Field Testing of *cis*-11-Tetradecenal as Attractant or Synergist in Tortricinae[1,2]

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Summary. Field studies have shown that *cis*-11-tetradecenal is an effective attractant for male *Choristoneura conflictana*, a pest of aspen. These studies also indicate that *cis*-11-tetradecenal is probably a secondary component in the sex pheromone systems of *Choristoneura rosaceana* and *Choristoneura fumiferana*.

The large aspen tortrix, *Choristoneura conflictana* occurs throughout the range of trembling aspen, *Populus tremuloides*, in eastern North America. Numerous outbreaks causing serious defoliation have occurred in Canada and have also been reported from the New England states, New York and Michigan. As a first step in the control of the pest, population levels could be monitored if a sex pheromone or a synthetic attractant were available.

It has been concluded[3] that attractants for tortricine species are generally 14-carbon compounds with a double bond in the 11 position. Consequently several 14-carbon monounsaturated compounds were tested as attractants for *C. conflictana*. Tests were carried out during June and July 1975, in mixed timber stands consisting of 30–50% trembling aspen, at 3 locations near Sault Ste. Marie, a) St. Joseph Island, b) Thessalon and c) Mile 56 north of Sault Ste. Marie. Initially both *cis*- and *trans*-isomers of Δ11-tetradecenal (TDAL), Δ11-tetradecen-1-ol (TDOL) and Δ11-tetradecen-1-ol acetate (TDAC) were dispensed in polyethylene vial caps, 100 µg/cap, at site a). During the period June 25 to July 3 traps (3 replicates) baited with *cis*-TDAL caught a total of 69 male *C. conflictana*. Traps containing the 5 other test compounds failed to catch any male aspen tortrix.

Aldehydes are involved in the sex pheromone systems of other lepidopteran pests. *Argyrotaenia citrana* has recently been shown to utilize *cis*-TDAL as a primary attractant[4]. In this species *cis*-TDAC is a secondary component. Previously it was reported that *trans*-TDAL is a sex pheromone of the eastern spruce budworm, *Choristoneura fumiferana*[5].

In an attempt to identify compounds having a synergistic (secondary components) or an inhibitory effect on *cis*-TDAL as an attractant for *Choristoneura conflictana* various mixtures of *cis*-TDAL/*cis*-TDOL, *cis*-TDAL/*cis*-TDAC and *cis*-TDAL/*trans*-TDAL were field tested.

It is evident from the results of these tests that *cis*-TDAC is inhibitory in all proportions (Table I). Similarly, if *cis*-TDOL is the major component of the aldehyde-alcohol blend the catch of *C. conflictana* males is distinctly reduced. The results from the St. Joseph Island site indicate that small amounts of *cis*-TDOL can apparently be tolerated in the blend but whether this compound is a secondary component cannot be defined from these results. Both sets of results of the *cis*/*trans*-TDAL mixtures exhibit a trend of antagonism with the presence of the *trans* isomer.

[1] *Christoneura conflictana* (Wlk.), *C. rosaceana* (Harris) and *C. fumiferana* (Clemens) (Lepidoptera: Tortricidae: Tortricinae).

[2] Contribution No. IPRI 296.

[3] W. L. ROELOFS and R. T. CARDÉ, *Pheromones* (Ed. M. C. BIRCH; North Holland, Amsterdam 1974), p. 96.

[4] A. S. HILL, R. T. CARDÉ, H. KIDO and W. L. ROELOFS, J. chem. Ecol. *1*, 215 (1975).

[5] J. WEATHERSTON, W. L. ROELOFS, A. COMEAU and C. J. SANDERS, Can. Entom. *103*, 1741 (1971).

Table I. Catches of male *Choristoneura conflictana* in traps baited with synthetic compounds[a]

Bait (100 µg)		St. Joseph Is. June 27–July 12	Thessalon July 2–July 12	Mile 56 July 4–July 17
cis-TDAL		7.7 (3)	22.6 (5)[b]	61.5 (2)
cis-TDAL/*cis*-TDOL	(100/1)	7.3 (3)	3.5 (2)	–
	(10/1)	7.0 (3)	7.0 (2)	–
	(1/1)	4.0 (3)	7.0 (2)	–
	(1/10)	0 (3)	0 (2)	–
	(1/100)	0 (3)	0.5 (2)	–
cis-TDOL		0 (3)	0 (2)	0 (2)
cis-TDAL/*cis*-TDAC	(100/1)	–	–	0 (2)
	(10/1)	–	–	0.5 (2)
	(1/1)	–	–	0 (2)
	(1/10)	–	–	0 (2)
	(1/100)	–	–	0 (2)
cis-TDAC		0 (3)	0 (2)	0 (2)
cis-TDAL/*trans*-TDAL	(100/1)	–	6.5 (2)	6.0 (2)
	(10/1)	–	4.5 (2)	1.0 (2)
	(1/1)	–	1.0 (2)	0 (2)
	(1/10)	–	3.5 (2)	0 (2)
	(1/100)	–	3.5 (2)	0 (2)
trans-TDAL		0 (3)	0 (2)	0 (2)

The figures indicate ♂♂/trap; figures in brackets = number of traps. [a]Isomer purity of the compounds tested was measured by GLC analysis on a 50 ft. SCOT column of PDEAS; *cis*-and-*trans* TDAL were greater than 99.5 in isomeric purity: *cis*-TDOL and *cis*-TDAC were greater than 99 isomerically pure. [b]The 113 ♂♂ were caught in 5 traps from June 28 to July 2.

Table II. Catches of male *Choristoneura rosaceana* with various *cis*-TDAC/*cis*-TDAL mixtures

Bait (100 µg)		Mile 56 July 4–July 17	
cis-TDAC		8	(2)
cis-TDAC/*cis*-TDAL	(100/1)	64	(2)
	(10/1)	35.5	(2)
	(1/1)	16	(2)
	(1/10)	4.5	(2)
	(1/100)	15	(2)
cis-TDAL		0	(2)

Figures indicate ♂♂/trap; figures in brackets = number of traps.

Table III. Catches of male *Choristoneura fumiferana* in traps baited with various isomer mixtures of TDAL

Bait (100 µg)		Mile 56 July 7–July 17		Thessalon July 2–July 12	
trans-TDAL		16.3	(3)	—	
trans-TDAL/*cis*-TDAL	(100/1)	107	(2)	50	(2)
	(10/1)	147.5	(2)	58	(2)
	(1/1)	22	(2)	7	(2)
	(1/10)	5.5	(2)	0.5	(2)
	(1/100)	1	(2)	1	(2)
cis-TDAL		0	(2)	—	

Figures indicate ♂♂/trap; figures in brackets = number of traps.

[6] W. L. ROELOFS and H. ARN, Nature, Lond. *219*, 513 (1968).
[7] W. L. ROELOFS and J. P. TETTE, Nature, Lond. *226*, 1172 (1970).
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At this time it is concluded that *cis*-11-tetradecenal is a potent attractant for male *Choristoneura conflictana*. Verification of this compound as the primary component of the sex pheromone of this insect, and elucidation of any secondary components, must await the results of laboratory studies now in progress.

From the field tests conducted at Thessalon and Mile 56 several interesting inferences may be made regarding the sex pheromone systems of 2 other *Choristoneura* species, the oblique banded leafroller *Choristoneura rosaceana* and the spruce budworm *Choristoneura fumiferana*. ROELOFS and ARN[6] identified *cis*-TDAC as the sex attractant of the red banded leafroller, *Argyrotaenia velutinana*. The same compound was later shown to be the sex attractant of the oblique banded leafroller[7]. These species have overlapping seasonal and diurnal cycles, and share the same host plants, and the authors were uncertain as to how specificity was effected. A reinvestigation of the sex pheromone system of the red banded leafroller has revealed that dodecyl acetate and a small amount of *trans*-TDAC are secondary components in the blend[8]. As shown in Table II the addition of approximately 1% of *cis*-TDAL to the primary *C. rosaceana* pheromone dramatically increases attractancy. It is postulated that a reinvestigation of extracts from female oblique banded leafrollers would reveal the presence of *cis*-TDAL as a secondary component, and a further means of effecting specificity (Table II).

The spruce budworm *Choristoneura fumiferana* was the first lepidopteran species shown to possess an aldehyde as a female produced sex attractant. The elucidation of the pheromone structure as *trans*-TDAL[5] was followed by a report that *trans*-TDOL and *trans*-TDAC exhibited significant inhibitory activity in the field when mixed with the budworm pheromone[9]. Results (Table III) from Mile 56 dispute the isomeric integrity of the budworm pheromone, and place the optimum amount of *cis* isomer between 1% and 9%. The trend, also borne out by the Thessalon data, indicates that greater than 9% of the *cis* compound reduces the effectiveness of the attractant.

Adenyl Cyclase Activity of Mouse Liver Membranes after Incubation with Endotoxin and Epinephrine

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Summary. Adenyl cyclase activity in isolated mouse liver cell membranes was stimulated two-fold by endotoxin. Furthermore, endotoxin inhibited epinephrine induction of adenyl cyclase activity, apparently through interruption of the phospholipid moiety of the enzyme complex.

Endotoxin, a lipopolysaccharide (LPS) extracted from gram-negative bacteria[1], has an affinity for the phospholipid portion of cell membranes[2–4]. In the liver, the interaction of endotoxin with cell membrane phospholipids could interfere with the synthesis of adenosine 3′,5′-monophosphate (cyclic-AMP), a compound essential in liver carbohydrate metabolism. Indeed, in vivo, endotoxin decreases total body carbohydrate by 80%[5,6] and a marked depletion of liver glycogen has been shown to be a contributing factor in the lethality of endotoxemia[7].

It was hypothesized that if endotoxin interacts with cell membranes, it may alter the activity of adenyl cyclase, an enzyme located within the plasma membrane. To determine if endotoxin altered the activity of liver cell adenyl cyclase, the amount of cyclic AMP formed was ascertained after the in vitro conversion of ^{14}C-adenosine labeled ATP to ^{14}C-labeled cyclic-AMP by adenyl cyclase. Additionally, the modifying action of LPS on epinephrine

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