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4-Pyridyl Carbonyl and Related Compounds as Thrips Lures: Effectiveness for Onion Thrips and New Zealand Flower Thrips in Field Experiments

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On the basis of structural and/or aroma analogies to known thrips (Thysanoptera: Thripidae) lures, 35 compounds (18 pyridine derivatives, 13 benzene derivatives, and 4 other compounds), consisting of both synthetic and naturally occurring compounds, were screened for their ability to bring about increased thrips capture in field experiments using water traps in Canterbury, New Zealand. Most of the thrips caught were New Zealand flower thrips (NZFT) (*Thrips obscuratus*) or onion thrips (OT) (*Thrips tabaci*). The greatest increase in capture for NZFT (158 times for ♀ cf. to water control) was for the known lure ethyl nicotinate, a 3-pyridyl ester. Ethyl isonicotinate, the 4-pyridyl regioisomer of ethyl nicotinate, not previously reported as a thrips lure, provided the greatest increases in capture for OT (31 times) of any of the compounds tested, significantly more than ethyl nicotinate. Other 4-pyridyl carbonyl compounds, including ethyl 4-pyridyl ketone, also increased OT capture significantly. The natural floral compound *cis*-jasmone, which increased trap capture of NZFT (♀ 42 times, ♂ 25 times) but not OT, is reported as a thrips lure for the first time.

KEYWORDS: ***Thrips obscuratus*; *Thrips tabaci*; lure; attractant; pyridine carbonyl; benzene carbonyl; flower aroma compounds; semiochemical**

INTRODUCTION

Thrips (Thysanoptera), especially flower-inhabiting species, are important pests of a number of agricultural and horticultural crops (*1*, *2*). Some thrips species are very difficult to control because of various biological attributes (e.g., polyphagy, vagility, rapid reproduction, cryptic behavior) and because they have become resistant to a range of insecticides (*3*, *4*). Consequently, there is a strong interest in developing alternative methods to insecticides for thrips pest management including the use of semiochemicals (chemicals involved in communication between organisms) (*5*, *6*) such as plant-derived allelochemicals (*7*−*14*) and alarm and sex pheromones (*15*−*19*) or their synthetic mimics. Such chemical lures could be used in a number of applications for thrips pest management including improved monitoring, mass trapping, push−pull, lure and kill, and lure and infect strategies (*16*, *19*, *20*). Nevertheless, the behavioral responses of thrips to these behavior-modifying chemicals are not well understood: thrips walk upwind in Y-tube olfactometers (attraction), but their flight is inhibited in wind tunnels (chemokinesis) (*12*, *20*−*22*) by certain chemicals. In this paper, we use the term "attractant" to refer to those compounds that bring about increased trap catch in comparison with control traps, even though the actual mechanism that brought about that increase may be different (e.g., an arrestant).

Various non-pheromone chemical attractants have been identified for several thrips species through the screening of odor chemicals derived from plants (especially flowers) and compounds reported to elicit responses in other insects (*10*, *12*, *13*, *23*−*27*). Additionally, Imai et al. (*14*) examined the response of thrips to compounds related to already known thrips attractants. Two compounds have given increases in thrips capture of >100 times in field experiments [methyl anthranilate for *Thrips hawaiiensis* (*14*) and ethyl nicotinate for *T. obscuratus* (*28*)], but the responses were generally much lower for other thrips species to these and a range of other compounds. In our search for new and potent thrips attractants for key thrips pests, we selected compounds related to known attractants by their chemical structures and/or by their aromas (as perceived by humans).

Most of the known non-pheromone thrips attractants contain a benzene ring conjugated to a carbonyl group (e.g., benzaldehyde, *p*-anisaldehyde, salicylaldehyde, **Figure 1**) (*29*, *30*). More recently further benzene carbonyl compounds have been reported as thrips attractants [e.g., 2-aminoacetophenone, methyl salicylate, and methyl anthranilate (*13*, *14*, *27*), **Figure 1**]. One

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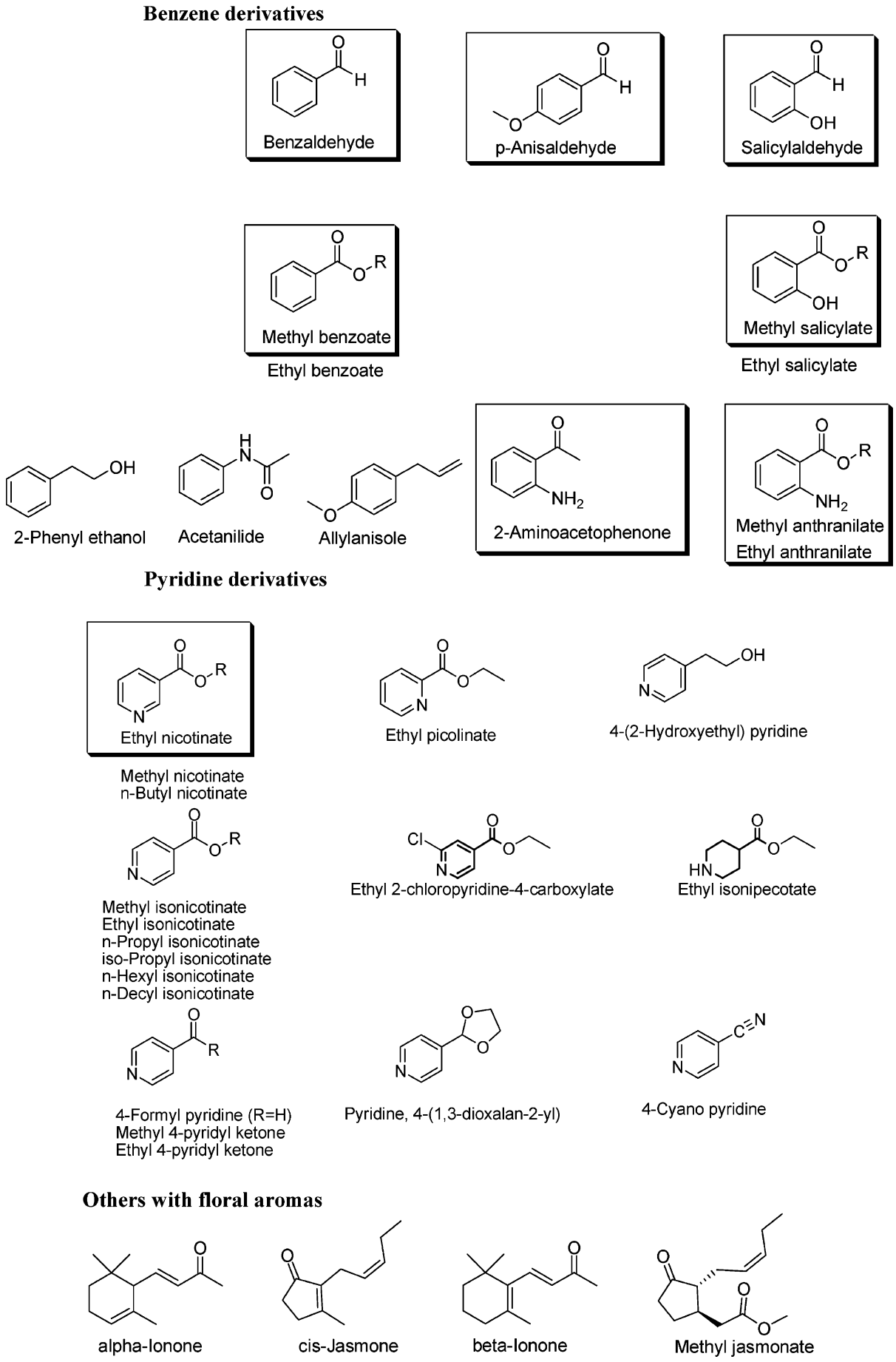

Figure 1. Compounds tested as thrips attractants in field trials (boxes indicate previously known attractants).

3-pyridyl carbonyl compound, ethyl nicotinate (**Figure 1**), has been reported as a thrips attractant (*9*, *28*). Most of the structural analogues we selected for testing were pyridine derivatives, based on ethyl nicotinate, including regioisomers such as ethyl isonicotinate, homologues such as methyl nicotinate, and analogues such as ethyl 4-pyridyl ketone (**Figure 1**). Ethyl benzoate was selected as a benzene analogue of ethyl nicotinate (and of ethyl isonicotinate, see below).

Several of the known thrips attractants have similar aromas as perceived by humans. Benzaldehyde, salicylaldehyde (diluted), and nitrobenzene all have bitter almond aromas (*31*, *32*). *p*-Anisaldehyde, benzyl alcohol (*30*), and geraniol (*33*) have sweet floral aromas (*31*, *32*). Ethyl nicotinate and 2-aminoacetophenone both have grainy corn-like aromas at low concentrations and grape-like aromas at high concentrations (*34*), and methyl anthranilate has both grape-like and floral aromas (*31*, *32*). Compounds selected for testing because of their floral aromas were 2-phenylethanol (also a benzene derivative), α- and β-ionone, *cis*-jasmone, and methyl jasmonate (**Figure 1**).

We used water traps to test the relative responses of thrips to selected compounds, as they are likely to include a combined flying and walking response of thrips, compared to Y-tube experiments, which measure only a walking response. Additionally, specimens caught in water traps are much easier to identify compared to specimens caught on sticky traps. The work targeted the New Zealand flower thrips (NZFT) (*Thrips obscuratus* Crawford), a polyphagous pest in New Zealand (*35*), and the onion thrips (OT) (*Thrips tabaci* Lindeman), a polyphagous and cosmopolitan pest (*1*). Both species are common in the Canterbury region (*35*, *36*) where these experiments were carried out. This work was carried out in association with testing of thrips responses to the same compounds in a Y-tube olfactometer (*37*).

MATERIALS AND METHODS

Sources of Compounds. Most of the 35 compounds tested were from commercial sources, and the others were synthesized (**Table 1**).

Isopropyl Isonicotinate and Related Esters. A solution of isonicotinic acid (Aldrich, 5 g) in CH_2Cl_2 (30 mL) was stirred with oxalyl chloride (10.4 mL) and pyridine (3.4 mL) under N_2 for 24 h. Isopropanol (20 mL) was added to the stirred solution, which was kept at room temperature for 2 h and then quenched by addition to aqueous $NaHCO_3$ (100 mL). Extraction into CH_2Cl_2 (2 × 100 mL), drying with $MgSO_4$, and then evaporation in vacuo gave isopropyl isonicotinate [CAS Registry No. 125294-42-0] as a creamy white solid (5.60 g, 83%): ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.75 (2H, d, J = 6 Hz), 7.82 (2H, d, J = 6 Hz), 5.26 (1H, septuplet, J = 6 Hz), 1.37 (6H, d, J = 6 Hz); UV (MeOH), λ_{max} (log ϵ) 212 (3.95), 274 (3.43) nm; >90% absolute purity by ^{1}H NMR spectroscopy. *n*-Propyl isonicotinate [λ_{max} (log ϵ) 274 (3.33) nm], hexyl isonicotinate [λ_{max} (log ϵ) 273 (3.54) nm], decyl isonicotinate [λ_{max} (log ϵ) 273 (3.36) nm], and methyl nicotinate [λ_{max} (log ϵ) 263 (3.48) nm] were synthesized by similar methods.

Ethyl-2-chloro-isonicotinate. The *N*-oxide of ethyl isonicotinate was prepared according to a literature method (*49*) and then selectively chlorinated at the 2-position. To a mixture of AcOH and H_2O_2 (30%, 14 mL) was added ethyl isonicotinate (10 g). The solution was heated to 75 °C for 24 h and then reduced in vacuo to a third of the volume, made basic with aqueous K_2CO_3, and extracted into CH_2Cl_2. This solution was dried and evaporated in vacuo to give the *N*-oxide as a white crystalline solid (10.5 g). The *N*-oxide (10.5 g) in $CHCl_3$ (25 mL) was refluxed for 12 h with phosphorus oxychloride (25 mL), cooled, and then poured onto ice. The product was extracted into CH_2Cl_2, dried, and evaporated to give ethyl-2-chloro-isonicotinate [CAS Registry No. 54453-93-9] as a pale yellow liquid with appropriate ^{1}H NMR signals (*50*): ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.53 (1H, d, J = 7 Hz), 7.87 (1H, d, J = 2 Hz), 7.76 (1H, dd, J = 2, 7 Hz), 4.42 (2H, q, J = 8 Hz), and 1.40 (3H, t, J = 8 Hz); >90% pure.

Table 1. Compounds Tested as Thrips Attractants (Structures in **Figure 1**): Sources and Field Trial Dates

compound	source	trial[a]
benzene derivatives		
benzaldehyde	unknown[b]	8, 10
p-anisaldehyde	Sigma-Aldrich	2, 8, 12
salicylaldehyde	unknown[b]	1
methyl benzoate	Hopkins & Williams	2
ethyl benzoate	Merck	1
methyl salicylate	Ajax Chemicals	2
ethyl salicylate	Merck	1
methyl anthranilate	Sigma-Aldrich	5
ethyl anthranilate	Merck	4
2-aminoacetophenone	Sigma-Aldrich	5
allylanisole	Sigma-Aldrich	3
acetanilide + $CHCl_3$[c]	BDH	7
2-phenylethanol	BDH	5, 10, 11
pyridine derivatives		
ethyl nicotinate (+ $CHCl_3$)[d]	Sigma-Aldrich	1–8, 12
methyl nicotinate + $CHCl_3$	synthesized	6
n-butyl nicotinate + $CHCl_3$	Sigma-Aldrich	6
ethyl isonicotinate	Sigma-Aldrich	7–9, 11, 12
methyl isonicotinate	Sigma-Aldrich	9
n-propyl isonicotinate	synthesized	9
isopropyl isonicotinate	synthesized	9
n-hexyl isonicotinate	synthesized	12
n-decyl isonicotinate	synthesized	12
ethyl picolinate	Merck	7
ethyl isonipecotate	Sigma-Aldrich	12
ethyl-2-chloropyridine-4-carboxylate	Synthesized	12
4-formylpyridine	Sigma-Aldrich	12
ethyl 4-pyridyl ketone	Lancaster	10, 11
methyl 4-pyridyl ketone	Sigma-Aldrich	12
pyridine, 4-(1,3-dioxalan-2-yl)	synthesized	12
4-cyanopyridine	Sigma-Aldrich	12
4-(2-hydroxyethyl)pyridine	Lancaster	10, 11
other floral aromas		
α-ionone	Fluka[e]	3
β-ionone	Riedel de Haen	3
methyl jasmonate	Sigma-Aldrich	4
cis-jasmone	Sigma-Aldrich	4

[a] Trials 1–4 used 2 mL of compound per trap, and trials 5–12 used 1 mL. Dates: 1, March 7–9, 2001 (48 h); 2, March 13–15, 2001 (48 h); 3, March 18–20, 2001 (48 h); 4, Nov 5–8, 2001 (74 h); 5, Dec 14–15, 2001 (25 h); 6, Feb 21–22, 2002 (24 h); 7, March 8–9, 2002 (25 h); 8, Dec 20–21, 2002 (24 h); 9, Jan 29–30, 2003 (24 h); 10, Feb 12–13, 2003 (24 h); 11, March 19–20, 2003 (25 h); 12, March 4–5, 2004 (29 h). [b] Unknown commercial source, >90% pure by ^{1}H NMR spectroscopy. [c] Placed into two vials per water trap. [d] Trial 6 included a treatment with 1 mL of pure compound and 1 mL of compound in $CHCl_3$. [e] Purity = 75–90%; balance is β-ionone.

Pyridine 4-(1,3-Dioxalan-2-yl). The acetal was produced according to a published method (*51*). A stirred solution of pyridine-4-carboxaldehyde (8.7 mL, 90 mmol), ethylene glycol (10 mL, 180 mmol), and *p*-toluenesulfonic acid (18.8 g, 99 mmol) in benzene (70 mL) was refluxed overnight, with removal of H_2O in a Dean−Stark apparatus. After 15 h, the mixture was cooled and then made basic with aqueous NaOH (20% w/v, 30 mL). The benzene layer was isolated, and the aqueous layer was washed with CH_2Cl_2 (3 × 60 mL). The combined organic phases were dried (Na_2SO_4), and solvent was removed in vacuo to give 4-(1,3 dioxolan-2-yl)pyridine [CAS Registry No. 61379-59-7] as a pale yellow liquid that solidified under vacuum (12.57 g, 92%) and showed appropriate ^{1}H NMR signals (*51*): ^{1}H NMR (300 MHz, $CDCl_3$), δ 4.06 [4H, m, O−$(CH_2)_2$−O], 5.82 (1H, s, O−CH−O), 7.39 (2H, d, J = 6 Hz, H-3, H-5), 8.63 (2H, d, J = 6 Hz, H-2, H-6); >90% pure.

Field Experiments. Experiments were conducted in a grass field at the Canterbury Agricultural Science Centre Campus, Lincoln, during the summer seasons of 2000−2001, 2001−2002, and 2002−2003 (**Table 1**). Grass and cereal fields surrounded the trial area on three sides with a *Poplar nigra* L. tree shelter row on the southeastern side.

The trial area was at least 100 m from any field boundary. Each field trial consisted of five replicates of five treatments in a Latin square design in a 10 × 10 m grid (i.e., 10 m between traps). Teulon et al. (*38*) pointed out the need for a sufficient distance between baited traps within a trial to minimize the influence of chemicals from one trap on an adjacent trap. Each trial included three test compounds, a water control, and either ethyl nicotinate (in most cases) or ethyl isonicotinate for comparison between experiments. Experiments were conducted from November to March and were between 24 and 74 h in duration (**Table 1**). These months included the highest records of thrips flight activity in Canterbury, New Zealand (*35*, *36*).

An additional experiment, modified to allow for a greater number of compounds to be tested at one time, was undertaken at Lincoln in March 2004 (**Table 1**). Three replicate 4 × 4 Latin squares were laid out in the grass field (see above). Each position of a square contained a water trap with 1 of 10 compounds (see **Table 1**), *p*-anisaldehyde (×2), ethyl isonicotinate (×2), and water (×2). $CHCl_3$ was tested by itself as this was used to dissolve several solid compounds in the first series of experiments (see below, **Table 1**). Traps were in position for 29 h from 9:00 a.m. on March 4 to 2:00 p.m. on March 5, 2004. Traps within Latin squares and between replicates were 10 m apart.

Traps. White plastic containers (16 cm square by 8.5 cm deep), containing between 1.5 and 1.7 l of water, 0.04 mL of formalin, and 0.08 mL of Tween 20, were placed above grass level on inverted plastic containers that were either 2 L white (16 × 16 × 8.5 cm), 4 L white (16 × 16 × 19 cm), or 3 L black (24 cm diameter × 13 cm tall). Trap supports were always of the same type for a given experiment. For each treatment, 1 or 2 mL of the compound (**Table 1**) or water was added to a glass vial (12 mm diameter × 32 mm deep) containing a piece of rolled filter paper (4.5 cm square, Whatman no. 1) that projected 1 cm above the top of the vial, creating a wick. The vial was suspended above the water in the center of the trap using wire (0.5 mm diameter). The vials were removed at the end of the sampling period, and water traps were sealed and transported to the laboratory. Compounds that were solid at room temperature were dissolved in a 1:1 or 1:2 ratio with $CHCl_3$ (**Table 1**) and placed in the glass vial for a total volume of 2 or 3 mL.

Thrips Subsamples and Identification. For all experiments, all thrips from each trap were counted and a subsample of thrips was mounted on microscope slides. Thrips were randomly subsampled using the following criteria: for <50 thrips per trap, all thrips were mounted; for 50−100 thrips per trap, 25 thrips were mounted; for 101−200 thrips per trap, 50 thrips were mounted; for >201 thrips per trap, 100 thrips were mounted. Terebrantian thrips species were identified under magnification (×100) according to the procedure of Mound and Walker (*39*) with allowance for several additions/corrections in thrips species since that time (L. Mound, personal communication). The total number of thrips (for a given species) per trap was estimated by multiplying the proportion of each species within a subsample with the total number of thrips.

Statistical Analysis. Estimated numbers per trap of NZFT ♂ and ♀ and OT ♀ were analyzed separately. Models were fitted using a generalized linear mixed model (GLMM) (*52*), which is a mixed model extension of the common Poisson generalized linear model with a logarithmic link for count data. Models were fitted using the GLMM procedure of Genstat (version 8 for Windows, VSN International Ltd., Hemel Hempstead, U.K., 2005). Each model had a fixed effect for treatment (compound) and random effects to account for differences in total thrips numbers between trials, location effects within trials, and differences in effectiveness of compounds between trials. Water was included as a treatment so the difference between the effects for the chemical compounds and water was calculated (on the log scale) and back-transformed into a ratio relative to water.

These differences (on the log scale) were compared to the standard errors of differences produced by Genstat, to assess which compounds were significantly more attractive than water. Because this involved 36 tests, the significance levels were Bonferroni-adjusted (i.e., for a difference to be declared significant at $p = 0.05$, the actual significance level had to be 0.05/36). The confidence intervals (CIs) presented are also Bonferroni adjusted, to give 95% simultaneous CIs.

Comparisons between specific treatments (e.g., between compounds, or pure compound versus compound dissolved in $CHCl_3$) were done by comparing the difference in effects with the standard errors of differences produced by Genstat. As there were far fewer of them, these comparisons were not adjusted for multiple testing.

RESULTS AND DISCUSSION

The majority (76−99%) of thrips caught were NZFT (*T. obscuratus*) males and females or OT (*T. tabaci*) females only. Female-only populations of OT are found throughout most of its worldwide distribution including New Zealand (*1*, *39*). Other thrips species found in low numbers included *Aeolothrips fasciatus* L., *Anaphothrips obscurus* Müller, *Chirothrips manicatus* Haliday, *Limothrips cerealium* Haliday, *Ceratothrips frici* Uzel, *Frankliniella intonsa* Trybom, *Frankliniella occidentalis* Pergande, *Thrips australis* Bagnall, *Thrips simplex* Morison, *Thrips vulgatissimus* Haliday, and unidentified *Tubulifera*. Both NZFT and OT have been previously reported as among the most common thrips found flying in Canterbury (*35*, *36*) during the months when the experiments were undertaken.

In total we report on 35 compounds (**Figure 1**), plus ethyl nicotinate dissolved in chloroform and chloroform by itself. The numbers of thrips (NZFT ♂ and ♀ and OT ♀) caught in baited traps are presented in **Tables 2**−**4** as ratios to the numbers in the control (water) traps to enable meaningful comparisons between experiments run over four summers, in different months and in different conditions. The mean number of thrips per trap for all trials is also listed. Compounds tested in only trial 12 had relatively wide confidence intervals for NZFT because this trial had only three replicates and the catches of thrips were relatively low. For NZFT 15 (male) and 18 (female) compounds and for OT 10 compounds significantly increased trap capture compared with the control (water only) traps.

Trap catches with chloroform alone were not significantly different from those with water for both thrips species. Additionally, trap catches for ethyl nicotinate with chloroform and ethyl nicotinate without chloroform were not significantly different from each other. Therefore, chloroform was a suitable inert solvent for testing solids, such as methyl nicotinate and *n*-butyl nicotinate.

New Zealand Flower Thrips (Tables 2 and 3). Ethyl nicotinate was expected to be a strong attractant for NZFT (*9*, *28*), and it did indeed give the highest capture ratios (mean 158× for ♀; mean 85× for ♂) of any of the compounds that we tested. Ethyl nicotinate remains one of the strongest attractants reported for any thrips species.

Several other compounds, not previously reported as thrips attractants but selected on the basis of structural and/or aroma analogies to known attractants, were also found to be strong attractants for NZFT. The best of these were two homologues of ethyl nicotinate, methyl nicotinate (♀ 111×, ♂ 50×) and *n*-butyl nicotinate (♀ 102×, ♂ 20×). One of the two regioisomers of ethyl nicotinate, ethyl isonicotinate, also caught significantly more NZFT than water (♀ 32×, ♂ 29×). Ethyl isonicotinate was also the strongest attractant for OT (see below). The other regioisomer of ethyl nicotinate, ethyl picolinate (**Figure 1**), was not significantly more attractive than water.

The benzene analogue of ethyl nicotinate, ethyl benzoate, was strongly attractive to NZFT (♀ 35×, ♂ 25×) and a homologue, methyl benzoate, was the strongest attractant for NZFT (♀ 49×, ♂ 51×) among the benzene derivatives. Methyl benzoate has previously been reported as a moderate attractant for *Thrips hawaiiensis* and *Thrips coloratus*, but not *Thrips flavus* (*14*). We also tested the 2-hydroxy and 2-amino derivatives of methyl

Table 2. Field Trapping Results for Female New Zealand Flower Thrips, *Thrips obscuratus*, Using Pyridine and Benzene Derivatives and Other Compounds

compound	ratio[a] (95% CI[b])	p^b	mean[c] (SD)
ethyl nicotinate + $CHCl_3$	179.1 (52.2, 614.8)	<0.001	76.5 (33.8)
ethyl nicotinate	157.6 (66.7, 372.2)	<0.001	199.8 (202.7)
methyl nicotinate + $CHCl_3$	111.2 (31.7, 390.2)	<0.001	47.7 (22.1)
n-butyl nicotinate + $CHCl_3$	102.4 (29.0, 361.8)	<0.001	42.7 (9.3)
methyl isonicotinate	44.1 (6.7, 290.6)	<0.001	8.0 (8.4)
ethyl isonicotinate	31.6 (11.6, 85.9)	<0.001	21.1 (32.3)
ethyl 4-pyridyl ketone	19.4 (1.9, 201.3)	0.002	1.3 (1.7)
pyridine, 4-(1,3-dioxalan-2-yl)	16.6 (0.0, 8544.4)	ns	0.3 (0.6)
ethyl 2-chloropyridine-4-carboxylate	15.1 (0.0, 7737.5)	ns	0.3 (0.6)
n-decyl isonicotinate	14.9 (0.0, 7639.1)	ns	0.3 (0.6)
n-propyl isonicotinate	9.0 (0.6, 129.9)	ns	1.6 (2.3)
isopropyl isonicotinate	9.0 (0.6, 128.4)	ns	1.6 (1.6)
4-formylpyridine	7.9 (0.0, 44876.5)	ns	0.2 (0.3)
ethyl picolinate	4.1 (0.4, 38.5)	ns	2.0 (2.0)
n-hexyl isonicotinate	0.0 (–)	ns	0.0 (0.0)
ethyl isonipecotate	0.0 (–)	ns	0.0 (0.0)
4-cyanopyridine	0.0 (–)	ns	0.0 (0.0)
4-(2-hydroxyethyl)pyridine	0.0 (–)	ns	0.0 (0.0)
methyl 4-pyridyl ketone	0.0 (–)	ns	0.0 (0.0)
methyl benzoate	49.1 (16.5, 146.5)	<0.001	130.9 (52.0)
ethyl salicylate	42.6 (12.1, 149.4)	<0.001	31.8 (14.3)
ethyl benzoate	35.4 (9.9, 126.4)	<0.001	26.7 (11.9)
methyl anthranilate	28.3 (9.2, 87.4)	<0.001	84.8 (25.8)
p-anisaldehyde	26.2 (9.9, 69.2)	<0.001	69.4 (38.9)
methyl salicylate	24.8 (8.1, 75.7)	<0.001	65.1 (24.7)
salicylaldehyde	20.7 (5.4, 79.6)	<0.001	15.5 (3.1)
2-aminoacetophenone	20.7 (6.6, 64.8)	<0.001	62.4 (24.7)
allylanisole	16.5 (3.6, 75.6)	<0.001	7.9 (8.7)
2-phenylethanol	9.8 (3.1, 31.3)	<0.001	10.5 (16.2)
benzaldehyde	5.0 (1.4, 17.6)	0.002	7.4 (10.6)
acetanilide + $CHCl_3$	2.4 (0.2, 37.6)	ns	1.1 (1.2)
ethyl anthranilate	1.6 (0.1, 21.2)	ns	1.3 (2.4)
cis-jasmone	42.1 (11.8, 150.5)	<0.001	36.9 (52.0)
β-ionone	1.8 (0.1, 40.4)	ns	0.9 (1.4)
α-ionone	1.8 (0.1, 40.1)	ns	0.9 (1.4)
methyl jasmonate	0.8 (0.0, 28.9)	ns	0.6 (0.9)
chloroform	0 (–)	ns	0 (0)
water	–		0.9 (1.8)

[a] Ratio (95% confidence interval) of thrips in baited traps compared to unbaited traps. [b] Bonferroni adjusted. [c] Mean number (SD) of thrips per trap in all trials.

Table 3. Field Trapping Results for Male New Zealand Flower Thrips, *Thrips obscuratus*, Using Pyridine and Benzene Derivatives and Other Compounds.

compound	ratio[a] (95% CI[b])	p^b	mean[c] (SD)
ethyl nicotinate	84.8 (33.4, 215.5)	<0.001	79.3 (94.4)
ethyl nicotinate + $CHCl_3$	56.9 (16.8, 192.2)	<0.001	19.6 (10.5)
methyl nicotinate + $CHCl_3$	49.8 (14.5, 171.1)	<0.001	17.4 (10.8)
ethyl isonicotinate	28.5 (10.1, 80.4)	<0.001	10.6 (15.1)
pyridine, 4-(1,3-dioxalan-2-yl)	20.4 (0.2, 2086.7)	ns	0.7 (0.6)
4-cyanopyridine	19.9 (0.2, 2103.4)	ns	0.7 (0.6)
n-butyl nicotinate + $CHCl_3$	19.9 (4.6, 86.6)	<.001	6.9 (2.1)
ethyl 2-chloropyridine-4-carboxylate	19.3 (0.2,1954.3)	ns	0.7 (0.6)
methyl 4-pyridyl ketone	10.3 (0.0, 5440.3)	ns	0.3 (0.6)
ethyl picolinate	5.9 (0.6, 54.4)	ns	1.9 (2.1)
methyl isonicotinate	5.1 (0.1, 426.1)	ns	0.4 (1.0)
4-formylpyridine	4.9 (0.0, 30734.2)	ns	0.2 (0.3)
isopropyl isonicotinate	0.0 (–)	ns	0.0 (0.0)
n-propyl isonicotinate	0.0 (–)	ns	0.0 (0.0)
n-hexyl isonicotinate	0.0 (–)	ns	0.0 (0.0)
n-decyl isonicotinate	0.0 (–)	ns	0.0 (0.0)
ethyl isonipecotate	0.0 (–)	ns	0.0 (0.0)
4-(2-hydroxyethyl)pyridine	0.0 (–)	ns	0.0 (0.0)
ethyl 4-pyridyl ketone	0.0 (–)	ns	0.0 (0.0)
methyl benzoate	50.5 (18.5, 137.6)	<0.001	74.7 (32.1)
ethyl salicylate	48.5 (15.4, 152.6)	<0.001	26.0 (29.7)
2-aminoacetophenone	26.7 (9.9, 72.1)	<0.001	69.9 (30.0)
ethyl benzoate	24.8 (6.3, 97.8)	<0.001	11.3 (5.2)
p-anisaldehyde	22.6 (8.2, 62.0)	<0.001	28.1 (19.0)
methyl anthranilate	22.1 (8.1, 60.2)	<0.001	59.0 (23.0)
allylanisole	17.2 (2.3, 126.3)	<0.001	2.8 (4.1)
salicylaldehyde	15.7 (4.1, 61.1)	<0.001	9.0 (3.5)
methyl salicylate	13.3 (4.3, 41.4)	<0.001	19.2 (2.5)
2-phenylethanol	9.5 (3.2, 27.9)	<0.001	13.2 (14.3)
benzaldehyde	3.6 (0.7,17.7)	ns	2.3 (4.2)
acetanilide + $CHCl_3$	2.5 (0.1, 61.0)	ns	0.8 (0.7)
ethyl anthranilate	0.6 (0.1, 7.8)	ns	1.4 (1.9)
cis-jasmone	24.5 (8.6, 70.1)	<0.001	55.6 (64.4)
β-ionone	3.8 (0.1, 144.6)	ns	0.6 (1.4)
methyl jasmonate	0.9 (0.1, 9.0)	ns	1.7 (2.3)
α-ionone	0.0 (-)	ns	0.0 (0.0)
chloroform	10.1 (0.0, 5457.6)	ns	0.3 (0.6)
water	–		0.8 (1.6)

[a] Ratio (95% confidence interval) of thrips in baited traps compared to unbaited traps. [b] Bonferroni adjusted. [c] Mean number (SD) of thrips per trap in all trials.

and ethyl benzoate (i.e., the salicylates and anthranilates, **Figure 1**). Ethyl salicylate (♀ 43×, ♂ 49×), methyl salicylate (♀ 25×, ♂ 13×) and methyl anthranilate (♀ 28×, ♂ 22×) were significantly attractive to NZFT, whereas ethyl anthranilate was not (♀ 2×, ♂ 1×). Murai and Imai reported that methyl anthranilate, which is a floral aroma compound in several plants, is a very strong attractant for *T. hawaiiensis* (especially females), less so for *T. coloratus*, but not for *T. tabaci* (*27*). They also studied the activity of structural analogues of methyl anthranilate (*14*) and did not find methyl salicylate to be significantly attractive to *T. hawaiiensis*, *T. coloratus*, or *T. flavus*.

Two of the best known thrips attractants are benzaldehyde and *p*-anisaldehyde (*9, 23, 27, 29*), which occur in flower aromas of several plant species that are hosts to thrips (*9*). These compounds are also benzene carbonyl derivatives, but with aldehyde rather than ester groups (**Figure 1**). *p*-Anisaldehyde (♀ 26×, ♂ 23×) was significantly attractive to NZFT in these trials, whereas benzaldehyde (♀ 5×, ♂ 4×) was for females but not for males. In previous field experiments Teulon et al. (*9*) found that both *p*-anisaldehyde (♀ 34×, ♂ 31×) and benzaldehyde (♀ 35×, ♂ 10×) were attractive to NZFT in summer (February) but much less so in spring (October) (*p*-anisaldehyde, ♀ 6×, ♂ 4×; benzaldehyde, ♀ 2×, ♂ 1×). Salicylaldehyde (♀ 21×, ♂ 15×), which is 2-hydroxybenzaldehyde (**Figure 1**), was more attractive than benzaldehyde (**Tables 2** and **3**). Another benzene carbonyl derivative, with a methyl ketone group, 2-aminoacetophone (**Figure 1**), was attractive to NZFT (♀ 21×, ♂ 27×). This compound was also tested by Imai et al. (*14*) and found to be significantly attractive to *T. hawaiiensis*, but not to *T. coloratus* or *T. flavus*.

Four of the compounds selected because of their floral aromas did not contain the pyridine or benzene ring plus carbonyl structure (**Figure 1**). Only one of these, *cis*-jasmone, showed significant attractant activity for NZFT (♀ 42×, ♂ 25×). *cis*-Jasmone has been reported as a repellant to aphids and an attractant to a ladybird species (*42*), but we could find no previous report of this compound as a thrips attractant

Onion Thrips (Table 4). The strongest attractants for OT (all ♀) reported from previous studies were *p*-anisaldehyde and benzaldehyde (*9, 23, 27*). These compounds were attractants for OT (*p*-anisaldehyde, 4×; benzaldehyde, 4×) in the experiments described here, but we identified several compounds that were much stronger attractants. Ethyl isonicotinate provided the greatest increases for OT trapping (31×) of any of the

Table 4. Field Trapping Results for Female Onion Thrips, *Thrips tabaci*, Using Pyridine and Benzene Derivatives and Other Compounds

compound	ratio[a] (95% CI[b])	p^b	mean[c] (SD)
ethyl isonicotinate	30.8 (14.3, 66.0)	<0.001	163.9 (216.0)
methyl isonicotinate	18.9 (6.3, 56.4)	<0.001	237.8 (256.9)
n-propyl isonicotinate	15.4 (5.1, 46.4)	<0.001	176.1 (170.9)
ethyl 4-pyridyl ketone	13.5 (5.1, 35.5)	<0.001	61.6 (29.7)
isopropyl isonicotinate	8.8 (2.7, 29.1)	<0.001	123.6 (99.9)
methyl 4-pyridyl ketone	7.6 (1.0, 58.7)	ns	8.7 (5.5)
n-decyl isonicotinate	6.8 (0.9, 53.4)	ns	8.7 (12.5)
pyridine, 4-(1,3-dioxalan-2-yl)	5.3 (0.6, 49.1)	ns	6.0 (3.5)
methyl nicotinate + $CHCl_3$	5.3 (0.6, 48.3)	ns	6.5 (2.8)
ethyl nicotinate + $CHCl_3$	4.2 (0.4, 41.4)	ns	5.2 (2.6)
ethyl isonipecotate	4.0 (0.4, 41.1)	ns	5.0 (2.7)
ethyl nicotinate	3.1 (1.4, 6.5)	<0.001	13.1 (20.6)
ethyl picolinate	2.8 (0.7, 10.5)	ns	7.1 (4.7)
4-cyanopyridine	2.4 (0.2, 36.0)	ns	3.0 (1.0)
ethyl-2-chloropyridine-4-carboxylate	1.7 (0.1, 32.3)	ns	2.3 (3.2)
4-formylpyridine	1.6 (0.1, 34.6)	ns	2.0 (1.7)
n-butyl nicotinate + $CHCl_3$	1.5 (0.1, 25.5)	ns	1.8 (2.9)
4-(2-hydroxyethyl)pyridine	1.3 (0.4, 4.2)	ns	5.7 (5.2)
n-hexyl isonicotinate	1.2 (0.0, 33.7)	ns	1.7 (1.5)
methyl benzoate	6.6 (1.5, 28.2)	0.001	116.2 (59.8)
2-aminoacetophenone	6.0 (0.8, 48.1)	ns	6.3 (3.7)
benzaldehyde	4.0 (1.1, 15.3)	0.031	13.9 (13.8)
p-anisaldehyde	4.0 (1.4, 11.6)	0.001	28.4 (41.2)
methyl salicylate	4.0 (0.9, 17.5)	ns	68.1 (38.1)
2-phenylethanol	3.8 (1.3, 11.4)	0.004	18.3 (15.7)
methyl anthranilate	3.5 (0.3, 34.6)	ns	3.6 (3.3)
ethyl salicylate	3.0 (0.6, 16.2)	ns	19.7 (7.8)
allylanisole	2.5 (0.4, 14.9)	ns	11.7 (9.1)
ethyl benzoate	2.1 (0.4, 11.9)	ns	13.8 (3.4)
salicylaldehyde	1.9 (0.3, 11.1)	ns	12.6 (3.1)
acetanilide + $CHCl_3$	1.2 (0.1, 9.6)	ns	3.7 (0.5)
ethyl anthranilate	1.1 (0.0, 86.8)	ns	0.6 (0.9)
β-ionone	2.6 (0.4, 15.4)	ns	12.8 (10.3)
α-ionone	1.3 (0.2, 9.2)	ns	6.1 (3.8)
cis-jasmone	1.2 (0.0, 83.7)	ns	0.7 (1.5)
methyl jasmonate	0.7 (0.0, 121.1)	ns	0.4 (0.6)
chloroform	1.1 (0.0, 40.8)	ns	1.3 (0.6)
water	–		4.7 (5.9)

[a] Ratio (95% confidence interval) of thrips in baited traps compared to unbaited traps. [b] Bonferroni adjusted. [c] Mean number (SD) of thrips per trap in all trials.

compounds tested and was significantly more attractive to OT than its regioisomer ethyl nicotinate (3×). Ethyl nicotinate was also found to be a relatively weak attractant for OT in earlier work (*9*). Neither the other regioisomer, ethyl picolinate (**Figure 1**), nor its reduced heterocyclic analogue, ethyl isonipecotate, was significantly attractive to OT.

Ethyl isonicotinate provided us with a new starting point in our search for alternative thrips attractants. We tested the methyl (19×), *n*-propyl (15×), isopropyl (9×), *n*-hexyl (1×), and *n*-decyl (7×) isonicotinate esters as homologues of ethyl isonicotinate. All of these except *n*-hexyl and *n*-decyl isonicotinate were significantly attractive to OT, but all except methyl isonicotinate were significantly less attractive than ethyl isonicotinate. A chlorinated analogue of ethyl isonicotinate, ethyl 2-chloropyridine-4-carboxylate (**Figure 1**), was not significantly attractive to OT.

Some ketones have similar aromas to analogous esters as perceived by humans (*43*), and other esters have been shown to give similar insect responses to analogous aldehydes (*44*). In the case of OT and 4-pyridyl carbonyl compounds, ethyl 4-pyridyl ketone (**Figure 1**) was as attractive (13×) as its ester analogue methyl isonicotinate (19×, no significant difference). The methyl 4-pyridyl ketone (8×) homologue fell just short of being significantly attractive ($p = 0.055$). The aldehyde analogue, 4-formylpyridine, and its nitrile analogue, 4-cyanopyridine (**Figure 1**), were not significantly attractive to OT.

The benzene analogue of ethyl isonicotinate (and of ethyl nicotinate, see above), ethyl benzoate (**Figure 1**), was not significantly attractive to OT, another difference from the preferences of NZFT (see above). However, methyl benzoate (7×) showed significant attractant activity to OT, and methyl salicylate (4×) was weakly attractive ($p = 0.099$).

We found that 2-phenylethanol, a non-carbonyl benzene derivative chosen because of its sweet floral aroma (*31*, *32*), was moderately attractive to OT (4×). However, the 4-pyridyl analogue, 4-(2-hydroxyethyl)pyridine (**Figure 1**), was not attractive. None of the other floral aroma compounds (neither benzene nor pyridine derivatives) (**Figure 1**) were significantly attractive to OT, even though *cis*-jasmone was attractive to NZFT (see above).

Variable Trap Catches. Ethyl nicotinate ($n = 9$ trials) and ethyl isonicotinate ($n = 5$ trials) were tested in several separate field trials (**Table 1**). Increased trap capture was quite variable between experiments, especially for NZFT and ethyl nicotinate (60−460× for ♀, 15−188× for ♂) and also for OT and ethyl isonicotinate (24−62×). We could not identify any experimental factors (month of year, duration of trial, volume of chemical compound) or environmental factors (temperature, wind speed, solar radiation) that might have contributed to these differences. Factors influencing trap capture, other than the chemical compound alone, are likely to be a fruitful area for future research so that optimal trap catches are obtained.

Pheromone or Allelochemical Mimics? The 3- and 4-pyridyl carbonyl compounds that brought about increased thrips trap capture might be natural compounds that are semiochemicals, but these compounds have not been reported from thrips, and records from plants are rare [ethyl nicotinate has been reported from some flowers and fruits (*40*, *41*), and methyl isonicotinate has been tentatively identified at a low level in sesame seed oil (*45*)]. Therefore, we suggest that these synthetic compounds bind to natural pheromone or allelochemical receptor proteins in the thrips' olfactory systems. This concept has been suggested to explain the activity of synthetic analogues of insect pheromones (*44*), and a synthetic, non-natural compound has been shown to give a strong response from a human olfactory receptor (*47*).

The only reported thrips aggregation pheromones, from *F. occidentalis* (*16*), are structurally very different from the 3- and 4-pyridyl carbonyl compounds. The strong correlation between the responses of NZFT males and females to the compounds that we tested (correlation coefficient = 0.8211, df 35, $p < 0.001$) suggests that these are unlikely to be thrips sex pheromone analogues. Furthermore, several of the compounds we tested (e.g., ethyl isonicotinate) were attractive to three different species: NZFT and OT in field experiments (see above) as well as *F. occidentalis* in Y-tube experiments (*37*).

We propose that the response of thrips to 3- and 4-pyridyl carbonyl compounds is the result of their structural similarity to allelochemical benzene carbonyl derivatives, such as benzaldehyde, 2-aminobenzaldehyde, methyl benzoate, methyl salicylate, and methyl anthranilate, which are some of the most common compounds in floral scents (*46*). The 3- and 4-pyridyl carbonyl compounds could bind to the same receptor proteins as these allelochemicals and may give more intense or long-lasting responses due to their different physical and chemical properties. The differences in preference between NZFT (especially 3-pyridyl) and OT (especially 4-pyridyl) for the

carbonyl compounds tested might reflect species differences in odors from their preferred host plants.

Summary. Of our two approaches for selecting potential thrips lures, the structural similarity approach was the most productive, leading us to discover several 4-pyridyl carbonyl compounds attractive to OT, with ethyl isonicotinate the most powerful attractant yet reported for this commercially important cosmopolitan species. Additionally, several of the compounds tested have also proved to be strongly attractive to *F. occidentalis* in Y-tube experiments (*37*). Patent protection is being sought for this group of compounds (*48*), and we are investigating their use for improved monitoring, mass trapping, lure and kill, and lure and infect systems for thrips pest management.

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