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(Z)-3-Tetradecenyl Acetate as a Sex-Attractant Component in Gelechiinae and Anomologinae (Lepidoptera: Gelechiidae)

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Sex-Attractant, Attraction-Inhibitor, Δ 3-Alkenyl Acetates, *Chionodes*, *Monochroa*, *Argolamprotes*, *Aproaerema*, Gelechiidae

The title compound, unreported as an insect pheromone component, effectively attracted certain male Gelechiidae (genera *Chionodes, Monochroa, Argolamprotes*) as a single chemical. Trap captures with this chemical decreased on addition of either (E)-3-dodecenyl acetate, (E)-3-tetradecenyl acetate or (Z)-3-tetradecen-1-ol, the sexual attractants of other, closely related species. Results on an *Aproaerema* test species showing a synergistic attraction response to combinations of (Z)-3-tetradecenyl acetate with its homologue (Z)-3-dodecenyl acetate are included.

Long-chain alkenyl acetates are the most common structural type among identified sex pheromone and attractant components in the Lepidoptera [1]. The title compound, (Z)-3-tetradecenyl acetate Z3-14:Ac, recently joined this group of semiochemicals when Willemse et al. [2] reported its attractiveness towards male Chionodes electella (Zell.) and Monochroa tenebrella (Hb.), members of the Gelechiidae subfamilies Gelechiinae and Anomologinae. Their report prompts a brief presentation of my own results obtained on this same and some structurally related compounds. The results define more closely the sex-attractant systems for the two species, demonstrate the attractiveness of Z3-14:Ac for further spp. of the same subfamilies, and provide evidence for involvement of this compound in synergistic attractant systems.

The response of certain male Gelechiidae to sources of Z3-14:Ac was discovered by simply including this compound in field screening tests, as in the study by Willemse *et al.* Sticky traps baited with 100 µg of Z3-14:Ac, set out in woodlands near Seewiesen (southwest of Munich, southern Germany) during June/July, caught large numbers of *C. electella*, *M. tenebrella* and another Anomologinae species, *Argolamprotes micella* (Den. & Schiff.). The three

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species feed on *Picea*, *Rumex* and *Rubus*, respectively, and their relative trap captures greatly varied between test sites, depending on host abundance; which may explain why one species (*A. micella*) was missing from the test by Willemse *et al*.

The outstanding effectiveness of the Z3-14: Ac for males of these gelechiid species was supported by electroantennogram measurements. These were made from males newly taken in Z3-14:Ac baited traps (with antennae not yet glued to the adhesive), using technical procedures as in other Microlepidoptera [3, 4]. In the series of (Z)- and (E)-alkenyl acetates, varied for chain length and double bond position, the Z3-14:Ac, at the test amount of 1 µg, elicited the greatest EAG response. This was followed by the geometric isomer (E3-14:Ac), the corresponding alcohol analogue (Z3-14:OH) and some positional isomers and shorter-chain homologues Z4-14:Ac, E4-14:Ac, (Z2-14:Ac,Z3-13:Ac, Z3-12:Ac). Evaluation of equipotent stimulus amounts [3, 4] showed that these compounds were between 10- to 300-fold less stimulating than the Z3-14:Ac, in all three species. EAG effectiveness decreased by > 1,000-fold when the double bond was beyond position 5 or chain length was altered by more than 2 carbons. These data supported the view that Z3-14:Ac may be the primary female pheromone in all three species.

Further field tests were designed to assess modifying effects of second compounds. Thus, 100 µg of Z3-14:Ac and a varying amount of another compound [5] were applied to the same rubber cap dispenser. Trap types and operating procedures were as in field studies on other Microlepidoptera [4, 6]. For the three gelechiids, no attraction synergism over Z3-14:Ac alone was found but some compounds strongly reduced the response. Results of a pilot study using 100 µg additions of other compounds are presented in Table I. They show strong inhibitory effects for E3-14:Ac and Z3-14:OH in all three species and for E3-12:Ac in C. electella, whereas the five other additives (Z3-10:Ac, Z3-12:Ac, Z5-14:Ac, E5-14:Ac, Z5-16:Ac) did not markedly alter capture rates.

The inhibitory effects of the E3-14:Ac and Z3-14:OH were further studied in subsequent tests. Results obtained for C. electella and A. micella in two test series using 3, 10, 30 and 100 μ g additions of these compounds are presented (Table II). The data show that a 30% addition of E3-14:Ac and a 3% one



Table I. Captures of male *Chionodes electella, Monochroa tenebrella* and *Argolamprotes micella* in tetratraps baited with 100 µg Z3-14:Ac alone or in combination with eight different additives. Seewiesen/Starnberg, June 19 to July 27, 1982; three replicates.

Additive	\overline{X} males/trap of			
[100 µg]	C. electella	M. tenebrella	A. micella	
none	71.0	17.7	26.7	
Z3-10:Ac	61.3	22.7	22.0	
Z3-12:Ac	80.3	14.0	34.0	
E3-12:Ac	0	9.3	23.3	
E3-14:Ac	0	0	0	
Z5-14:Ac	49.7	23.0	22.0	
E5-14:Ac	53.3	11.7	19.7	
Z5-16:Ac	45.7	17.0	16.7	
Z3-14:OH	0	0	0	

Table II. Effect of varying amounts of E3-14:Ac or Z3-14:OH on captures of male Chionodes electella and Argolamprotes micella with 100 µg Z3-14:Ac. Seewiesen/Starnberg, July 3 to 29, 1983 (series A) and June 25 to July 24, 1984 (series B); tetratraps, four replicates per series.

Additive, μg		X males/trap of C. electella		A. micella	
		A	В	Α	В
none		92.75	55.0	17.5	28.5
E3-14:Ac,	3	53.0	18.0	9.25	9.0
	10	18.5	9.25	2.0	0
	30	0.25	0	0	0
	100	0	-	0.25	_
Z3-14:OH,	3	0	0	0	1.75
	10	0.5	0	0	0
	30	0	_	0	_
	100	0	_	0	_

of Z3-14:OH were sufficient to suppress captures, in both species. In these tests the main flight of *M. tene-brella* had already passed when traps were set. A separate test conducted on this species (Table III) revealed inhibitory effects of the two compounds comparable to the two other species.

The abolition of captures by adding to the Z3-14:Ac source only 3% of the alcohol analogue Z3-14:OH was an unexpected discovery, as the Z3-14:Ac samples used contained almost 1% of this parent alcohol [7]. This suggests that Z3-14:Ac sources free of alcohol might be even more attractive for these gelechiids. Related alcohols, such as Z3-12:OH or E3-14:OH, showed only weak inhibitory effects.

Table III. Effect of varying amounts of E3-14:Ac or Z3-14:OH on captures of male *Monochroa tenebrella* with 100 μg Z3-14:Ac. Seewiesen/Starnberg, June 10 to July 12, 1985; tetratraps, three replicates.

Additive, µg	\overline{X} males/trap
none	37.7
E3-14:Ac, 3	10.7
10	3.3
30	0.3
100	0
Z3-14:OH, 3	2.0
10, 30, 100	0

On extending these tests further to various other structural analogues, E3-13:Ac was established as another strong inhibitor for C. electella (but not the two other species). Both E3-12:Ac and E3-13:Ac are identified sex pheromone or attractant components for some other Gelechiinae and Anomologinae [8–11]. No further strong inhibitor was found for the three test species. Particularly noteworthy is the failure of various chain length homologues (from Z3-10:Ac to Z3-18:Ac) to modify captures by Z3-14:Ac. Two of these homologues, Z3-13:Ac and Z3-12:Ac, even caught small numbers of C. electella and M. tenebrella (but not A. micella) when offered as single chemicals. A similar pattern of attraction specificity as for C. electella was obtained for two other Chionodes spp. responsive to Z3-14:Ac, C. luctuella (Hb.) and C. nebulosella (Hein.), at other central European test sites.

When testing binary combinations between Z3-14: Ac and another (Z)-3-alkenyl acetate, numerous male Aproaerema anthyllidella (Hb.) (Gelechiinae) were caught by the 100/100 mixture of Z3-14:Ac / Z3-12:Ac. The species was absent from neighbouring traps containing the single chemicals alone, indicating a synergistic attraction response. In subsequent tests of different mixtures of the two compounds, maximum attraction occurred with Z3-14:Ac / Z3-12:Ac ratios ranging from 100/10 to 100/100; the 10/100 mixture produced only poor captures and the single chemicals alone again were nonattractive (Table IV). Male A. anthyllidella were also caught by 100/100 combinations of Z3-14:Ac with either Z3-13:Ac or E3-12:Ac (data not shown), though at far lower numbers than with the 100/100 Z3-14:Ac / Z3-12:Ac combination. Third components were tested on this species as 100 µg amounts

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Table IV. Captures of male *Aproaerema anthyllidella* in tetratraps baited with varying amounts of Z3-14:Ac and Z3-12:Ac. Seewiesen/Starnberg, July 15 to August 21, 1985; three replicates.

Amount [µg/ Z3-14:Ac	trap] of Z3-12:Ac	\overline{X} males/trap		
100	0	0		
100	3	6.7		
100	10	25.7		
100	30	18.3		
100	100	23.7		
30	100	9.0		
10	100	1.3		
3	100	0		
0	100	0		

added to this binary mixture. Only the alcohol Z3-14:OH reduced but did not fully suppress captures; various other third components tested (including Z3-10:Ac, E3-10:Ac, E3-12:Ac, Z5-12:Ac, Z3-13:Ac, E3-13:Ac, E3-14:Ac, Z5-14:Ac, Z3-16:Ac, Z5-16:Ac and Z3-12:OH) did not markedly modify capture rates. In this species, using a synergistic attractant system, attraction-inhibition thus appears to be less pronounced, compared to the other gelechiids treated above.

Potent inhibitors discovered in lepidopterous sexattractant systems have often turned out to be essential attractant components in other, taxonomically related species. The E3-13:Ac and E3-12:Ac, highly inhibitory to male *C. electella*, are indeed the reported pheromones or attractants of certain other gelechiids ([8-11]; see also above). To further test potential attractive or synergistic properties for these two compounds, and also for E3-14:Ac and Z3-14:OH, traps containing 100 μg amounts of these chemicals either alone or in different combinations with 100 µg Z3-14:Ac were set out at various central European test sites for some years. A number of further Gelechiinae and Anomologinae spp. (representing the genera Apodia, Athrips, Bryotropha, Caryocolum, Chionodes, Metzneria, Monochroa, Recurvaria, Scrobipalpa and Scrobipalpopsis), all unresponsive to pure Z3-14:Ac, were effectively captured by some of these baits. For example, male Chionodes holosericella (H. Sch.) responded specifically to E3-12:Ac and male C. perpetuella (H. Sch.) to E3-14:Ac, with Z3-14:Ac (the C. electella attractant) acting inhibitorily on these species. Such data indicated a role for the various inhibitors in reproductive species isolation. Results obtained on species from the two gelechiid subfamilies responsive to $\triangle 3$ -alkenyl attractants other than Z3-14:Ac will be presented elsewhere.

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