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(11*Z*,13*E*)-Hexadecadien-1-yl Acetate: Sex Pheromone of the Grass Webworm *Herpetogramma licarsisalis*—Identification, Synthesis, and Field Bioassays

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Abstract The grass webworm *Herpetogramma licarsisalis* (Lepidoptera: Crambidae), which has recently established in pasture in Northland, New Zealand, is an important pest of many tropical and subtropical grasses. Two pheromone components, (*Z*)-11-hexadecen-1-yl acetate (*Z*11–16:Ac) and (11*Z*,13*E*)-hexadecadien-1-yl acetate (*Z*11,*E*13–16:Ac), were identified in pheromone gland extracts of female moths by gas chromatography (GC), GC-electroantennographic detection, and GC-mass spectrometry in conjunction with micro-chemical tests (dimethyldisulfide and 4-methyl-1,2,4-triazoline-3,5-dione derivatizations). *Z*11,*E*13–16:Ac and its geometric isomer (11*E*,13*Z*)-hexadecadien-1-yl acetate (*E*11,*Z*13–16:Ac) were synthesized via stereoselective Wittig reactions, and the identity of the diene present in the pheromone glands was confirmed to be *Z*11,*E*13–16:Ac. Field bioassays at Indooroopilly in Brisbane, Australia, established that *Z*11,*E*13–16:Ac was necessary and sufficient for attraction of male grass webworm moths and that the corresponding alcohol, (11*Z*,13*E*)-hexadecadien-1-ol (*Z*11,*E*13–16:OH), had a strong inhibitory effect on trap catches at the ratios tested. When mixed with *Z*11,*E*13–16:Ac in various ratios, *Z*11–16:Ac had no effect on the attractiveness of lures.

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Introduction

The grass webworm *Herpetogramma licarsisalis* (Walker, 1859) (Lepidoptera: Crambidae) is an important pest of many tropical and subtropical grasses used for pasture and ornamental turf. *H. licarsisalis* is widely distributed globally as it is present in central Africa, Sierra Leone, Egypt, Saudi Arabia, India, Japan, Southeast Asia, Hawaii, and northern Australia (Tashiro, 1976; Common, 1990; Goater and Knill-Jones, 1999). Infestations have also been reported from Spain and Portugal, and the species has recently been recorded in Britain and Sweden (Goater and Knill-Jones, 1999; Svensson, 2003).

In 1999, *H. licarsisalis* larvae were confirmed in kikuyu (*Pennisetum clandestinum* Hochst. Ex Chiov. South) dairy pasture on the Aupouri Peninsula in Northland, New Zealand (Hardwick et al., 2000). During the outbreak, densities of up to 1,500 caterpillars per square meter were recorded that were associated with significant damage to kikuyu swards (S. Hardwick, personal communication). Despite the fact that the infestation was considered to be at the margins of the moth's climatic and geographical range (Hardwick et al., 2000; Willoughby and Barns, 2002; Jensen and Cameron, 2004), low-density grass webworm populations still persist on the Aupouri Peninsula.

Our objective was to identify the sex pheromone of *H. licarsisalis* to use as a monitoring tool of the existing populations for deployment in delimitation surveys and for collection of phenological data for pest management. A pheromone attractant would also be useful as a basis of an early warning system for any future outbreaks in the Northland area, including the detection of new incursions from the east coast of Australia (Fox, 1978).

To date, sex pheromone attractants for more than 40 crambid moth species have been identified (El-Sayed, 2006), but none is known from the genus *Herpetogramma*. We report in this study the identification of two compounds in pheromone gland extracts of *H. licarsisalis* and the evaluation of their biological activity in a series of field bioassays in Queensland, Australia.

Methods and Materials

Insects Approximately 50 *H. licarsisalis* pupae were obtained from AgResearch, Ruakura (see Jensen and Cameron, 2004 for a review). A colony was established at HortResearch, Lincoln, and maintained for five generations at 22°C and 60% relative humidity. Freshly emerged adults were placed in 400×600 mm polyethylene bags (one to two males and one to two females per bag). Each of the bags was supported by a stainless steel wire frame. Each bag contained six 'Pioneer' hybrid maize (*Zea mays* ssp. *mays*) seedlings on which female moths readily deposited egg batches. Maize leaves infested with egg batches were collected daily and placed into 680 ml plastic containers (Huhtamaki Henderson Ltd., Auckland, NZ).

After eclosion, groups of ca. 10 early-instar larvae were transferred to additional plastic containers to avoid cannibalism. The larvae were supplied with fresh maize leaves as required. Pupae were collected and held individually until adult emergence in 35 ml plastic containers (Lily® portion cups with lids; Huhtamaki Henderson Ltd.). The antennae of males were used for coupled gas chromatographic-electroantennographic detection (GC-EAD),

whereas females had their pheromone glands excised and extracted for analysis by GC-EAD, GC, and GC-mass spectrometry (MS).

Pheromone Gland Extraction and Analyses Pheromone glands were removed from actively calling 24- to 48-hr-old female *H. licarsisalis* during the third and fourth hours of the scotophase. Excised glands were extracted in 20–40 μl of *n*-hexane for 5 min. The resulting supernatant was stored at −20°C until analysis. For quantitative analysis, the pheromone glands of 10 48-hr-old females were extracted with a 40-μl aliquot of *n*-hexane containing 4 ng of tetracosane as an internal standard. Two pheromone gland extracts were also derivatized, with either 4-methyl-1,2,4-triazoline-3,5-dione (MTAD; Sigma-Aldrich, NSW, Australia) or dimethyldisulfide (DMDS; Merck, Darmstadt, Germany), to determine the double-bond positions of the two MS-detectable compounds that elicited EAD responses. For the MTAD derivatization of a 26-female gland extract, we followed the procedure of McElfresh and Millar (1999). For the DMDS derivatizations of a 96-female gland extract, and (11*Z*)-hexadecen-1-yl acetate (*Z*11–16:Ac) and (11*E*)-hexadecen-1-yl acetate (*E*11–16:Ac) standards, we followed the procedure described by Buser et al. (1983).

Gas Chromatography-Electroantennographic Detection We analyzed pheromone gland extracts (five batches of 10, 13, 27, 18, and 10 pheromone glands) by GC-EAD, with a Varian 3800 GC coupled to an EAD Recording Unit (Syntech, Hilversum, The Netherlands). For details of the preparation of moth antennae, and our setup of associated equipment for GC-EAD analyses, see the work of Gibb et al. (2006). Extracts were run on DB-5 (30 m × 0.25 mm i.d. × 0.5 μm film; Agilent Technologies, Palo Alto, CA, USA) and DB-Wax columns (30 m × 0.25 mm i.d. × 0.5 μm film; Agilent) with 1:1 split outlets. Helium was used as the carrier gas (1 ml min^{-1}), and injections were splitless for 0.6 min. Injector and detector temperatures were 220° and 300°C, respectively, and the GC temperature program was 80°C for 1 min, 10°C min^{-1} to 240°C, and held for 35 min. Kováts retention indexes (KIs) (Kováts, 1965; Marques et al., 2000) were calculated for the compounds that elicited antennal responses to compare relative retention times and, thus, to obtain rudimentary information about the identity of the EAD-active compounds.

Gas Chromatography-Mass Spectrometry We compared the retention times and mass spectra of the EAD-active compounds detected in a gland extract (1 μl, ca. 18-female equivalents) with those of known standards by using a Varian 3800 GC coupled to a Varian 2200 mass spectrometer (GC-MS). Helium was used as the carrier gas (1 ml min^{-1}), and injections were splitless for 0.6 min. Transfer line and ion trap temperatures were 250° and 200°C, respectively. The GC injector temperature was 220°C, and the temperature program was 100°C for 1 min, 10°C min^{-1} to 210°C, and held for 18 min using a VF-5ms column (30 m × 0.25 mm i.d. × 0.25 μm film; Varian Inc., Walnut Creek, CA, USA). The MTAD- and DMDS-derivatized pheromone gland extracts, and the DMDS-derivatized standards, were also analyzed by GC-MS (injector temperature 250°C; 8 min solvent delay for MS) on the VF-5ms column, using oven ramps of 15°C min^{-1} from 100° to 300°C, and held for 20 min (MTAD), or 15°C min^{-1} from 100° to 260°C, and held for 20 min (DMDS).

Chemicals *Z*11–16:Ac and E11–16:Ac (both >98% isomerically pure by GC analysis) were obtained from Pherobank (Wageningen, The Netherlands). (10*E*,12*Z*)-Hexadecadien-1-yl acetate (*E*10,*Z*12–16:Ac) and (10*E*,12*Z*)-hexadecadien-1-ol (*E*10,*Z*12–16:OH) were available from previous work (Suckling et al., 2005). (11*Z*,13*E*)-Hexadecadien-1-ol (*Z*11,*E*13–16:OH) and the corresponding acetate (11*Z*,13*E*)-hexadecadien-1-yl acetate (*Z*11,*E*13–16:

Ac) were synthesized as shown in Scheme 1 and as described in detail in the online supplement. The synthesis of (11*E*,13*Z*)-hexadecadien-1-yl acetate (*E*11,*Z*13–16:Ac) is also described in the online supplement.

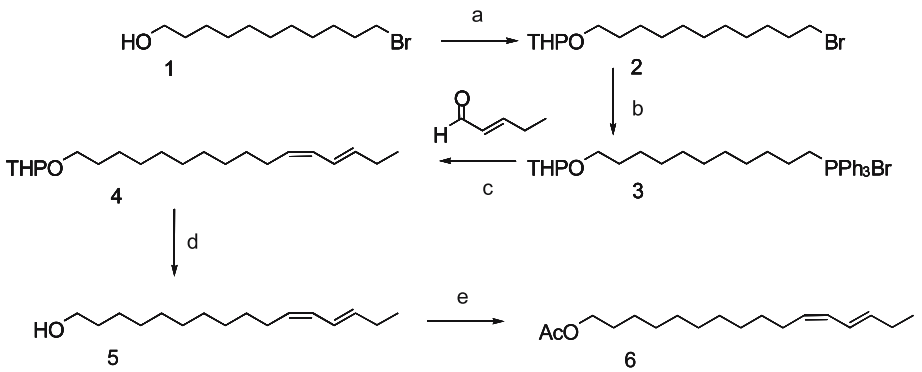
Field Bioassays We undertook a series of field bioassays in kikuyu turf at the Indooroopilly Golf Course (27.5090° S, 152.9948° E), Brisbane, Australia (trials A, B, and C). Test compounds, based on ratios established from GC analyses of *H. licarsisalis* gland extracts, were loaded onto red rubber septa (Thomas Scientific Inc., Philadelphia, PA, USA). In all trials, green delta traps (Clare et al., 2000) were attached to fencing wires, at a height of ca. 0.5 m, with 10 m spacings between treatments and >50 m spacings between replicates. Trap positions within each replicate were rerandomized, and sticky inserts were replaced, at each check for capturing male *H. licarsisalis*.

In trial A (April 8–28, 2005), the attraction of *H. licarsisalis* males to various combinations of the three sex pheromone candidate compounds was investigated. Traps were checked seven times at intervals of 1–4 d. Treatments were (1) blank control, (2) 100:0:0, (3) 0:100:0, (4) 0:0:100, (5) 30:70:0, (6) 30:70:1, and (7) 30:70:10 μg loadings of *Z*11–16:Ac, *Z*11,*E*13–16:Ac, and *Z*11,*E*13–16:OH ($N = 5$).

In trial B (January 24 to February 15, 2006), the attraction of *H. licarsisalis* males to 100 μg of *Z*11,*E*13–16:Ac was compared with the attraction of *H. licarsisalis* males to binary mixes comprising 100 μg of *Z*11,*E*13–16:Ac and various doses of *Z*11–16:Ac. Traps were checked six times at intervals of 1–5 d. Treatments were (1) blank control, (2) 100:0, (3) 100:11, (4) 100:25, (5) 100:42, and (6) 100:66 μg loadings of *Z*11,*E*13–16:Ac and *Z*11–16:Ac ($N = 4$).

Trial C was a dose response trial based on treatment 3 from trial A. Traps were checked four times at intervals of 3 d from February 21 to March 5, 2006. Treatments were (1) blank control, (2) 10, (3) 100, and (4) 1000 μg doses of *Z*11,*E*13-16:Ac ($N = 5$).

Statistical Analyses Only treatments that attracted moths were included in the statistical analyses. For each trial, the sum of moths captured per trap was analyzed for treatment and block effects using two-way analysis of variance (ANOVA) (MINITAB, version 14). Residual plots were used to check the validity of the ANOVA assumptions, and square root



Scheme 1 Syntheses of (11*Z*,13*E*)-hexadecadien-1-ol (**5**) and (11*Z*,13*E*)-hexadecadien-1-yl acetate (**6**). Reaction conditions: (**a**) Amberlyst 15, *t*-butylated hydroxyanisole (BHA), 3,4-dihydropyran, diethyl ether, 0°C to room temperature (RT); (**b**) PPh_3, MeCN, reflux; (**c**) sodium ethoxide, THF, reflux then −100°C, addition of (*E*)-2-pentenal, then to RT; (**d**) Amberlyst 15, BHA, MeOH; 45°C; (**e**) Ac_2O/pyridine, RT

($x + 0.5$) transformations of the summed captures were undertaken to remove variance heterogeneity. Means were compared by Fisher's protected least-significant difference test ($P = 0.05$) (MINITAB, version 14).

Results and Discussion

Identification of Gland Components Eliciting Antennal Responses In GC-EAD assays, male *H. licarsisalis* antennae responded repeatedly to three compounds in pheromone gland extracts. Only two of these compounds (X and Y, Fig. 1) were visible in the flame ionization detector (FID) trace (KIs of 2001 and 2037, respectively, on the DB-5 column, and 2365 and 2508, respectively, on the DB-Wax column). Antennal response times were the only indication of the presence of compound Z in the extracts. On the DB-5 column, no peak for compound Z was visible in the FID trace, whereas on the DB-Wax column, the antennal response time suggested that the compound was co-eluting on the tail of another unidentified compound (Fig. 1).

The retention times of compound X on DB-5 and DB-Wax columns suggested the presence of a monounsaturated hexadecen-1-yl acetate (Marques et al., 2000), and KIs were identical with those of the *Z*11–16:Ac standard. In addition, the mass spectrum of compound X [*m*/*z* (relative intensity—rel. int.) 222 (4), 166 (2), 137 (5), 123 (13), 109 (23), 95 (56), 81 (100), 67 (98), 61 (7), and 55 (49)] was virtually identical with that of *Z*11–16:Ac, and the retention time of X was the same as the retention time of *Z*11–16:Ac on the VF-5ms column. A comparison of the retention times of the DMDS adducts of *Z*11–16:Ac and *E*11–16:Ac, with the DMDS derivatization products of a grass webworm pheromone gland extract, unequivocally confirmed that compound X was *Z*11–16:Ac rather than *E*11–16:Ac. Both hexadecen-1-yl acetate DMDS adducts have a molecular ion at *m*/*z* (rel. int.) 376 (7) and diagnostic ions at *m*/*z* (rel. int.) 117 (20, $[C_5H_{10}SCH_3]^+$) and 259 (100, $[O_2C_{13}H_{24}SCH_3]^+$) corresponding to the addition of DMDS to a double bond at position 11.

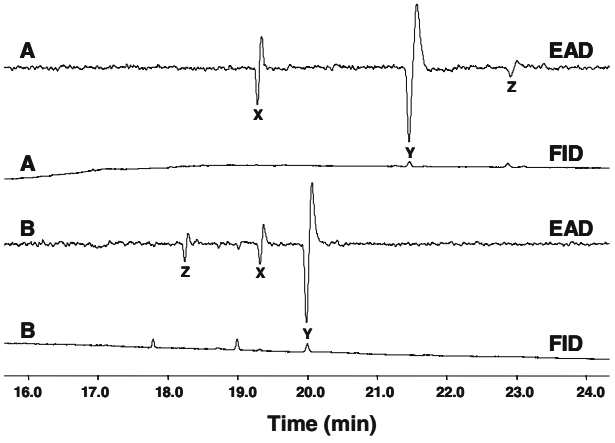


Fig. 1 Coupled gas chromatogram-electroantennograms of *Herpetogramma licarsisalis* male antennae responding to compounds (X = (*Z*)-11-hexadecen-1-yl acetate, Y = (11*Z*,13*E*)-hexadecadien-1-yl acetate, and Z = tentatively identified as (11*Z*,13*E*)-hexadecadien-1-ol), in pheromone gland extracts (ca. 1-female equivalents), eluting from DB-Wax (**A**) and DB-5 (**B**) columns

The retention times of compound Y on the DB-5 and DB-Wax columns suggested a C_{16}-conjugated dien-1-yl acetate after a comparison with a number of C_{16}-conjugated and C_{16}-nonconjugated dien-1-yl acetate standards. Similarly, the antennal response time for compound Z on the DB-5 and DB-Wax columns suggested a C_{16}-conjugated dien-1-ol by comparison with a number of C_{16}-conjugated and C_{16}-nonconjugated dien-1-ol standards. Furthermore, the retention times of *E*10,*Z*12–16:Ac and *E*10,*Z*12–16:OH were the same as those of compounds Y and Z, respectively. Both of these standards elicited strong EAD signals from male grass webworm antennae, and when *E*10,*Z*12–16:Ac was added to an aliquot of pheromone extract, it co-eluted with compound Y on both columns. However, a trapping trial in Northland in early 2003, using these two conjugated dienes in various combinations with *Z*11–16:Ac, failed to trap any moths at a time when moths were observed flying (Willoughby, unpublished data).

We hypothesized that although compounds Y and Z were C_{16}-conjugated dienes, the diene was probably at either the 9,11 or 11,13 position. The analysis of the MTAD-derivatized pheromone gland extract by GC-MS revealed an adduct with a molecular ion at *m*/*z* (rel. int.) 393 (1), and diagnostic ions at *m*/*z* (rel. int.) 364 (21, $[C_{19}H_{30}N_3O_4]^+$) and 194 (100, $[C_9H_{12}N_3O_2]^+$), indicative of a C_{16} dien-1-yl acetate with the diene in the 11,13 position. Thus, compound Y was identified as an 11,13-hexadecadien-1-yl acetate. We could not confirm the identity of compound Z due to the small amount of material in gland extracts (not detectable by GC-FID or GC-MS), but we hypothesized that compound Z was likely to be the C_{16} dien-1-ol precursor of the insect-produced C_{16} dien-1-yl acetate (see Jurenka, 2004 for a review).

Stereoselective syntheses of the (*Z*,*E*) and (*E*,*Z*) isomers of 11,13-hexadecadien-1-yl acetate were carried out. These syntheses also made the (*Z*,*Z*) and (*E*,*E*) isomers as trace by-products, giving us access to all four stereoisomers. A comparison of the spectrum [*m*/*z* (rel. int.) 280 (1, M^+), 220 (4), 177 (3), 163 (4), 149 (8), 135 (15), 121 (27), 107 (14), 95 (43), 81 (54), 67 (100), 55 (21), and 43 (44)] and retention times of compound Y in pheromone gland extract, with the four spectra of the 11,13-stereoisomers, unambiguously confirmed compound Y as *Z*11,*E*13–16:Ac. Analysis of an *H. licarsisalis* gland extract by GC on the DB-Wax column showed that *Z*11,*E*13–16:Ac and *Z*11–16:Ac were present in a ca. 70:30 ratio. The amount of *Z*11,*E*13–16:Ac and *Z*11–16:Ac per female was calculated to be ~280 and 100 pg, respectively ($N = 10$).

Synthesis of Pheromone Compounds The synthesis of (11*Z*,13*E*)-hexadecadien-1-ol **5** (Scheme 1) and the corresponding acetate **6** (Scheme 1) started with 11-bromoundecanol **1**, which was protected using dihydropyran with Amberlyst 15 as catalyst (Santangelo et al., 2002). The THP-protected bromide **2** was transformed to the phosphonium salt **3** with PPh_3 (Legrand et al., 2004). A Wittig reaction between **3** and (*E*)-2-pentenal in the presence of sodium ethoxide made, after deprotection, the (*Z*,*E*)-dien-1-ol **5** as the major product. Acetylation of **5** using acetic anhydride in pyridine produced acetate **6** (Santangelo et al., 2002).

Field Bioassays In the field bioassays, we established *Z*11,*E*13–16:Ac as the main sex pheromone component of *H. licarsisalis*. In trial A, the treatments with *Z*11,*E*13–16:Ac as a single component or in combination with *Z*11–16:Ac (treatments 3 and 5, respectively) were equally attractive to male moths ($P < 0.05$) (Fig. 2a). Single-component lures loaded with *Z*11,*E*13–16:OH were not attractive, and the addition of *Z*11,*E*13-16:OH to the binary mix of *Z*11,*E*13-16:Ac and *Z*11–16:Ac was strongly inhibitory at the ratios tested ($P < 0.05$).

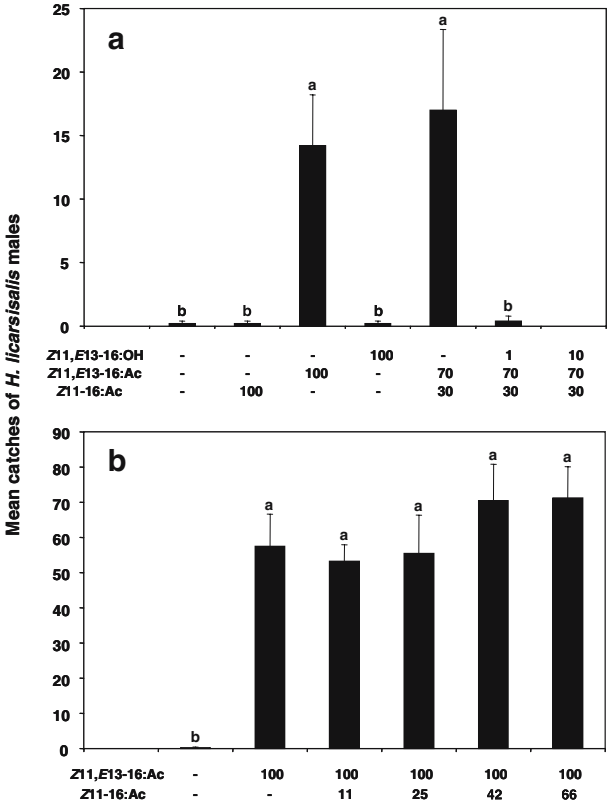


Fig. 2 Mean (+SEM) total catches of *Herpetogramma licarsisalis* male moths at Indooroopilly Golf Course (Brisbane, Australia) in a blend trial (trial A) of the three compounds that elicited responses from moth antennae (two-way ANOVA for treatment effect, $F = 23.18$; $df = 5, 29$; $P < 0.001$, and for block effect $F = 2.9$; $df = 4, 29$; $P = 0.048$, followed by Fisher's protected least significant differences (PLSD test), and in a two-component blend trial (trial B), using (11*Z*,13*E*)-hexadecadien-1-yl acetate and (*Z*)-11-hexadecen-1-yl acetate (two-way ANOVA for treatment effect, $F = 53.29$; $df = 5, 23$; $P < 0.001$, and for block effect $F = 5.4$; $df = 3, 23$; $P = 0.01$, followed by Fisher's PLSD test). Amounts on the *x*-axis are micrograms per lure, and treatments labeled with the *same letter* are not significantly different ($P > 0.05$)

Although we identified *Z*11–16:Ac from gland extracts, male grass webworm moths were not attracted to lures loaded with this compound only. Furthermore, *Z*11–16:Ac, when added to *Z*11,*E*13–16:Ac over a range of ratios, did not increase attraction to lures ($P > 0.05$) (Fig. 2b).

In trial C (Fig. 3), we tested the optimal dose of *Z*11,*E*13–16:Ac required for attracting male grass webworm moths. Lures loaded with 10 μg of *Z*11,*E*13–16:Ac attracted few moths ($P < 0.05$), and a 1,000-μg dose was not better than the 100-μg dose ($P > 0.05$).

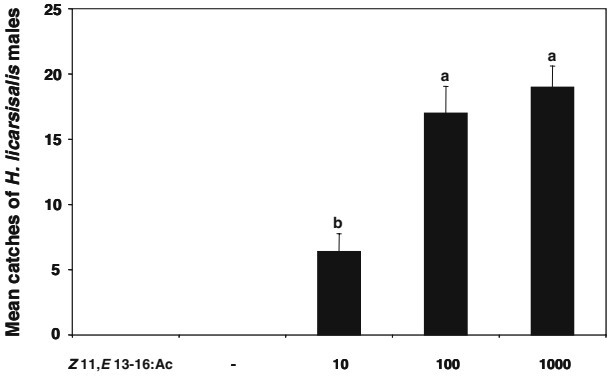


Fig. 3 Mean (+SEM) total catches of *Herpetogramma licarsisalis* male moths to various doses of (11*Z*,13*E*)-hexadecadien-1-yl acetate (trial C) at Indooroopilly Golf Course (Brisbane, Australia) (two-way ANOVA for treatment effect, $F = 25.98$; $df = 2, 14$; $P < 0.001$, and for block effect $F = 2.28$; $df = 4, 14$; $P = 0.149$, followed by Fisher's PLSD test). Amounts on the *x*-axis are micrograms per lure, and treatments labeled with the *same letter* are not significantly different ($P > 0.05$)

*Z*11,*E*13–16:Ac has already been used for monitoring male grass webworm moths in the infested area in Northland. Lures containing 100 μg of *Z*11,*E*13–16:Ac have also successfully attracted male grass webworm moths in Hawaii (Suckling, unpublished data), where the insect is the major pest of turf grass (Tashiro, 1977). Although the 11,13 position for a C_{16}-conjugated diene has previously been reported for pheromone components of moths in the family of Crambidae (Arai et al., 1982; Millar et al., 2002), this is the first identification of an (11,13)-hexadecadien-1-yl acetate as a sex pheromone component of a crambid moth. *Z*11,*E*13–16:Ac also has been found as a minor component in the pheromone glands of two Notodontidae (Bestmann et al., 1991, 1993).

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