ol acetate	+	+	+
3-hexen-1-ol acetate			+
acetic acid, cyclohexyl ester	+		
acetic acid, hexyl ester	+	+	+
butanoic acid, 3-hexenyl ester		+	+
hexanoic acid, 3-hexenyl ester			+
aliphatic aldehydes			
2-methyl-4-pentenal			+
2-hexenal	+	+	+
2,2-dimethylhexanal	+	+	+
2,6-dimethyl-5-heptenal			+
aliphatic ketones			
3-octanone	+	+	+
1-methoxy-3-methylene-2-pentanone			+
2,2,5,5-tetramethyl-3,4-hexanedione			+
diphenylmethanone			+
aliphatic alcohols			
2,4-hexadien-1-ol	+		
3-hexen-1-ol	+	+	+
1-hexanol	+	+	+
7-octen-4-ol	+	+	+
3-octanol	+		
1-nonen-3-ol			+
unsaturated hydrocarbons			
3-tetradecene		+	+
1-dodecene		+	
3,5,5-trimethyl-2-hexene		+	
terpenoids			
trans-ocimene		+	+
linalool			+
anisole			
methoxybenzene			+

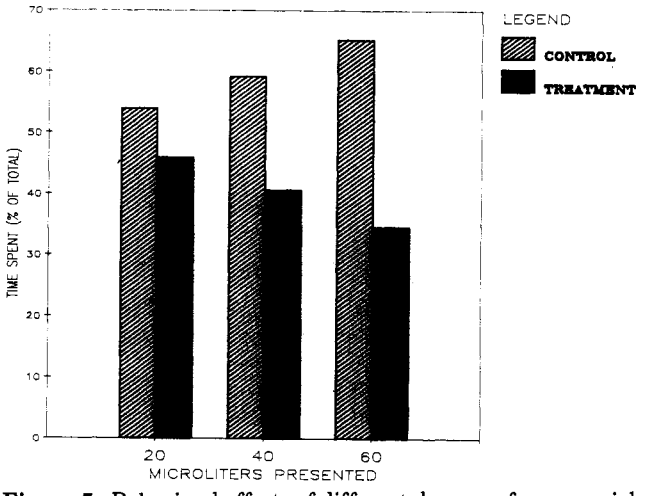

Figure 7. Behavioral effects of different dosages of commercial dodecene (0.015%) on CL female adults: 20 μL, NS; 40 μL, $P = 0.05$ level different; 60 μL, $P = 0.01$ level (t-test).

of Henderson volatiles to assayed insects is that the individual attractive and repellent components effectively cancel each other so that the net effect on the insect's behavioral responses is zero.

Both qualitative and quantitative differences play important roles in the overall functions of plant volatiles in insect orientations. Thus, the net effects of given plant volatiles depend on whether the major components are repellent (PI 227687), attractant (Davis), or neutralized (Henderson).

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Registry No. Acetic acid, 64-19-7; 4-hexen-1-ol acetate, 72237-36-6; 3-hexen-1-ol acetate, 1708-82-3; acetic acid, cyclohexyl ester, 622-45-7; acetic acid, hexyl ester, 142-92-7; butanoic acid, 3-hexenyl ester, 2142-93-0; hexanoic acid, 3-hexenyl ester, 84434-19-5; 2-methyl-4-pentenal, 5187-71-3; 2-hexenal, 505-57-7; 2,2-dimethylhexanal, 996-12-3; 2,6-dimethyl-5-heptenal, 106-72-9; 3-octanone, 106-68-3; 1-methoxy-3-methylene-2-pentanone, 55956-45-1; 2,2,5,5-tetramethyl-3,4-hexanedione, 4388-88-9; diphenylmethanone, 119-61-9; 2,4-hexadien-1-ol, 111-28-4; 3-hexen-1-ol, 544-12-7; 1-hexanol, 111-27-3; 7-octen-4-ol, 53907-72-5; 3-octanol, 589-98-0; 1-nonen-3-ol, 21964-44-3; 3-tetradecene, 36587-78-7; 1-dodecene, 112-41-4; 3,5,5-trimethyl-2-hexene, 26456-76-8; *trans*-ocimene, 27400-72-2; linalool, 78-70-6; methoxybenzene, 100-66-3.

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Synthesis of Methylene-Linked Pyrethroids

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In a simplified approach, new methylene-linked pyrethroid esters and ketones, lacking an ester bridge, are synthesized from (*E*)-(*R,S*)-2,2-dimethyl-3-(2-methylpropenyl)cyclopropane-, (*E*)-(*R,S*)-3-(cyclopentylidenemethyl)-2,2-dimethylcyclopropane-, (*E*)-(*R,S*)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-, and (*R,S*)-1-(4-chlorophenyl)-2,2-dimethylethane-1-carboxylic acids and 3-phenoxybenzyl and 5-benzyl-3-furylmethyl halides. The keto esters are prepared via a Meldrum's acid intermediate and classical alkylation of the β-keto ester with a halide. An aqueous, phase transfer (PTA) catalyzed or sodium hydride–1,2-dihydroxypropane decarbethoxylation at 80 °C is used to complete the synthesis. The β-keto esters and subsequent ketones express various biological activities in *Oncopeltus fasciatus* (large milkweed bug), *Tenebrio molitor* (yellow mealworm), and *Spodoptera frugiperda* (fall armyworm).

Pest insects adversely impact on and significantly affect the production and quality of agricultural products (Harein, 1982; Ouye, 1984), and the recent and potential removal of several accepted fumigants and stored product protectants may introduce further critical problems for agriculture (Brady, 1982). Also, because a number of these pests have developed resistance (Elliott et al., 1978; Beard et al., 1985; Bangston et al., 1983; Riskallah, 1983), new, improved, and environmentally safe chemicals are needed

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