EXPOSURE, FATE AND POTENTIAL RESIDUES IN FOOD OF APPLIED LEPIDOPTERAN PHEROMONES

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ABSTRACT

Chemical pesticide registration regulations in most of the world require extensive toxicity, environmental and residue testing of proposed active ingredients. These definitions currently include insect pheromone components used to disrupt or confuse mating cycles. Negligible residues are predicted for lepidopteran pheromones used in fruit production as only small amounts are employed, and in discrete point source formulations applied in use patterns that preclude direct contact with the fruit. In this study, fruits (apples, peaches, grapes) treated with a variety of pheromones were analyzed for their respective component residues. Fruit samples were blended and extracted with acetone; following the addition of water, the analytes were extracted into hexane, concentrated, and adsorbed onto a Florisil Sep-pak. Elution was with 10% acetone/hexane. Chromatography of Z-9-DDA (Z-9-Dodecen-1-ol Acetate), Z-11-TDA (Z-11-Tetradecen-1-ol Acetate) and E-11-TDA (E-11-Tetradecen-1-ol Acetate) utilized a H-P Model 5890 equipped with a Restek Stabilwax 10 capillary column, 30 m x 0.25 mm x 0.25 µm coating. Temperature program: 80°-130°C @ 5°/min, 130°-200°C @ 4°/min, hold 9 min. Detection by HP-MSD Model 5970B was in the selective ion mode. Retention times were 16.3, 21.1 and 20.9 min, respectively. EZ-3,13-ODA (E-Z-3,13-Octadecadien-1-ol Acetate) and ZZ-3,13-ODA (Z-Z-3,13-Octadecadien-1-ol Acetate) were chromatographed on a H-P Model 5890B using a Silar 10C, 50m x 0.25 mm x 0.25 µm column. Temperature program: initial temperature 80°C, hold 2 min.; 80°-130°C @ 10°C/min., hold 15 min. Detection was by HP-MSD Model 5970C operated in the selective ion mode. Retention times were 18.4 and 18.6 min., respectively. Recoveries were generally 80%, or better, at a minimum sensitivity of <5 ppb for all components analyzed. No residues have been detected on any commodity samples.

INTRODUCTION

The large number of insect pheromones being evaluated or proposed for formal submission and registration as commercial pest control agents poses a problem since in most countries current regulations require that each component in the formulation be subjected to the same testing and toxicity standards as are all potential chemical pesticide active ingredients. This is prohibitively expensive, both because of the large number of active ingredients needed, and because of the relatively small market potential for each specific pheromone mixture. Not only are pheromone compositions unique for a given target species, they are applied at lower rates than traditional insecticides (gram/hectare vs. kilogram/hectare). Couple these factors with the separate registration and tolerance

required for each commodity on which a given pheromone component may be used, and the commercial future for this whole area of endeavor is bleak. Clearly, each step of the traditional chemical pesticide regulatory process must be examined with regard to the use patterns and chemical characteristics of the proposed pheromone components so that those procedures that could be modified, minimized or combined without compromising the safety and intent of the law might be so amended. This paper considers pheromone residues on food, an area that must be addressed in present chemical pesticide registration protocols.

Previous work at our laboratory had shown no detectable residues (<2 ppb) of either Z-9-DDA or Z-11-TDA on grapes (see Table I) after season-long application programs as high as 141 g/ha (Spittler et al., 1988). However, there is little other available literature on pheromone residues in and on raw agricultural commodities: obviously this one report constitutes insufficient evidence for consideration of regulatory relief from residue studies. Accordingly, we acquired treated fruit samples from several 1990 lepidopteran pheromone field trials for residue analysis--the intent being to expand the pheromone residue data base. The similarity of many components in commercial lepidopteran mating disruption formulations simplified the analytical complexity of the study (Figure 1). Our preliminary attempts to chromatograph the free alcohols were discouraging, but agreed with previous observations of problems with quantitative measurements of underivatized alcohol pheromone components (Charlton, personal communications). However, if conversion of the alcohols to their respective acetates could be effected quantitatively and with acceptable recoveries, five of the eight alcohols could be determined as analytes already present in the scheme. Only data for the acetate pheromone components are available for this presentation. Measurement of the alcohol pheromone component residues will be conducted and reported in future work.

PRODUCTION OF FIELD SAMPLES

All field trials except the New York State grape berry moth studies were part of the 1990 field testing program of Biocontrol Ltd., Davis, CA 95616 USA. All pheromones tested were formulated in polyethylene twist-tie dispensers at load rates described in this paper. Formulations were prepared for Biocontrol Ltd. by Shin-Etsu Chemical Company, Tokyo, Japan. Species information on four of the insect pheromones being assessed is proprietary and confidential. Thus, these insects have been code named 9OUSEX1, 9OUSEX2, 9OUSEX3 and 9OUSEX4 in this publication to protect trade information. See Tables for full names and percentages of pheromone components.

Grapes, New York

Details on the 1986 program are found in Spittler et al., 1988. For T. J. Dennehy's 1990 trials, vineyards of Seyval and Elvira varieties were hung with Grape Berry Moth pheromone in tie-on polyethylene applicators at a rate of 493 ties/ha on April 15, 1990. Each tie contained 69 mg of a mixture of 90% Z-9-DDA and 10% Z-11-TDA; total application rate 34 g/ha. Fresh samples were delivered within several hours of harvest, on September 20, 1990, to the Cornell Analytical Laboratories. Samples were stored at -20°C until analysis. See Tables 1 and 2.

Grapes, Virginia

Two Chardonnay vineyards were hung with 493 Grape Berry Moth ties/ha (see above)--Prince Michel on April 21, 1990 and Meredith on April 22, 1990--by D. Pfeiffer. On August 30, 1990, samples were taken from row #15 (center row) and row

#6 of the Prince Michel vineyard. On September 9, 1990, a sample was taken from the center row of Meredith vineyard. Samples were frozen for shipping, and held at -20°C upon receipt. See Table 3.

Apples, Virginia

One orchard (Bryant) of Golden Delicious variety was treated on April 12, 1990 by D. Pfeiffer with 986 ties/ha of Codling Moth pheromone (63% EE-8,10-DDOH, 31% DDOH, 6% TDOH). Each tie contained 170 mg of formulation; total application 168 g/ha. Both the Bryant orchard and a Wine Sap variety orchard (Crown Spring Valley) were hung on April 12-13, 1990 with 986 ties/ha of 9OUSEX4 pheromone. One hundred and thirty mg/tie yields 129 g/ha. Two replicate samples from Bryant were harvested September 4, 1990, frozen for shipping, and maintained at -20°C until analysis. One sample from Crown Spring Valley was taken October 11, 1990, and handled in a similar manner. See Tables 4 and 8.

Apples, New York

Orchard blocks of Tydeman, McIntosh, Cortland and Ida Red variety apples were hung on June 1, 1990 with 986 ties/ha of 9OUSEX1 pheromone by A. Agnello. Each tie contained 160 mg of Z-11-TDA. Harvest dates were Tydeman-August 22, 1990; McIntosh-September 17, 1990; Cortland-September 21, 1990; and Ida Red-October 5, 1990. Samples were delivered fresh to the laboratory on their harvest dates where they were pulverized, subsampled and frozen at -20°C. See Table 5.

Apples, Pennsylvania

9OUSEX2 pheromone formulations were under investigation by L. Hull. "Generic" ties contained 67% E-11-TDA, 29% Z-11-TDA, 1% E-11-TDOH, 1% Z-11-TDOH and 2% Z-9-DDA. Two blocks (Tyson and Oyler) of Yorking variety were hung with generic ties on April 18, and 17, 1990, respectively: 1972 ties/ha x 160 mg/tie = 316 g/ha. "High E" ties contained 90% E-11-TDA and 10% E-11-TDOH. Orchards and rates were Yorking-Hall (1479 ties/ha x 160 mg/tie = 237 g/ha), Yorking-Raff and Rome-Hickey (985 ties/ha x 160 mg/tie = 158 g/ha). Harvests were on September 27, October 6, October 3, October 2, and October 15, 1990, in the order presented. Samples were frozen for shipment and maintained at -20°C until analyzed. See Table 6.

Peaches, New Jersey

Two variety blocks, Marqueen and Rio-Oso-Gem, were treated by D. Polk with 247 ties/ha of 9OUSEX3 pheromone on April 1-2, 1990. Each 50 mg tie was 70% EZ-3,13-ODA and 30% ZZ-3,13-ODA. Total application 12.5 g/ha. The Marqueen block was sampled August 21, 1990, and the Rio-Oso-Gem block on August 29, 1990. Encore variety samples were taken on this latter date as untreated check. Samples were frozen for shipping and stored at -20°C. See Table 7.

ANALYSIS

Sample Preparation

Fruit was pulverized in a Hobart chopper, either upon receipt or immediately before analysis. Fifty gram samples were taken from the homogeneous slurry. Each 50g sample was blended for two min with 2.5g Hyflo-Supercel and 60 ml redistilled acetone. Each extraction mixture was filtered in a sintered glass funnel and the resultant pad rinsed with acetone. Fifty ml H_2O, 15 ml saturated NaCl and 50 ml n-hexane were added to the

filtrate in a one-liter separatory funnel, and shaken. After phase separation, the hexane was removed and the aqueous phase was sequentially extracted with two more 50 ml portions of n-hexane--these were then combined with the original and dried over Na_2SO_4. Volume was reduced to 5.0 ml by rotovap @ 35°C. Any waxy precipitants were centrifuged out, and a 2.0 ml (20g equivalent) aliquot was placed on a Florisil Sep-pak (Waters Assoc, Milford, MA USA). After first washing with 5.0 ml of n-hexane, the pheromone containing fraction was eluted with 2.0 ml of 10%-acetone/90% n-hexane. The sample was evaporated under dry N_2 to 1.0 ml.

Standards

Analytical standards were obtained from Shin-Etsu Chemical Company, Ltd., Tokyo: Z-9-DDA, Lot #04008; Z-11-TDA, Lot #98007; EE-8,10-DDOH, Lot #03050; DDOH, Lot #03065; TDOH, Lot #03066; E-11-TDA, Lot #03066; E-11-TDOH, Lot #03037; Z-11-TDOH, Lot #83023; EZ-3,13-ODA, Lot #93006; ZZ-3,13-ODA, Lot #16280.

Chromatography: Z-9-DDA; Z-11-TDA; E-11-TDA

The samples (1.0 µl) were injected on a Hewlett-Packard Model 5890 B Capillary Gas Chromatograph utilizing a split-splitless injector at 245°C. Column was a Restek Stabilwax 10, 30m x 0.25 mm I.D. x 0.25 µm coating with a He carrier velocity of 30 cm/sec. Temperature program: initial temperature 80°C, hold 1.0 min; 80°C to 130°C @ 10°C/min; 130°C to 200°C @ 4°C/min, hold 9.0 min; 200°C to 250°C @ 30°C/min, hold/recycle. Transfer line to the H-P 5970B detector was via a butt connector/guard column maintained at 280°C.

Chromatography: EZ-3,13-ODA; ZZ-3,13-ODA

Samples (1.0 µl) were injected on a Hewlett-Packard 5890B Capillary Gas Chromatograph utilizing a split-splitless injector at 220°C. Column was Silar 10C, 50m x 0.25 mm x 0.25 µm coating with a He carrier velocity of 25 cm/sec. Temperature program: 80°C, hold 2 min.; 80°C to 220°C @ 10°C/min.; hold 15 min.; recycle. Transfer line to the H-P 5870C detector was via a butt connector/guard column maintained at 250°C.

Detection

Quantitation was with Hewlett-Packard Model 5970B or 5970C Mass Selective Detectors run in the SIM (Selective Ion Mode) at the major unique M/E (Mass/Charge Ratio) for each component (See Figures 2-9). These figures give the SIM response for the various analytes. Untreated check materials for each commodity were run at M/E's determined for the base peaks of each pheromone, as were spiked checks. For all acetates investigated, the strongest ion corresponded to M-60, the ion formed by the loss of an acetate fragment. Figures 5 and 9 illustrate samples receiving the higher application rates of selected pheromone components. See Spittler, 1988 for Z-9-DDA and Z-11-TDA analytical details on grapes.

Recovery and Sensitivity

In Table 9 are found the results of recovery spikes run for pheromone components on check samples. In those situations where no control samples of a particular variety were available, the test samples were spiked after determining the retention windows of interest to be free of interference at the designated M/E's.

Figure 1

Simplification of Leidopteran Pheromone Analytical Scheme

PHEROMONE COMPONENTS		ANALYTES
GBM	Z-9-DDA Z-11-TDA	
		Z-9-DDA (2)
9OUSEX1	Z-11-TDA	
		Z-11-TDA (3+2*)
9OUSEX4	Z-11-TDOH* E-11-TDOH*	
		E-11-TDA (2+3*)
9OUSEX2 GENERIC	E-11-TDA Z-11-TDA E-11-TDOH* Z-11-TDOH* Z-9-TDA	
9OUSEX2 HIGH E	E-11-TDA E-11-TDOH*	
CM	EE-8,10-DDOH* DDOH* TDOH*	EE-8,10-DDA DDA TDA
9OUSEX3	EZ-3,13-ODA ZZ-3,13-ODA	EZ-3,13-ODA ZZ-3,13-ODA

*If Acetylated to Corresponding Acetate

TABLE 1

Residues of Grape Berry Moth Pheromone* on Grapes in New York State -- 1986.

	RATE		DATE(month/day)		RESIDUE (ppb)	
VARIETY-SITE	TIES/ha	(g/ha)	APPLICATION	HARVEST	Z-9-DDA	Z-11-TDA
CONCORD-HAYWARD	985	(86)	5/15	10/1	<5	<5
CONCORD-HAYWARD	986	(86)	5/15 & 7/15	10/1	<5	<5
CONCORD-HAYWARD	0	(0)	---	10/1	<5	<5
CONCORD-FRANCIS	986	(86)	5/15	10/1	<5	<5
CONCORD-FRANCIS	493	(43)	5/15	10/1	<5	<5
CONCORD-FRANCIS	0	(0)	---	10/1	<5	<5
CONCORD-DEGOLIER	1972	(172)	5/15 & 7/15	10/1	<5	<5
CONCORD-DEGOLIER	986	(86)	5/15	10/1	<5	<5
CONCORD-DEGOLIER	0	(0)	---	10/1	<5	<5

FROM: Spittler, Leichtweis and Dennehy, ACS, 6156/88/0379
*Grape Berry Moth Peromone = 90% Z-9-Dodecen-1-ol Acetate (Z-9-DDA)
88 mg/TIE 10% Z-11-Tetradecen-1-ol Acetate (Z-11-TDA)

TABLE 2

Residues of Grape Berry Moth Pheromone* on Grapes in New York State -- 1990.

VARIETY-SITE	RATE TIES/ha	RATE (g/ha)	DATE(month/day) APPLICATION	DATE(month/day) HARVEST	RESIDUE (ppb) Z-9-DDA	RESIDUE (ppb) Z-11-TDA
SEYVAL-DRESDEN	493	(34)	5/15	9/20	<5	<5
SEYVAL-DRESDEN	0	(0)	---	9/20	<5	<5
ELVIRA-DRESDEN	493	(34)	5/15	9/20	<5	<5
ELVIRA-DRESDEN	0	(0)	---	9/20	<5	<5

Field Research: Dennehy, Cornell University

*Grape Berry Moth Pheromone = 90% Z-9-Dodecen-1-ol Acetate (Z-9-DDA)
69 mg/TIE 10% Z-11-Tetradecen-1-ol Acetate (Z-11-TDA)

TABLE 3

Residues of Grape Berry Moth Pheromone* on Grapes in Virginia -- 1990.

VARIETY-SITE	RATE TIES/ha	RATE (g/ha)	DATE(month/day) APPLICATION	DATE(month/day) HARVEST	RESIDUE (ppb) Z-9-DDA	RESIDUE (ppb) Z-11-TDA
CHARDONNAY-PRINCE MICHEL #15	493	(34)	5/21	8/30	<2	<5
CHARDONNAY-PRINCE MICHEL #6	493	(34)	5/21	8/30	<2	<5
CHARDONNAY-MEREDITH	493	(34)	5/23	9/9	<2	<5

FROM: Pfeiffer, Virginia Polytechnical Institute

*Grape Berry Moth Pheromone = 90% Z-9-Dodecen-1-ol Acetate (Z-9-DDA)
69 mg/TIE 10% Z-11-Tetradecen-1-ol Acetate (Z-11-TDA)

TABLE 4

Residues of Codling Moth Pheromone* on Apples in Virginia -- 1990.

VARIETY-SITE	RATE TIES/ha	RATE (g/ha)	DATE(month/day) APPLICATION	DATE(month/day) HARVEST	RESIDUE (ppb) EE-8,10-DDOH	RESIDUE (ppb) DDOH	RESIDUE (ppb) TDOH
GOLDEN DELICIOUS -BRYANT #1	986	(168)	4/12	9/4/90	Analyses Incomplete		
GOLDEN DELICIOUS -BRYANT #2	986	(168)	4/12	9/4/90			

Field Research: Pfeiffer, Virginia Polytechnical Institute

*Codling Moth Pheromone = 170 mg/TIE
63% E,E-8,10-Dodecadien-1-ol (EE-8,10-DDOH)
31% Dodecan-1-ol (DDOH)
6% Tetradecan-1-ol (TDOH)

TABLE 5

Residues of 9OUSEX-1 Pheromone* on Apples in New York -- 1990.

VARIETY-SITE	RATE TIES/ha	RATE (g/ha)	DATE(month/day) APPLICATION	DATE(month/day) HARVEST	RESIDUE (ppb) Z-11-TDA**
TYDEMAN-OAKS	986	(158)	6/1	8/22	<5
TYDEMAN-OAKS	0	(0)	---	8/22	<5
MCINTOSH-PADDOCK	986	(158)	6/1	9/17	<5
MCINTOSH-PADDOCK	0	(0)	---	9/17	<5
CORTLAND-STAPLES	986	(158)	6/1	9/21	<5
CORTLAND-STAPLES	0	(0)	---	9/21	<5
IDA RED-STAPLES	986	(158)	6/1	10/5	<5
IDA RED-STAPLES	0	(0)	---	10/5	<5

Field Research: Agnello, Cornell University

*9OUSEX-1 Pheromone = 160 mg/TIE
100% Z-11-Tetradecen-1-ol Acetate (Z-11-TDA)

**Samples run in duplicate

TABLE 6

Residues of 9OUSEX-2 Pheromone* on Apples in Pennsylvania -- 1990.

VARIETY-SITE	RATE TIES/ha	RATE (g/ha)	DATE(month/day) APPLICATION	DATE(month/day) HARVEST	RESIDUE (ppb) E-11-TDA	Z-11-TDA	E-11-TDOH	Z-11-TDOH	Z-9-DDA
YORKING-TYSON	1972	(316)	5/18	9/27	<5	<5			<5
YORKING-OYLER	1972	(316)	5/17	10/6	<5	<5	Analyses Incomplete		<5
YORKING-HALL	1479	(237)	5/18	10/3	<5	--	For Alcohols		--
YORKING-RAFF	985	(158)	5/15	10/2	<5	--			--
YORKING-RAFF	0	(0)	---	10/2	<5	<5			<5
ROME-HICKEY	985	(158)	7/27	10/15	<5	--			--
ROME-HICKEY	0	(0)	---	10/15	<5	--			--

Field Research: Hull, Pennsylvania State University

*9OUSEX-2 Pheromone, Generic = 160 mg/TIE	100% E-11-Tetradecen-1-ol Acetate	(E-11-TDA)
	29% Z-11-Tetradecen-1-ol Acetate	(Z-11-TDA)
	1% E-11-Tetradecen-1-ol	(E-11-TDOH)
	1% Z-11-Tetradecen-1-ol	(Z-11-TDOH)
	2% Z-9-Dodecen-1-ol Acetate	(Z-9-DDA)
*9OUSEX-2 Pheromone, High E = 160 mg/TIE	90% E-11-Tetradecen-1-ol Acetate	(E-11-TDA)
	10% E-11-Tetradecen-1-ol	(E-11-TDOH)

TABLE 7

Residues of 9OUSEX-3 Pheromone* on Peaches in New Jersey -- 1990.

VARIETY-SITE	RATE TIES/ha	RATE (g/ha)	DATE(month/day) APPLICATION	DATE(month/day) HARVEST	RESIDUE (ppb) EZ-3,13-ODA	RESIDUE (ppb) ZZ-3,13-ODA
MARQUEEN-RFRDC	247	(12.5)	5/1-2	8/21	<5	<5
RIO-OSO-GEM-RFRDC	247	(12.5)	5/1-2	8/29	<5	<5
ENCORE-RFRDC	0	(0)	---	8/29	<5	<5

Field Research: Polk, Rutgers University

*9OUSEX-3 Pheromone = 50 mg/TIE
70% E-Z-3,13-Octadecadien-1-ol Acetate (EZ-3,13 ODA)
30% Z-Z-3,13-Octadecadien-1-ol Acetate (ZZ-3,13 ODA)

TABLE 8

Residues of 9OUSEX-4 Pheromone* on Apples in Virginia -- 1990.

VARIETY-SITE	RATE TIES/ha	RATE (g/ha)	DATE(month/day) APPLICATION	DATE(month/day) HARVEST	RESIDUE (ppb) Z-11-TDOH	RESIDUE (ppb) E-11-TDOH
WINE SAP-CROWN SPRING VALLEY	986	(129)	4/13	10/11		
GOLDEN DELICIOUS-BRYANT #1	986	(129)	4/12	9/4	Analyses Incomplete	
GOLDEN DELICIOUS-BRYANT #2	986	(129)	4/12	9/4		

Field Research: Pfeiffer, Virginia Polytechnical Institute

*9OUSEX-4 Pheromone = 130 mg/TIE
30% Z-11-Tetradecen-1-ol (Z-11-TDOH)
70% E-11-Tetradecen-1-ol (E-11-TDOH)

TABLE 9

Retention Times, Recoveries and Sensitivities for Pheromone/Commodity Analytical Methods

PHEROMONE	COMMODITY-VARIETY	R.T. (min)	SPIKE (ppb)	RECOVERY (%)	MINIMUM (ppb)*
Z-9-DDA	GRAPE-CONCORD	17.7	10,5	98,80	2
Z-9-DDA	GRAPE-SEYVAL	16.3	5	79	2
Z-9-DDA	GRAPE-ELVIRA	16.3	10	88	2
Z-11-TDA	GRAPE-CONCORD	22.7	10,5	90,80	2
Z-11-TDA	GRAPE-SEYVAL	21.2	5	74	5
Z-11-TDA	GRAPE-ELVIRA	21.2	10	89	5
Z-11-TDA	APPLE-MCINTOSH	21.2	10,5	100,89	2
E-11-TDA	APPLE-YORKING	20.9	10,5	106,124	5
Z-11-TDA	APPLE-YORKING	21.1	10,5	92,104	5
Z-11-TDA	APPLE-ROME	---	10,5	---	---
E-11-TDOH	APPLE-YORKING	---	10,5	---	---
E-11-TDOH	APPLE-ROME	---	10,5	---	---
Z-9-DDA	APPLE-YORKING	16.3	10,5	87,116	2
EE-8,10-DDOH	APPLE-GOLDEN DELICIOUS	---	10,5	---	---
DDOH	APPLE-GOLDEN DELICIOUS	---	10,5	---	---
TDOH	APPLE-GOLDEN DELICIOUS	---	10,5	---	---
Z-11-TDOH	APPLE-GOLDEN DELICIOUS	---	10,5	---	---
E-11-TDOH	APPLE-GOLDEN DELICIOUS	---	10,5	---	---
Z-11-TDOH	APPLE-WINE SAP	---	10,5	---	---
E-11-TDOH	APPLE-WINE SAP	---	10,5	---	---
EZ-3,13-ODA	PEACH-ENCORE	18.4	10,5	78	5
ZZ-3,13-ODA	PEACH-ENCORE	18.6	10,5	80	5

*Minimum measurable concentration

---Data Incomplete

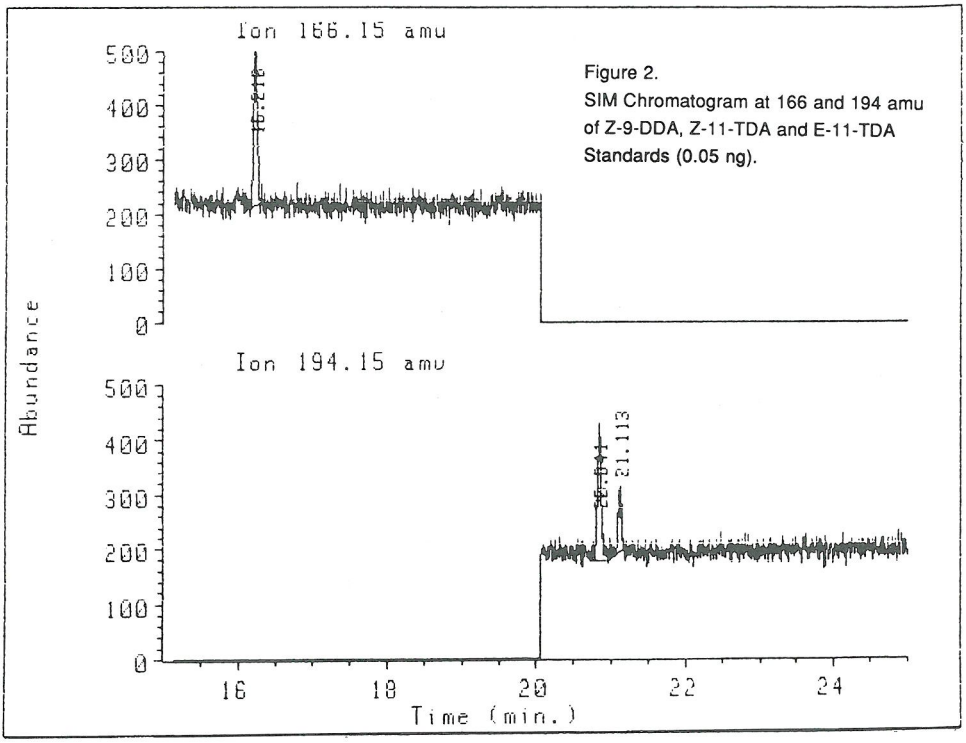

Figure 2.
SIM Chromatogram at 166 and 194 amu of Z-9-DDA, Z-11-TDA and E-11-TDA Standards (0.05 ng).

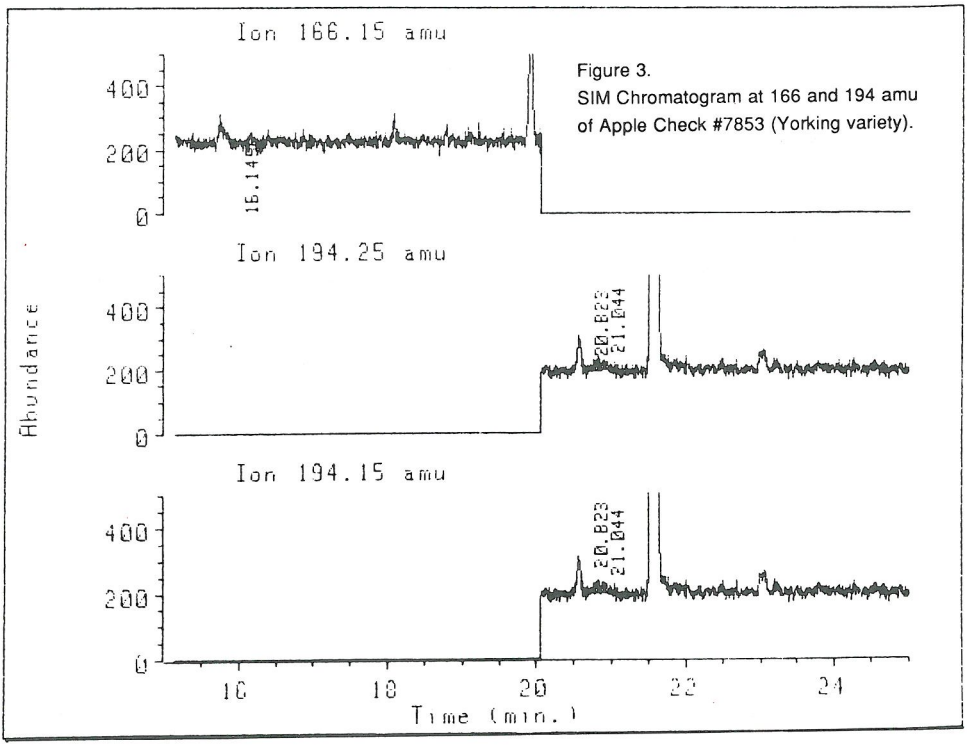

Figure 3.
SIM Chromatogram at 166 and 194 amu of Apple Check #7853 (Yorking variety).

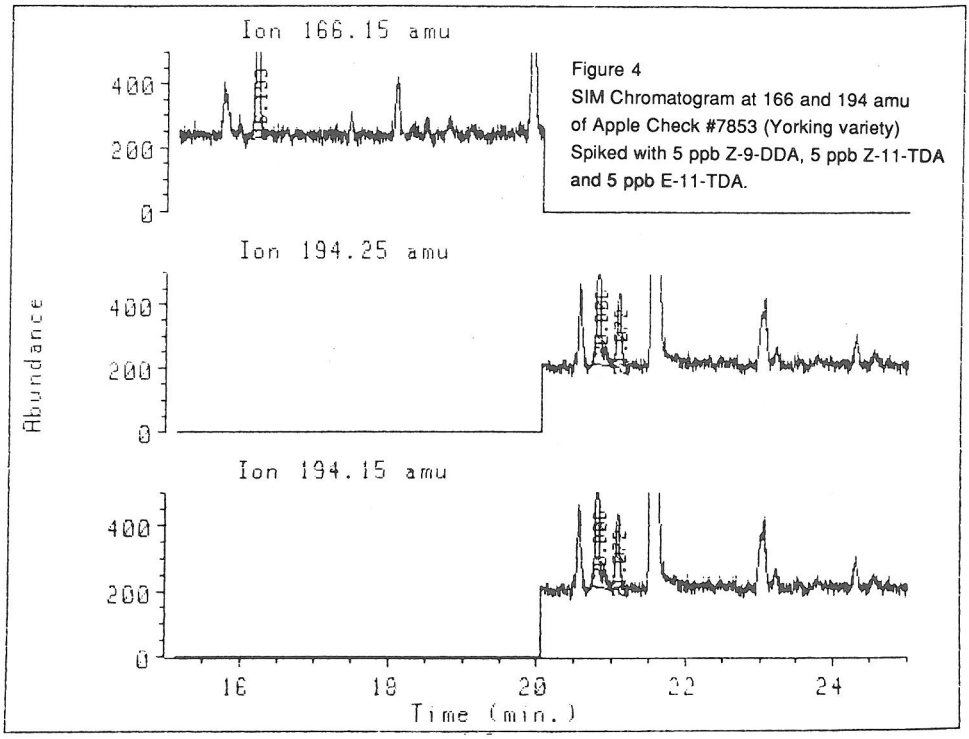

Figure 4
SIM Chromatogram at 166 and 194 amu of Apple Check #7853 (Yorking variety) Spiked with 5 ppb Z-9-DDA, 5 ppb Z-11-TDA and 5 ppb E-11-TDA.

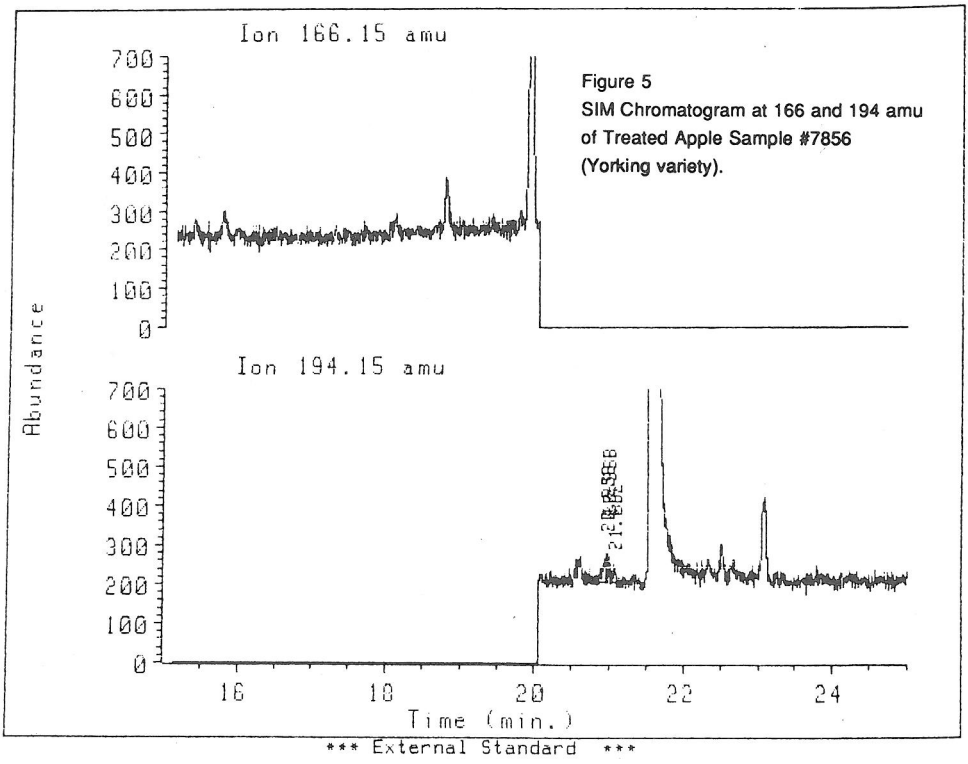

Figure 5
SIM Chromatogram at 166 and 194 amu of Treated Apple Sample #7856 (Yorking variety).

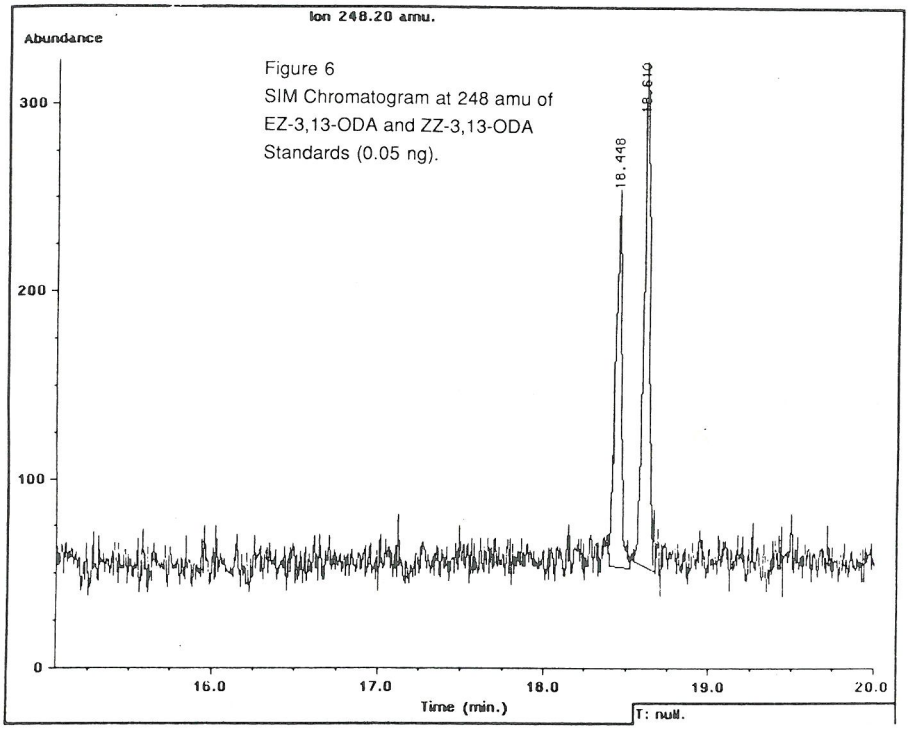

Figure 6
SIM Chromatogram at 248 amu of EZ-3,13-ODA and ZZ-3,13-ODA Standards (0.05 ng).

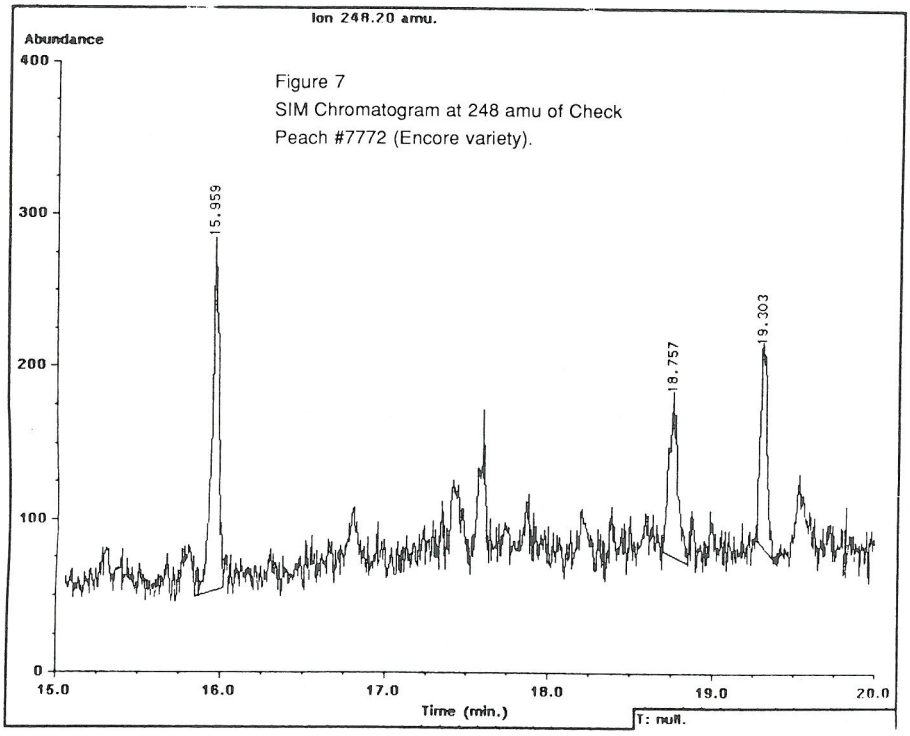

Figure 7
SIM Chromatogram at 248 amu of Check Peach #7772 (Encore variety).

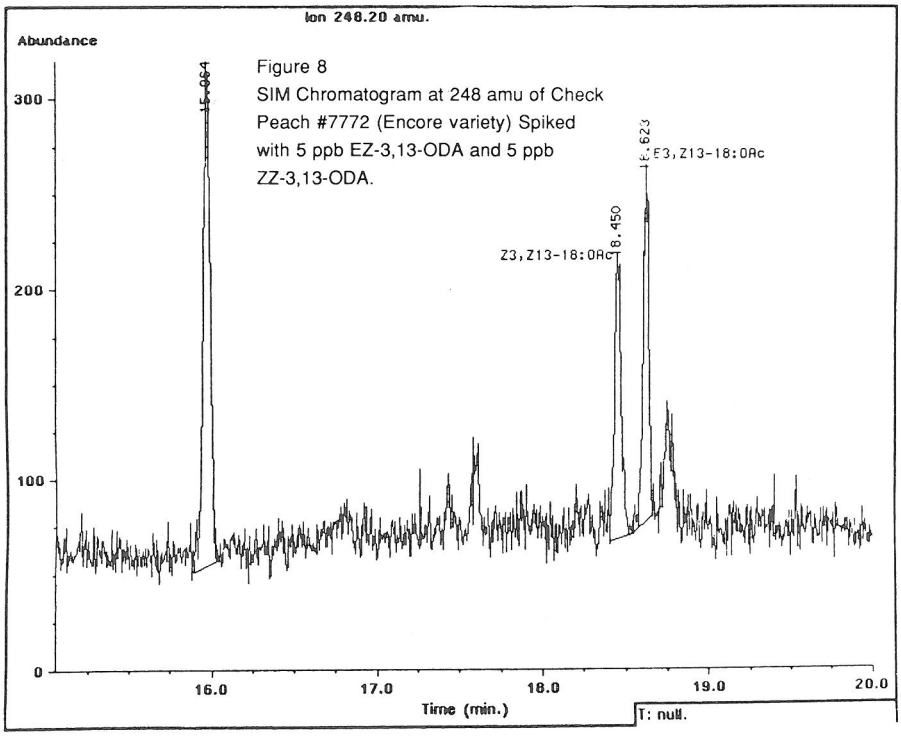

Figure 8
SIM Chromatogram at 248 amu of Check Peach #7772 (Encore variety) Spiked with 5 ppb EZ-3,13-ODA and 5 ppb ZZ-3,13-ODA.

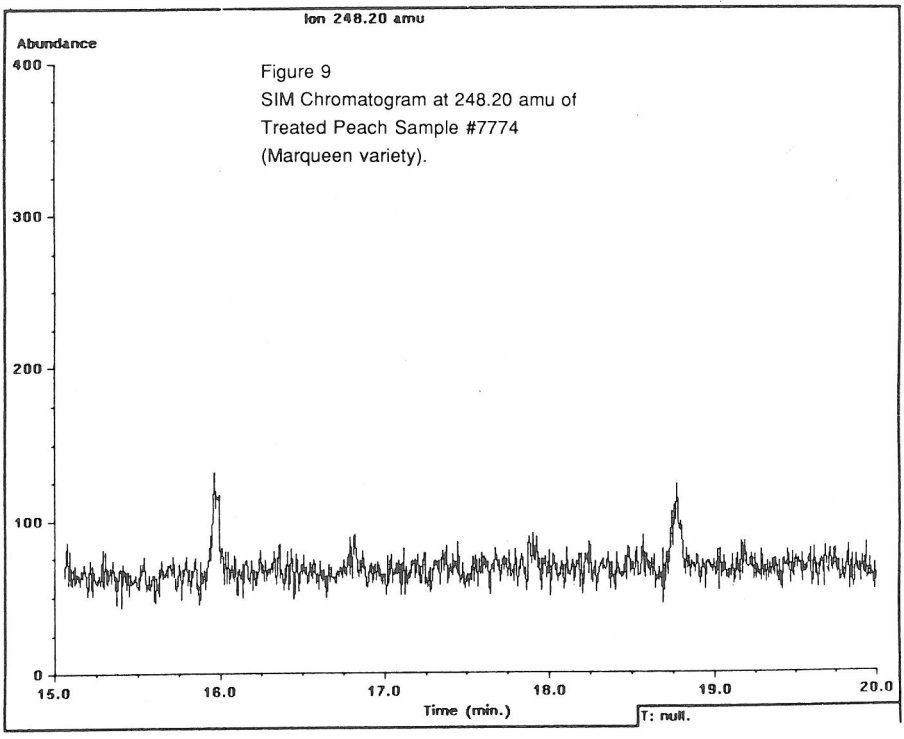

Figure 9
SIM Chromatogram at 248.20 amu of Treated Peach Sample #7774 (Marqueen variety).

DISCUSSION

Inspection of Tables 1-8 reveals that there have been no detectable residues of any applied pheromone acetate found on any treated sample. This is in agreement with results of our 1988 study. Further, in light of the use pattern of these pheromones (discrete point source dispensers), the results are not at all unexpected considering the highly unlikely probability of any measurable amount of volatilized pheromone selectively condensing on the edible portion of the biomass in an orchard or vineyard. Even a uniform residue distribution of applied pheromones over the entire canopy floor and foliage is a highly improbable event--it would be like attempting to store a few micrograms of a volatile chemical for six months in an open beaker.

The work is incomplete; because the less volatile alcohols are still to be determined, the argument exists that residues may still be found. However, with the exception of EE-8,10-DDOH, all alcohols in this study are 10% or less of the formulation--thus diminishing the likelihood of their being found as residues by a factor of ten.

With increased resources and effort we could confidently extend our sensitivity for these analytes down to the ppt (pg/g) range. This claim could be made for almost any chemical pesticide under scrutiny--frequently it is important that it be done. But, excessive outlays for pheromone residue schemes are probably not the best use for research funds, nor do pheromone residues in this range (if present at all) constitute a significant threat to human or animal health.

A review of lepidopteran pheromone toxicology shows that most pheromone components show no adverse effects up to the NOEL (No Observable Effect Level), a number generally dictated by the maximum amount that the test system (animal) can physically accommodate (Kirsch, 1988). It is less a matter of toxicological response, than an illustration of an exclusion principle. But, they are not inert substances, and they would be expected to undergo common biological oxidations to long chain carboxylic acids (i.e. fatty acids). Plus, there is nothing obvious in the structure of any of the pheromone components in this study that would disqualify them from metabolism by beta oxidation and complete mammalian digestion (Ernster et al., 1965; Griffiths, 1965; Nicholls et al., 1964). In fact, in light of todays health concerns, the worst that might be said against potential (or unmeasurable) lepidopteran pheromone residues is that they might be slightly fattening.

So are we wasting our time and money by conducting these studies? Not really. It is important to document the absence of residues under these conditions to backup anticipated requests for tolerance exemptions or waivers of residue data requirements. Plus, studies demonstrating no residues on food (or foliage, soil and adjacent water, for that matter), would go a long way towards justifying requests for relief from non-target organism studies. Finally, a point of caution, these studies are limited to analysis of fruit crops that have been treated with discrete point source formulations of pheromone. The analyses reported in this study demonstrate no detectable residues under this use pattern, however, these results do not suggest that residues would be absent on crops treated with pheromone formulations that were broadcast or sprayed directly onto the fruit. Research examining the potential of residues from broadcast formulations still needs to be undertaken.

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