

Short Communication

(7Z,11Z)-7,11-Hexadecadienal:
Sex Attractant of the Citrus
Leafminer Moth,
Phyllocnistis citrella STAINTON
(Lepidoptera, Phyllocnistidae)

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The chemical structure-activity relationship for the sex pheromones in Lepidoptera¹⁾ indicates that some dienic compounds are characteristically secreted from the taxonomically related species. Namely, 5,7-dodecadienes, 8,10-dodecadienes and 3,13-octadecadienes with alcohol, acetate or aldehyde functions are known to be some pheromonal components in the family Lasiocampidae, the subfamily Olethreutinae and the family Sesiidae, respectively. Field screening tests with each diene in different environments has revealed a new attraction of the other related species.^{2,3)} On the other hand, the sex pheromone of the pink bollworm moth is a mixture of (7Z,11Z)-7,11-hexadecadienyl acetate and (7Z,11E)-isomer,^{4,5)} and the latter has also been identified from the female of the Angoumois grain moth.⁶⁾ These two species belong to the family Gelechiidae. Field trials in Australia with the pheromonal components of the pink bollworm moth showed the attraction of two other species in Gelechiidae.⁷⁾ This information prompted us to test 7,11-hexadecadienic com-

pounds for the male moths in Gelechiidae distributed in Japan, and the random screening tests have been conducted. In addition to the attraction of some species in Gelechiidae to 7,11-hexadecadienic compounds, however, we interestingly observed that (7Z,11Z)-7,11-hexadecadienal powerfully attracted the male moths of the citrus leafminer, *Phyllocnistis citrella* STAINTON, in the family Phyllocnistidae. This insect is a harmful pest for the citrus as the larva mines into the epidermis of the young leaf, shoot and fruit. This larva mining in the tissue not only prevents growth of the leaf and shoot, but induces the plant disease, citrus canker by *Xanthomonas citri* (HASSE) DOWSON. The life cycle of the species is partly shrouded, and the attractant should be ideal for monitoring its occurrence. In this paper, we report the results of field screening tests.

Using silica gel column chromatography impregnated with silver nitrate, (7Z,11Z)-hexadecadienyl acetate and (7Z,11E)-isomer were separated from their mixture in a ratio of 1:1, the synthetic pheromone of the pink bollworm moth being supplied by Shin-etsu Chemical Co.⁸⁾ Hydrolysis of each acetate with potassium carbonate in methanol gave hexadecadien-1-ol, which was oxidized with pyridinium chlorochromate in methylene chloride to obtain hexadecadienal. Each compound was analyzed by GC on a capillary column, and by GC-MS, NMR and IR, the geometrically pure samples (>98%) being submitted to field tests conducted in the same manner as that described earlier^{9,10)} in a forest in Tokyo (Hachioji-shi).^{*1}

Table I shows the results of the field test with the traps baited with 1 mg of (7Z,11Z)-7,11-hexadecadienic compound(s) as a single-component or two-component lure. The male moths of the citrus leafminer were particularly attracted to (7Z,11Z)-7,11-hexadecadienal. (7Z,11Z)-7,11-Hexadecadien-1-ol and its acetate attracted no males, and did not show the synergistic effect on the attraction activity of

*1 Asakawa Experimental Forest, Forestry and Forest Products Research Institute.

the aldehyde when they were added to it. The flight of the male moths in the field was observed from early June to November, and mainly in September. Table II shows the effect of the (7*Z*,11*E*)-isomer on the activity of (7*Z*,11*Z*)-7,11-hexadecadienal. The (7*Z*,

11*E*)-isomer, which attracted no males of this species, did not possess synergistic activity.

In our systematic screening tests with monoene compounds in the same forest, the males of the citrus leafminer moth were not caught by any lures.^{9,10} Accordingly it is strongly indicated that the sex pheromone of this species may consist of the dienic compound, (7*Z*,11*Z*)-7,11-hexadecadienal. Furthermore, the results shown in Tables I and II

TABLE I. FIELD ATTRACTION OF MALE MOTHS OF THE CITRUS LEAFMINER, *Phyllocnistis citrella* STANTON, TO (7*Z*,11*Z*)-7,11-HEXADECADIENIC COMPOUNDS

Treatment ^a (mg)			Number of attracted males ^b	
A	B	C	Trap I	Trap II
0	1.0	0	0	0
0.1	0.9	0	29	23
0.5	0.5	0	41	164
0.9	0.1	0	135	187
1.0	0	0	162	208
0.9	0	0.1	149	196
0.5	0	0.5	53	70
0.1	0	0.9	28	44
0	0	1.0	0	0
0	0	0	0	0

^a In rubber septa. A, (7*Z*,11*Z*)-7,11-hexadecadienal; B, (7*Z*,11*Z*)-7,11-hexadecadienyl acetate; C, (7*Z*,11*Z*)-7,11-hexadecadien-1-ol.

^b Data were obtained between June 5 and November 6, 1983.

TABLE II. FIELD ATTRACTION OF MALE MOTHS OF THE CITRUS LEAFMINER, *Phyllocnistis citrella* STANTON, TO 7,11-HEXADECADIENAL

Treatment ^a (mg)		Number of attracted males ^b	
A	D	Trap I	Trap II
1.0	0	129	206
0.9	0.1	119	191
0.5	0.5	70	46
0.1	0.9	12	25
0	1.0	0	0
0	0	0	0

^a In rubber septa. A, (7*Z*,11*Z*)-7,11-hexadecadienal; D, (7*Z*,11*E*)-7,11-hexadecadienal.

^b Data were obtained between August 30 and October 4, 1984.

TABLE III. SEX ATTRACTANTS DISCOVERED BY FIELD TESTS OF 7,11-HEXADECADIENIC COMPOUNDS IN 1983

[Family]	Species	Attractant ^a	Number of attracted males (1984)	Flight period
[Phyllocnistidae]				
	<i>Phyllocnistis citrella</i> STANTON	Z7,Z11-16: Ald	370 (335)	June ~ Nov.
	<i>Phyllocnistis</i> sp.	Z7,E11-16: Ald	151	June ~ Sept.
[Argyresthiidae]				
	<i>Argyresthia beta</i> FRIESE & MORIUTI	Z7,E11-16: OH	29	May ~ June
[Gelechiidae]				
	<i>Dichomeris oceana</i> MEYRICK	Z7,E11-16: OAc	10	June ~ July
	<i>Sitotroga cerealella</i> OLIVER	Z7,E11-16: OAc + Z7,E11-16: Ald (9:1)	40	May ~ June
	Gen. et sp. 1	Z7,Z11-16: OAc	222	Oct. ~ Dec.
	Gen. et sp. 2	Z7,Z11-16: OAc + Z7,E11-16: OAc (5:5)	— (94)	Sept.

^a The chemical formulae are symbolized by the *Z*=*Z* isomer and *E*=*E* isomer, the number before the hyphen giving the position of unsaturation, and the number after the hyphen giving the carbon atoms in the chain. OH=alcohol; OAc=acetate; Ald=aldehyde.

suggest that the pheromone may not include its functional derivatives, acetate and alcohol, and (7*Z*,11*E*)-isomer as minor components. The attraction of Lepidoptera to 7,11-hexadecadienal has not been reported, so an investigation of the real sex pheromone is important. We are now collecting the females of the citrus leafminer moth from the citrus grove. A comparison of the attractive activity between the virgin female and the synthetic attractant, and the preparation of (7*E*,11*Z*)- and (7*E*,11*E*)-isomers are also under way.

Other species attracted to 7,11-hexadecadienic compounds are listed in Table III. Although some species in Gelechiidae*² were attracted by the traps baited with 7,11-hexadecadienic compounds according to expectation, (7*Z*,11*E*)-7,11-hexadecadienal and the alcohol attracted another species in the family Phyllocnistidae and *Argyresthia beta* in the family Argyresthiidae, respectively. The 7,11-hexadecadienes may also be one group of the sex pheromone in other families such as Phyllocnistidae, which is not closely related to Gelechiidae.

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*² Only (7*Z*,11*E*)-7,11-hexadecadienyl acetate was identified from the female extract of the Angoumois grain moth, *Sitotroga cerealella*, but in our field tests this species was more strongly attracted by the mixture of the acetate and the corresponding aldehyde than by the unmixed acetate.