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4-Pyridyl Carbonyl Compounds as Thrips Lures: Effectiveness for Western Flower Thrips in Y-Tube Bioassays

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In a search for chemical lures to manage the cosmopolitan crop pest western flower thrips (WFT), *Frankliniella occidentalis*, a Y-tube olfactometer was used to screen 20 compounds, including 18 4-pyridyl compounds. Comparison of Y-tube results for New Zealand flower thrips (NZFT), *Thrips obscuratus*, with field trapping data for ethyl nicotinate and ethyl isonicotinate, suggested that the minimum attractive dose (MAD) of an odor compound, where significantly ($p < 0.05$) more than 50% of thrips walked up the odor-laden arm, provided a measure for selecting compounds to evaluate for potential lure efficacy in the field. Eighteen synthetic 4-pyridyl compounds were tested on female WFT in a Y-tube olfactometer and four 4-pyridyl carbonyl compounds had MADs lower than the known WFT attractants *p*-anisaldehyde (MAD 10^{-3} μL) and ethyl nicotinate (10^{-2} μL): methyl isonicotinate (10^{-6} μL), ethyl-2-chloropyridine-4-carboxylate (10^{-6} μL), ethyl isonicotinate (10^{-4} μL) and methyl 4-pyridyl ketone (10^{-5} μL). The suitability of MAD for selecting compounds for further evaluation of practical lure efficacy is discussed. Comparisons of activities within homologous series of esters and ketones showed that attractant activity decreased with chain length. 4-Formyl pyridine was an attractant at a dose of 10^{-5} μL, but was repellent at higher doses (10^{-2}–10^{0} μL).

KEYWORDS: Western flower thrips; *Frankliniella occidentalis*; New Zealand flower thrips; *Thrips obscuratus*; pyridine derivative; olfactometer; attractant; repellent

INTRODUCTION

Western flower thrips (WFT), *Frankliniella occidentalis* Pergande (Thysanoptera), are major cosmopolitan pests on a variety of vegetable, fruit and ornamental crops (*1*). WFT are difficult to manage because of their small size (<3 mm), cryptic habits and resistance to a number of insecticides (*2*). As with other thrips pest species, their response to color has been exploited through the use of colored sticky traps for monitoring populations (*3, 4*). Thrips have also been shown to respond to olfactory cues, including alarm, sex, and aggregation pheromones (*5–7*) and plant-derived compounds (*8–11*). These responses could be used in pest management applications. Attractants could be used as lures with colored sticky traps to measure a thrips population in a crop (improved monitoring) (*12*), to remove thrips from a crop (mass trapping) (*13*), to attract thrips to an insecticide or predator/parasitoid (lure and kill), or to bring thrips into contact with a pathogen/virus that infected thrips then spread to others in a population [autodissemination (*14*) or lure and infect (*15*)]. Attractants and repellents could be used in push–pull strategies, in which a repellent pushes thrips off a crop and an attractant pulls thrips to a trap (*16*).

We have discovered a new class of thrips lures, 4-pyridyl carbonyl compounds, effective at increasing trap capture of onion thrips (OT), *Thrips tabaci* Lindeman, and New Zealand flower thrips (NZFT), *Thrips obscuratus* Crawford, in field trials using water traps (*17*). The purpose of this study was to investigate the responses of WFT toward this class of compounds. In New Zealand, WFT are a key pest in greenhouses but are not found in very high numbers outdoors, so outdoor water trap bioassays were not appropriate. Screening compounds in greenhouses is problematic because, with the restricted area and reduced airflow, an active compound in one trap can interfere with catches of neighboring traps. We therefore needed a method to screen a large number of compounds that would indicate which compounds could warrant further testing in the greenhouse.

Y-tube olfactometers have been used to test the responses of WFT to various compounds (*11, 18*). Y-tube testing has several advantages: assays are not dependent on variable natural thrips populations; dose–response measurements can be done; both repellent and attractant activities can be investigated; and only small amounts of compounds are needed (milligrams versus grams for field trials using water traps). On the other hand,

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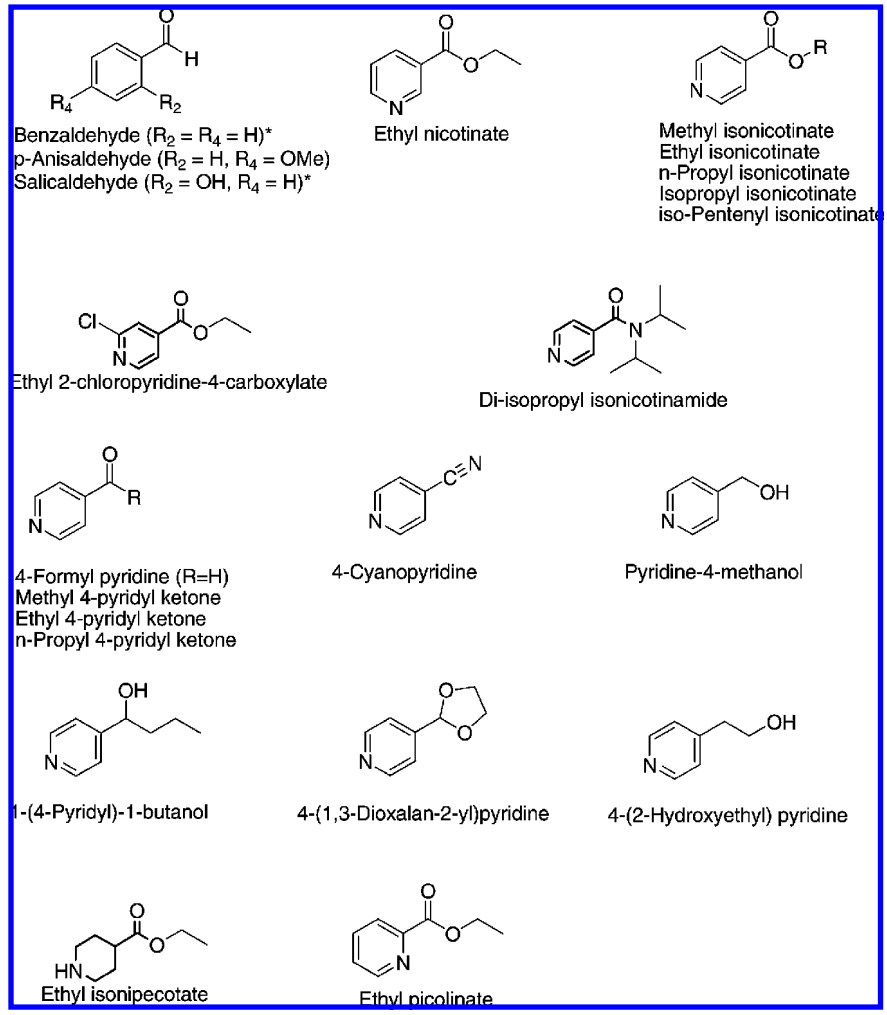

Figure 1. Compounds tested as thrips attractants in a Y-tube olfactometer [* see Koschier et al. (*11*)].

Y-tube experiments only measure a walking response whereas thrips in the field or greenhouse are likely to be both flying and walking, so it is not obvious that Y-tube results will predict practical potencies. However, pheromones which attracted WFT in Y-tube experiments (*19*) also increased catches on blue sticky traps in greenhouses (*6*). Furthermore, both *p*-anisaldehyde and ethyl nicotinate were significantly attractive to WFT in Y-tube experiments at a range of doses (*11*) and both of these compounds have given increased trap catches of WFT in greenhouse and open field experiments (*9, 10*).

Here we report close similarity of Y-tube results between laboratories, results on NZFT suggesting a Y-tube measure for indicating which compounds may be worth testing in a commercial greenhouse, and results for 18 4-pyridyl carbonyl and related compounds showing both attractant and repellent activities toward WFT in a Y-tube olfactometer.

MATERIALS AND METHODS

Sources of Compounds. Eleven of the 20 compounds tested (**Figure 1**) were from the commercial sources previously listed (*17*) and pyridine 4-methanol was from Merck, all with stated purities of 97−99%. *n*-Propyl isonicotinate (estimated by ^{1}H NMR to be 98% pure), isopropyl isonicotinate (98% pure), ethyl 2-chloropyridine-4-carboxylate (99% pure), and 4-(1,3-dioxolan-2-yl)pyridine (98% pure) were synthesized as described elsewhere (*17*). iso-Pentenyl isonicotinate (3-methyl-but-2-enyl isonicotinate [CAS Registry No. 638203-02-8], 96% pure) was synthesized by a method similar to that for isopropyl isonicotinate (*17*).

1-(4-Pyridyl)-1-butanol was prepared by a Grignard reaction. Magnesium turnings (5.1 g, 3.2 eq.), a few crystals of I_2 and a stirring bar were placed in a 500 mL three-necked round-bottom flask. The flask was fitted with a dropping funnel containing propyl bromide (17.8 mL, 3 eq.) in anhydrous Et_2O, a dropping funnel containing anhydrous Et_2O (100 mL) and a condenser. The reaction was carried out under N_2. Once the Grignard reagent had been made, Et_2O was added (∼100 mL) and the reaction was cooled to −5 °C. 4-Formylpyridine (6.24 mL, 65.4 mmol) in anhydrous Et_2O (30 mL) was added dropwise over 40 min at −5 °C. The mixture was stirred for 2 h, then poured onto crushed ice. Sulfuric acid (15% v/v) was added until the solution had pH ∼1 and the mixture was stirred for 10 min. The solution was made basic again with aqueous NaOH (20% w/w). The layers were separated and the aqueous layer was extracted with 10% MeOH/$CHCl_3$ (2 × 300 mL). The combined organic extracts were dried (Na_2SO_4) and solvent removed *in vacuo* to give the crude product as a brown oil (∼10 g). The oil was purified by silica gel column chromatography (gradient elution from CH_2Cl_2 to EtOAc) to give 1-(4-pyridyl)-1-butanol [18085−89−7] as a pale yellow oil (5 g, 50% yield) with appropriate ^{1}H NMR (300 MHz, $CDCl_3$) signals: δ 0.94 (3H, t, J 7 Hz), 1.41 (2H, m), 1.70 (2H, m), 4.70 (1H, dd, J 5, 7 Hz), 7.27 (2H, d, J 6 Hz), 8.54 (2H, d, J 6 Hz) ppm; 96% pure by ^{1}H NMR.

n-Propyl 4-pyridyl ketone was synthesized by oxidation of 1-(4-pyridyl)-1-butanol. Pyridinium chlorochromate (4.27 g, 19.84 mmol) was suspended in dry CH_2Cl_2 (50 mL) in a round-bottom flask under N_2. After stirring for 5 min, 1-(4-pyridyl)-1-butanol (2.0 g, 13.23 mmol) in dry CH_2Cl_2 (10 mL) was added. After 2 h anhydrous Et_2O (70 mL) was added, the supernatant was decanted and the residual black gum was washed with anhydrous Et_2O (4 × 100 mL). The combined organic fractions were concentrated *in vacuo*, and the black tar-like substance

was subjected to two stages of silica gel column chromatography (3:1 EtOAc:hexanes, then EtOAc as eluants) to give *n*-propyl 4-pyridyl ketone [1701-71-9] as a yellow-green oil (520 mg, 27% yield) with appropriate ^{1}H NMR (300 MHz, $CDCl_3$) signals: δ 1.01 (3H, t, J 7 Hz), 1.78 (2H, sextuplet, J 7 Hz), 2.95 (2H, t, J 7 Hz), 7.72 (2H, d, J 5 Hz), 8.81 (2H, d, J 5 Hz) ppm; 96% pure.

Di-isopropyl isonicotinamide was obtained during an unsuccessful attempt to prepare ethyl 3-bromopyridine-4-carboxylate by the method of Epsztajn et al. (*20*). *n*-Butyl lithium (8.27 mL, 1.6 M in hexanes, 13.23 mmol) was added to di-isopropylamine (13.36 mmol, 1.95 mL) in dry THF (10 mL) at −78 °C and stirred for 0.5 h (to make lithium di-isopropylamine, LDA). The mixture was warmed to room temperature for 20 min, then cooled to −78 °C again. Ethyl isonicotinate (1.00 g, 6.62 mmol, 0.91 mL) was dissolved in dry THF (30 mL) and cooled to −78 °C under Ar, and the freshly prepared LDA was added dropwise. The mixture was stirred for 1 h, then allowed to warm to room temperature for 0.5 h. The reaction mixture was cooled to −78 °C again and 1,2-dibromotetrafluoroethane (6.62 mmol, 0.79 mL) in THF (10 mL) was added slowly. The reaction was stirred at −78 °C for 1 h, then stirred at room temperature overnight. Water (40 mL) was added, the organic layer was separated, and the aqueous layer was washed with $CHCl_3$ (3 × 100 mL). The combined organic solutions were dried (Na_2SO_4) and the solvent removed to give the crude compound, which was subjected to silica gel column chromatography (8:2 benzene:acetone) to give di-isopropyl isonicotinamide (220 mg, 16% yield) [77924−05−1] with appropriate ^{1}H NMR (300 MHz, $CDCl_3$) signals: δ 8.66 (2H, d, J 6 Hz), 7.19 (2H, d, J 6 Hz), 3.69 (1H, bs), 3.55 (1H, bs), 1.54 (6H, bs) and 1.16 (6H, bs); 95% pure.

Insects. A laboratory colony of WFT was maintained on potted flowering chrysanthemums, *Dendranthema grandiflora* (cv. Onyx time yellow). The colony was established in 2001 from thrips collected from commercial greenhouses (Auckland, New Zealand), with yearly introductions of WFT from greenhouses (Canterbury and Auckland, New Zealand). The plants used for the colony were held in three temperature-controlled Perspex cages (5 plants per cage) with a temperature maintained at 25 °C under a 16:8 h light:dark cycle. A fresh uninfested plant was placed in each cage every 3 days and the oldest plant was removed at the same time. Female *Thrips obscuratus* were collected from flowering gorse (*Ulex europaeus* L.) or cabbage trees (*Cordyline australis* Forst f.) near Lincoln, Canterbury the day before the Y-tube experiments.

Y-Tube Olfactometer. The responses of thrips toward odor compounds were evaluated in a glass Y-tube olfactometer following the method described by Koschier et al. (*11*). Briefly, the Y-tube had two branching arms at an angle of approximately 45° leading into a single tube (stem), all 60 mm long with an internal diameter of 5 mm. The Y-tube was held at an inclining position of 25°. Glass vials (4 mL) were attached to each arm via Wheaton Micro Kit adapters. Air was drawn through activated charcoal before entering the vials and the Y-tube apparatus, using a suction pump (AR Harris Co. Ltd., New Zealand) producing an airflow of 5 cm/s through each arm and 10 cm/s through the stem of the Y-tube. Air was drawn through the Y-tube for 30 min before introducing the first thrips. Connections between the activated charcoal, vials, Wheaton adapters, Y-tube and suction pump were with silicone tubing. The Y-tube and Wheaton adapters were held within a box, the interior of which had been painted gray in order to prevent external stimuli influencing thrips behavior, which was located in a darkened room at 22 ± 2 °C. The Y-tube was lit from above (approximately 42 cm away from a light source) with a halogen light providing 780 lx at the Y-tube level. The vial on the clean-air arm of the Y-tube contained filter paper (1 cm^2 Whatman no. 1) dosed with 10 ° μL of either hexane or chloroform (Pronalys AR), depending on which solvent was used to dilute a compound. Preliminary assays had shown that these solvents did not elicit a response from female WFT in the Y-tube. The vial for the odor-laden arm contained filter paper (1 cm^2 Whatman no. 1) dosed with 10 ° μL of a diluted or undiluted volatile compound. Generally an undiluted sample of a compound was tested first, then 10X or 100X dilutions until the percentage of thrips walking up each arm was similar. Most compounds were diluted in hexane to obtain different concentrations, but 4-formylpyridine, and 4-(2-hydroxyethyl) pyridine were not soluble in hexane and were diluted in $CHCl_3$. 4-(1,3-Dioxolan-2-yl)pyridine, pyridine 4-methanol, and 4-cyanopyridine were solid at room temperature and were first dissolved in $CHCl_3$ (1:1).

Bioassay. An individual female thrips of unknown age that had been starved for 24 h was released into the base of the stem of the Y-tube using a small aspirator, after disconnecting the silicone tubing connecting the base of the Y-tube to the pump. Most thrips walked up into the stem of the Y-tube within a few seconds, at which time the silicone tubing was reconnected to the base of the glass Y-tube. The end position of a thrips was recorded when the thrips had reached the far end of one arm (odor or clean-air) and only those thrips that walked to the end of an arm within 3 min were recorded. Generally more than 90% of thrips introduced into the Y-tube walked to the end of one of the arms. After every five recorded thrips the Y-tube and vials were rotated 180° to avoid position effects. After 25 recorded thrips, the Y-tube and vials were thoroughly cleaned with acetone (99.5%, Merck) and allowed to dry before repeating the experiment. For each dose there were three replicates of 25 recorded thrips.

Statistical Analysis. Data were analyzed with a binomial generalized linear model with a logit link (*21*), with the number to chose the odor-laden arm as the positive response, out of the total number of thrips to walk up either arm. Comparisons between different doses of a given compound were made as contrasts within the analysis of deviance done as part of the analysis (*21*). Tests for preference for a given dose over the control were made with *t* tests of the parameters estimated on the transformed (logit) scale. On the logit scale, 50% has a value of zero, so if the parameter for a given dose is significantly greater than zero on the logit scale, significantly more than 50% of the thrips walked up the odor or clean-air arm. Confidence limits of 95% for the percentage of thrips walking up the odor arm were calculated on the transformed (logit) scale, and then back-transformed. A significance level of 5% ($p < 0.05$) was used in all analyses.

RESULTS AND DISCUSSION

Female WFT and NZFT were used, rather than both males and females, because a lure for female thrips could reduce egg laying and thus population growth (unmated females can lay viable eggs) (*1*). We previously found a strong correlation between the responses of male and female NZFT to the compounds tested in water traps outdoors (*17*). Furthermore, females are larger than males and thus easier to manipulate.

Y-Tube Interlaboratory Comparisons. *p*-Anisaldehyde and ethyl nicotinate (structures in **Figure 1**) are the most studied thrips attractants (*17*), so we tested these in the Y-tube olfactometer as positive controls for comparisons with results from other laboratories. The responses of female WFT to these compounds reported by Koschier et al. (*11*) fell within the 95% confidence limits calculated in the present study (**Figure 2**). This shows that thrips behavior in Y-tube olfactometers can be consistent between laboratories, and between thrips populations. However, there were differences between the two studies. For example, Koshier et al. found that 63% ($p < 0.05$) of female WFT walked up the odor-laden arm containing 10^{-5} μL *p*-anisaldehyde, but in the present study, only 52% walked up the odor-laden arm at this dose ($p = 0.36$) (**Figure 2**). This could be due to differences in the solvents used for the dilutions. Koschier et al. used paraffin, which does not evaporate as quickly as hexane or chloroform, the solvents used in the present study.

We also tested isobornyl valerate as an aggregation pheromone for WFT in our Y-tube olfactometer, and found significant attractant activity (results not shown) at the same levels as reported by Hamilton and Kirk, despite differences in Y-tube designs (*22*).

Interpreting Y-Tube Results for Evaluating Lure Efficacy. The aim of this study was to use Y-tube screening results to select compounds for further evaluation of their efficacy as thrips

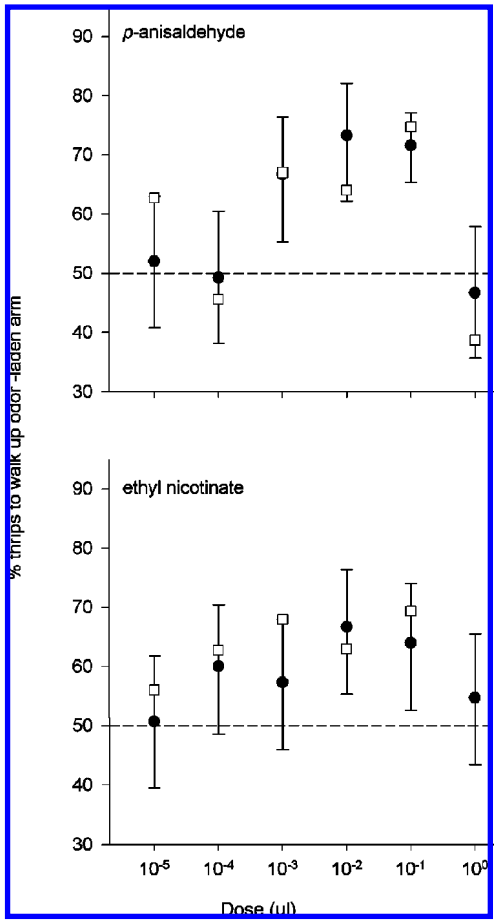

Figure 2. Mean percentage (95% confidence limits) of western flower thrips females to walk up an odor-laden arm containing known thrips attractants in a Y-tube olfactometer. Open squares are values from Koschier et al. (*11*).

lures in practical applications. The dose−response curves from Y-tube experiments, e.g. for *p*-anisaldehyde and ethyl nicotinate in **Figure 2**, offer several measures of potency: the range of doses at which significantly ($p < 0.05$) more than 50% of the thrips walked up the odor-laden arm; the minimum attractive dose within this range; or the maximum proportion of thrips to walk up the odor-laden arm. Furthermore, some compounds can be attractants at lower doses, but repellents at higher doses (see below).

The concentration of a compound in the atmosphere around a lure will depend very strongly on air flow [see discussion and references in Miller et al. (*23*)], but this concentration will always decline with distance from the lure, by diffusion into a greater volume of air. Therefore, a compound that is attractive at a lower concentration (i.e., a lower dose in the Y-tube) may be detected by thrips at a greater distance from the lure, so potentially more thrips will be attracted. Based on this argument, the minimum dose to result in significantly ($p < 0.05$) more than 50% of thrips walking up the odor-laden arm in the Y-tube (minimum attractive dose, MAD) seems a logical choice for indicating a compound's potential lure efficacy if it remains attractive at higher doses. However, the MAD, as with the response of thrips toward all of the doses tested, is based on a significance test and is thus necessarily affected by trial size, i.e. number of thrips per replicate, number of replicates per dose per compound. Therefore, the response of thrips toward doses of a given compound, including the MAD, must be interpreted cautiously between this and other studies.

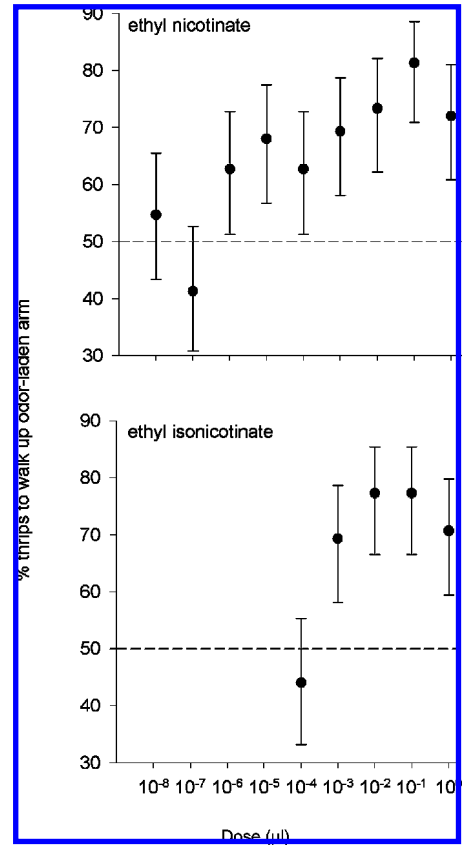

Figure 3. Mean percentage (95% confidence limits) of New Zealand flower thrips females to walk up the odor-laden arm containing regioisomeric pyridyl esters in a Y-tube olfactometer.

We have shown highly significant differences in catches of female NZFT in water traps baited with either ethyl nicotinate (average of 158 times more than control) or ethyl isonicotinate (average of 32 times more than control) (structures in **Figure 1**) (*17*). When we tested these compounds in the Y-tube with female NZFT we found that ethyl nicotinate had a thousand-fold lower MAD (10^{-6} μL) than the regioisomeric ethyl isonicotinate (10^{-3} μL) (**Figure 3**), corresponding to the significantly higher efficacy in the field bioassay. Therefore we discuss the results of our screening compounds against WFT in the Y-tube (below) primarily in terms of the MAD, as an indication of lure efficacy.

4-Pyridyl Esters as WFT Attractants. The three isomeric esters ethyl picolinate, ethyl nicotinate and ethyl isonicotinate (structures in **Figure 1**) were tested at a range of doses in the Y-tube on WFT females (**Figures 2** and **4**). Ethyl isonicotinate showed the lowest MAD (10^{-4} μL) so further work focused on 4-pyridyl derivatives. The reduced heterocyclic analogue of ethyl nicotinate, ethyl isonipecotate (**Figure 1**), was significantly attractive at 10 ° μL but not at 10^{-2} μL (**Table 1**, only tested at these two doses) so no further work was done on this class of compound.

Five other 4-pyridyl esters were tested (**Figure 4** and **Table 1**). The methyl homologue was more active (MAD 10^{-6} μL) than ethyl isonicotinate, and the n-propyl homologue was less active (MAD 10^{-3} μL). The branched chain isopropyl isonicotinate had a similar MAD (10^{-2} μL) to its straight chain isomer, n-propyl isonicotinate (**Figure 4**). The higher molecular weight iso-pentenyl isonicotinate was inactive at the highest (10 ° μL) dose tested (**Table 1**). Thus MAD decreased with decreasing molecular weight. One possible explanation for this structure−activity relationship is the decrease of vapor pressure

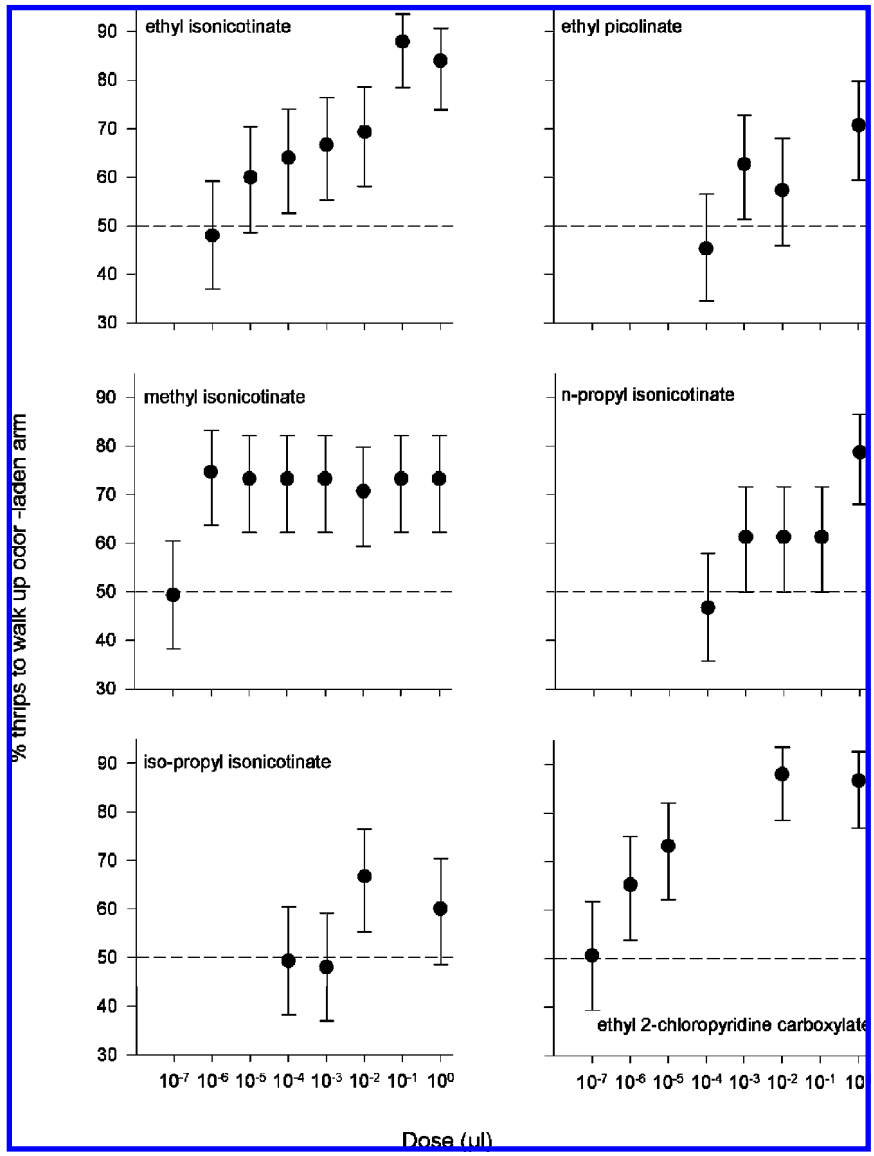

Figure 4. Mean percentage (95% confidence limits) of western flower thrips females to walk up an odor-laden arm containing 4-pyridyl esters in a Y-tube olfactometer.

Table 1. Mean Percentage (95% Confidence Limits) of Female Western Flower Thrips To Walk up an Odor-Laden Arm of a Y-Tube Olfactometer for Pyridyl Compounds Tested at One, Two, or Three Doses

	dose (μL)						
compound	5×10^{-4}	10^{-3}	5×10^{-3}	10^{-2}	10^{-1}	5×10^{-1}	10°
ethyl isonipecotate				49 (38, 60)			63 (51, 73)
iso-pentenyl isonicotinate							49 (38, 60)
di-isopropyl isonicotinamide[a]						81 (71, 89)	
propyl 4-pyridyl ketone					47 (36, 58)		55 (43, 65)
4-cyanopyridine[a]						39 (28, 50)	
4-(1,3-dioxolan-2-yl)pyridine[a]	48 (37, 59)		63 (51, 73)			61 (50, 72)	
1-(4-pyridyl)-1-butanol							47 (36, 58)
pyridine 4-methanol[a]							52 (41, 63)
4-(2-hydroxyethyl) pyridine[b]		48 (37, 59)		59 (47, 69)			79 (68, 86)

[a] Solid at room temperature, dissolved in chloroform (1:1). [b] Not soluble in hexane, diluted in chloroform.

with increasing molecular weight (**Figure 6**), resulting in fewer molecules of higher molecular weight compounds per unit volume to affect the thrips' behavior. Bengtsson et al. (*24*) and Heath and Tumlinson (*25*) have discussed the importance of taking vapor pressures into account for insect pheromones. However, ethyl 2-chloropyridine carboxylate (MAD 10^{-6} μL) was about a hundred times more active than its nonchlorinated analogue ethyl isonicotinate (**Figure 4**), despite having a much lower predicted vapor pressure (**Figure 6**). A GC-MS analysis confirmed the 99% purity of the ethyl 2-chloropyridine carboxylate sample, with a 1% level of an isomer. The GC retention time, which is related to vapor pressure (*25*), was much greater than the retention time of ethyl isonicotinate, confirming the relative vapor pressures.

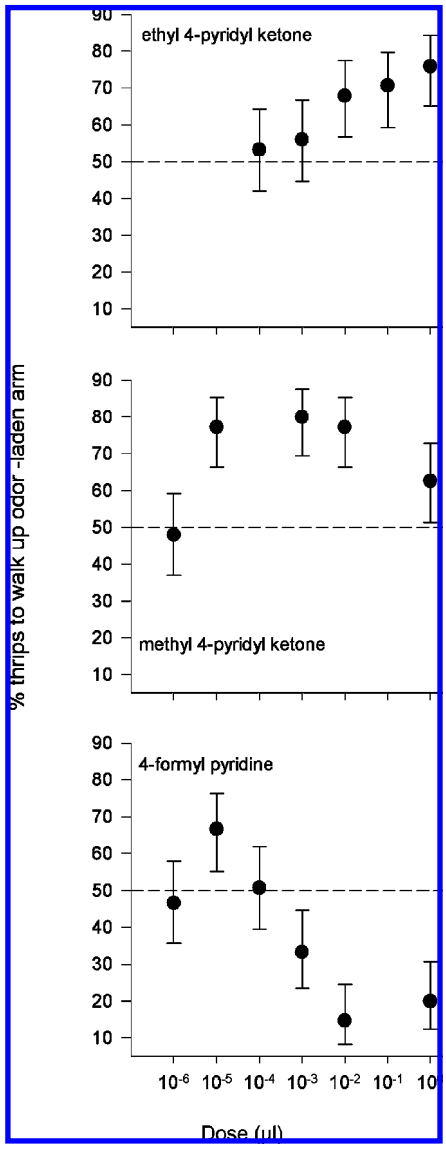

Figure 5. Mean percentage (95% confidence limits) of western flower thrips females to walk up an odor-laden arm containing 4-pyridyl ketones or an aldehyde in a Y-tube olfactometer.

4-Pyridyl Ketones and an Aldehyde as WFT Attractants and Repellents. Ethyl 4-pyridyl ketone, which we found to be attractive to NZFT and onion thrips in field trapping experiments (*17*), is an analogue of methyl isonicotinate (**Figure 1**). We tested methyl, ethyl and n-propyl 4-pyridyl ketones against WFT in the Y-tube (**Table 1** and **Figure 5**). The MAD decreased along the homologous series: methyl 10^{-5} µL; ethyl 10^{-2} µL; and propyl was not active at the doses tested (**Table 1**). As with the isonicotinate esters (above), this decline in activity could be due to decreasing vapor pressure (**Figure 6**). Ethyl 4-pyridyl ketone has a very similar molecular size and shape to methyl isonicotinate, but is about ten thousand times less active (**Figure 6**).

4-Formyl pyridine is both a homologue of the 4-pyridyl ketones, with hydrogen instead of the alkyl groups, and an analogue of benzaldehyde (**Figure 1**). 4-Formyl pyridine was significantly attractive at a dose of 10^{-5} µL, but was significantly repellent at higher concentrations: only 15% of thrips chose the odor arm of the Y-tube at a 10^{-2} µL dose (**Figure 5**). Terry et al. (*26*) found that β-myrcene, a compound found in cones of the cycad, *Macrozamia lucida*, attracted its obligate pollinator, *Cycadothrips chadwicki*, at low doses in a Y-tube, but repelled

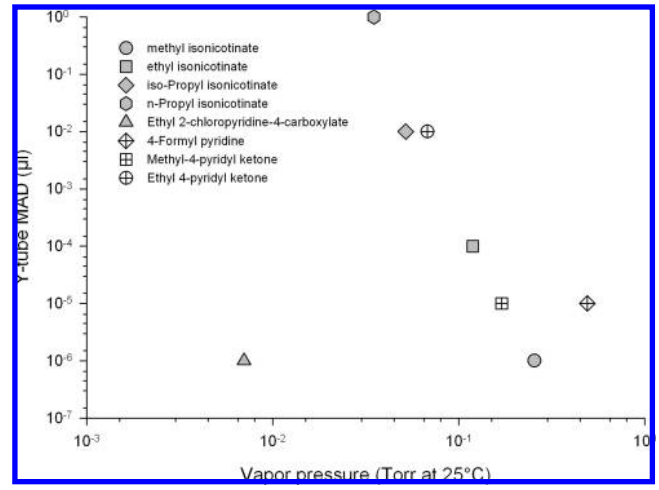

Figure 6. 4-Pyridyl carbonyl compounds' effects on WFT females in the Y-tube bioassay (log minimum attractive dose, MAD; $p < 0.05$) and vapor pressures (log Torr at 25 °C, calculated by ACD software, in the Chemical Abstracts Registry file). 4-Formylpyridine was repellent at higher doses.

it at higher doses. Koschier et al. found that another aromatic aldehyde, salicaldehyde (**Figure 1**), was significantly repellent to WFT at two doses in their Y-tube tests, but did not show significant attractant activity at lower doses (*11*). The repellent activity of compounds such as salicaldehyde and 4-formyl pyridine could be used in push−pull strategies, with a repellent to push thrips off a crop and an attractant to pull thrips to a trap (*16*).

In the light of this finding of a dose-dependent bimodal response for 4-formyl pyridine, the decrease in attractiveness of *p*-anisaldehyde at the highest dose tested (10 ° µL) observed by us (**Figure 2**) and by Koschier et al. (*11*) is interesting. In our results (**Figure 2**) the decrease in attractiveness between 10^{-1} and 10 ° µL is statistically significant, so *p*-anisaldehyde may be repellent at higher doses. This result means that compounds that we only tested at one or two doses (**Table 1**) could show attractant or repellent activities at other doses (see below).

4-Pyridyl Alcohols and Other Derivatives as WFT Attractants and Repellents. 4-(1,3-Dioxolan-2-yl)pyridine is an acetal derivative of 4-formyl pyridine (**Figure 1**) that was significantly attractive to WFT at 5×10^{-1} and 5×10^{-3} µL doses (**Table 1**). 4-Cyanopyridine is an analogue of 4-formyl pyridine (**Figure 1**) that was significantly repellent to WFT at the single 5×10^{-1} µL dose tested (**Table 1**). This compound was not tested further because it is classified as a harmful chemical, which would limit practical applications (the other 4-pyridyl compounds in this study are generally classified as irritants, rather than harmful, in Material Safety Data Sheets). Another alcohol, 4-(2-hydroxyethyl) pyridine (**Figure 1**) attracted WFT at a 10 ° µL dose, but not at two lower doses (**Table 1**). This compound is a 4-pyridyl analogue of 2-phenylethanol, a common component of floral scents that has been shown to attract NZFT and onion thrips (*17*).

The unplanned synthesis of *N*,*N*-di-isopropyl isonicotinamide (**Figure 1**) led to the discovery of thrips attractant activity for another type of 4-pyridyl carbonyl compound, the isonicotinamides. *N*,*N*-Di-isopropyl isonicotinamide was significantly attractive to WFT at the one 5×10^{-1} µL dose tested (**Table 1**), which is surprising from a compound with two isopropyl substituents and a low predicted vapor pressure (<0.001 Torr at 25 °C, calculated by ACD software, in the Chemical Abstracts

Registry file). *N*,*N*-Diethyl isonicotinamide (not yet tested) is a 4-pyridyl analogue of the most well-known insect repellent, *N*,*N*-diethyl *m*-toluamide (DEET), active against many insect species including mosquitoes (*27*).

Selected 4-Pyridyl Carbonyl Compounds as Efficacious WFT Lures. From the Y-tube results discussed above, we selected four 4-pyridyl carbonyl compounds for testing in a commercial greenhouse as potential WFT lures. These were methyl and ethyl isonicotinate, methyl-4-pyridyl ketone, and ethyl-2-chloropyridine-4-carboxylate, which had the lowest MADs and no significant repellent activity. Yellow sticky traps treated with methyl or ethyl isonicotinate did trap significantly more female WFT (up to 14 times) than untreated traps (*28*). Traps treated with methyl-4-pyridyl ketone trapped more female WFT (up to 4.5 times) than control traps, but traps treated with ethyl-2-chloropyridine-4-carboxylate did not increase the capture of female WFT (*28*).

The result for ethyl-2-chloropyridine-4-carboxylate was surprising, since it was a potent attractant for WFT in Y-tube experiments (**Figure 4**). The predicted vapor pressure for ethyl-2-chloropyridine-4-carboxylate is much lower than for the other selected compounds (**Figure 6**) so it could be that the odor plume emanating from this compound was small and/or short-lived in the greenhouse. Also, in the Y-tube there is a continuous airflow carrying molecules that do vaporize directly to the thrips. Therefore, we propose future selection criteria for thrips attractants for field trials are a low MAD in Y-tube experiments combined with moderate vapor pressure.

The WFT results given above, taken with the results for OT and NZFT in our field trial study (*9*), show that 4-pyridyl carbonyl compounds are potent attractants for several thrips species. We now have an example of a 4-pyridyl amide as an attractant, in addition to the ester and ketone derivatives, and the aldehyde (4-formyl pyridine) was found to be an attractant at a low dose. In our field trial paper we pointed out that thrips may never have encountered such 4-pyridyl carbonyl compounds in nature, since they have not been reported from thrips, and only rarely recorded at low levels in plants (references in (*9*)). We propose that the synthetic 4-pyridyl carbonyl compounds bind to olfactory receptors for natural allelochemicals, because of their structural similarity to benzene carbonyl derivatives commonly found in flower scents (see ref *9*).

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