Synthesis and field experiments of the female sex pheromone of sweet potato weevil, *Cylas formicarius*

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Abstract. (*Z*)-3-dodecen-1-yl (*E*)-2-butenoate (**1**) identified as the sex pheromone of sweet potato weevil, *Cylas formicarius* Fabricius, has been successfully synthesized from 3-butyn-1-ol and 1-bromooctane as starting materials. The overall yield via four steps was 60 % calculated on 3-butyn-1-ol. The primary step of the scheme was the stereoselective reduction reaction for $Pd_2(dba)_3$-catalyzed alkyne cis-hydrogenation without using molecular hydrogen. And, this reaction was carried out efficiently with KOH/DMF as the hydrogen source. Next, field trapping experiments were conducted from February to June 2021 at Tien Thuy ward - Chau Thanh district (Ben Tre province) to develop a simple, easy-to-construct, cost-effective, and efficient sex pheromone-baited trap. The main experiments gave positive results such as the relative to sweet-potato foliage, the trap designs, doses of pheromone lure from 0.1 mg to 0.8 mg, and the effect of lure traps with a dose of 0.4 mg. These values can be used well to control the dosage of pheromone in field experiments.

Keywords: (*Z*)-dodec-3-en-1-yl (*E*)-2-butenoate, *Cylas formicarius* Fabricius, $Pd_2(dba)_3$/KOH/DMF, 1-decyne, 1-bromooctane, 3-butyn-1-ol, (*Z*)-configuration, the average number of captured individuals, sweet potato weevil.

Classification numbers: 1.1.4, 4.4.7.

1. INTRODUCTION

In addition to rice and maize, sweet potato is one of the food crops with economic value in Viet Nam. If farmers comply well with VietGAP safety standards for the production model,

sweet potatoes will become a kind of root with high export potential to fastidious markets. Currently, sweet potatoes are being grown in large areas in many provinces of Viet Nam including Vinh Long, Dong Thap, Can Tho, Da Lat, Ha Tinh, and Ben Tre. However, the annual production of sweet potatoes is severely reduced due to weevils as the primary pest. They can kill the vines or render the roots unusable when harvested [1].

The sex pheromone of *C. formicarius* was identified to be (*Z*)-3-dodecen-1-yl (*E*)-2-butenoate (**1**) by R. Heath *et al*. [2] and has been synthesized by many researchers. Notably, the product from the coupling between ethylene oxide (EO) and 1-decyne was reduced to a double bond by the Lindlar catalyst with a yield of over 88 %, [2]. However, the toxicity of EO that produces carcinogens at concentrations above 0.1 *ppm* was a limitation in this synthetic route [3]. The Wittig reaction between 2-(2-bromoethyl)-1,3-dioxolane and oleic acid has been investigated for the synthesis of (*Z*)-alkene including compound (**1**) with a total yield of 48.5 % [4]. In a similar fashion to the coupling, pheromone (**1**) has been synthesized from propane-1,3-diol with a yield of 18.1 % by Pham *et al*. [5]. However, the products from the Wittig reaction contained a ratio of more than 10 % of (*E*)-configuration [6].

Herein, we have described the synthesis and field test of the sex pheromone of sweet potato weevil using 3-butyn-1-ol and 1-bromooctane as starting materials via four steps. The reduction of alkyne was performed in the presence of $Pd_2(dba)_3$ catalyst and hydrogenation source of the KOH/DMF system to obtain cis-alkene as a key step.

2. MATERIALS AND METHODS

2.1. Materials

All commercially available reagents were purchased from Acros Organics Co. and were purified, when necessary, according to the usual procedures described in the literature.

2.2. Methods

2.2.1. Equipment

A Hei-Tec Heidolph heated magnetic stirrer was used for the reactions. Thin layer chromatography (TLC) on aluminum sheets adsorbed layer was performed with Merck silica gel 60F-254. Column chromatography on Merck silica gel 60 (70 - 230 mesh) and flash column chromatography on Merck silica gel 60 (230 - 400 mesh) were used. Nuclear Magnetic Resonance (NMR): ^{1}H NMR, ^{13}C NMR was measured on BRUKER AC 500MHz and 125MHz (Institute of Chemistry - Vietnam Academy of Science and Technology).

2.2.2. Field tests

Test method: In the experimental sweet potato field, the trap was fixed by a wooden bar with the trap door placed across the potato leaves, and rubber stoppers impregnated with pure hexane were the control samples [7, 8]. All baits were placed in opaque plastic bottles containing soap solution (5 g soap in 1200 mL water).

Test site: The test was performed on 1500 m^2 of the sweet potato field for all the biological tests - Tien Thuy ward, Chau Thanh district, Ben Tre province, Viet Nam.

Trap design: Plastic bottles (2 L volume) with 8-10 windows (about 3 cm in diameter and 10 cm from the lid bottle) were used. The traps were always covered with a lid in the field and numbered in order or according to the dose of bait. A soap solution was added about 2 - 3 cm from the trap window of the bottle and was changed every week to avoid the reduced efficiency of decaying individuals [9].

Making a lure for the trap: Clean rubber septa (1.5 cm diameter) as a carrier material were impregnated with pheromone loaded (**1**) in *n*-hexane. The lure solvent in the septa was evaporated for 10 min, and these septa were carefully packed into aluminum bags, labeled, and stored at 0 - 5 °C until testing.

The effect of insect attractant doses: These included five treatments randomly arranged and replicated three times with doses of 0.1, 0.2, 0.4, and 0.8 mg of pheromone (**1**), each dose consisted of three traps and one control sample (*n*-hexane usage) (Figure 1E*)* [10]. All baits were placed in opaque plastic bottles containing soap solution. In addition, some commercial lures (purchased from Can Tho University) were further tested with a dosage of 0.4 mg pheromone. A trial period of 4 weeks (February 22 - March 22, 2021) was applied. Sweet potatoes were grown for 45 days.

The effect of insect attractant duration: Three treatments of the same dose (0.4 mg pheromone (**1**)) and one control sample (*n*-hexane) were arranged and replicated three times. A trial period of 6 weeks (March 1 - April 15, 2021) was applied. Sweet potatoes were grown for 60 days.

The effect of the window height: Five treatments were randomly arranged and replicated three times with NT1: trap window was placed 20 cm below the sweet potato leaves; NT2: trap windows were placed horizontally on the leaves surface; NT3, NT4, and NT5: trap window was 20, 40, and 60 cm higher than the leaves surface; and NT6: control sample (*n*-hexane), respectively. The decoy dose was 0.4 mg of pheromone (**1**). A trial period of 4 weeks (May 15 - June 11, 2021) was applied. Sweet potatoes were grown for about 60 days.

Figure 1. A: opaque plastic trap (OPT); B: clear plastic trap (CPT); C: setup pheromone traps of *Cylas formicarius* in fields; D: *Cylas formicarius* caught with pheromone lures; E: control sample.

The effect of trap material types: Trap windows, consisting of four treatments randomly arranged and replicated three times, were settled horizontally on the surface of sweet potato leaves (*Figure 1C*) with an OPT (opaque plastic trap) (Figure 1A), one OPT-C (control sample 1: soap solution), one CPT (clear plastic trap) (Figure 1B), and one CPT-C (control sample 2:

soap solution). Sweet potatoes were grown for about 60 days. The decoy dose was 0.4 mg of pheromone (**1**). A trial period of 4 weeks (May 15 - June 11, 2021) was applied.

Statistics: The experimental results were treated with SPSS software via One-ANOVA analysis, Duncan's test, with $P < 0.05$ as a significant difference.

2.3. Experimental

Stains of thin-layer chromatography appeared with an aqueous solution of permanganate or 10 % sulphuric acid in ethanol. Tetrahydrofuran (THF) and diethyl ether were distilled in sodium benzophenone under nitrogen before use. The ^{1}H-NMR spectral data were presented in terms of chemical shifts (multiplicity, coupling constant, number of hydrogen). The chemical shifts (δ) and coupling constants (J) were described in *ppm* and hertz (Hz), respectively. The abbreviations of the symbol for multiplicities of splitting patterns included *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), and *br.* (broad). All samples for NMR measurements were dissolved in $CDCl_3$. The deuterated solvent residue $CHCl_3$ was used as the internal standard and calibrated at δ 7.26 *ppm* in ^{1}H-NMR spectra and δ 77.2 *ppm* in ^{13}C-NMR spectra, respectively.

Synthesis of 2-(but-3-ynyloxy)-tetrahydro-2H-pyran (**2**)

The synthesis procedure according to the literature [7] was applied as the preparation method of 6-bromohex-1-yl tetrahydropyran-2-yl ether (or 2-(6-bromohexyloxy)tetra hydrogen-2*H*-pyran) with 3-butyn-1-ol (4.3 g, 60.8 mmol), toluene-*p*-sulfonic acid (104.3 mg, 0.55 mmol) (instead of *p*PTS), 3,4-dihydro-2*H*-pyran (6.64 g, 79.04 mmol) in CH_2Cl_2 (50 mL). The product was cleaned by silica gel column chromatography (10 % diethyl ether/*n*-hexane as eluent solvent) to obtain (**2**) (8.89 g, 95 % yield). Boiling point: 95 $^{\circ}$C/20 mmHg; $n_D^{29} = 1.457$. ^{1}H NMR (*500 MHz, CDCl₃, δppm*): 4.65 (*dd, J* = 3.5 Hz, 1H), 3.81-3.91 (*m*, 2H), 3.49-3.59 (*m*, 2H), 2.50 (*dt, J* = 7.0 Hz, 2.5 Hz, 2H), 1.97 (*t, J* = 2.5 Hz, 1H), 1.69-1.85 (*m*, 2H), 1.51-1.64 (*m*, 4H). ^{13}C NMR (*125 MHz, CDCl₃, δppm*): 98.8, 81.4, 69.2, 65.3, 62.2, 30.5, 25.4, 19.9, 19.4.

Synthesis of 2-(dodec-3-yn-1-yloxy)tetrahydro-2H-pyran (**3**)

A solution of 2 M *n*-BuLi/*n*-hexane (30 mL) was slowly introduced dropwise to a solution of (**2**) (4.9 g, 32 mmol) in anhydrous THF (20 mL) and stirred for 30 min. under argon atmosphere at -78 °C. The reaction mixture was warmed to *r.t* and blended for another 2 hrs. And then, KI (0.66 g, 04 mmol) and 1-bromooctane (5.8 g, 30 mmol) in anhydrous THF (40 mL) were added to the reaction mixture before being refluxed for 16 hrs. After cooling to *r.t*, the reaction was quenched with a sat. $NaHCO_3$ solution. After the separation of the organic layer, the aqueous layer was extracted with *n*-hexane (50 mL × 3). Gathering the organic layers was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to obtain a crude product. Purification of the product by silica gel column chromatography (10 % diethyl ether/*n*-hexane as eluent solvent) gave (**3**) (0.76 g, yield 89 %). Boiling point: 150 - 153 $^{\circ}$C/2 mmHg. ^{1}H NMR (*500 MHz, CDCl₃, δppm*): 4.64 - 4.65 (*m*, 1H), 3.76 3.91 (*m*, 2H), 3.48 - 3.55 (*m*, 2H), 2.43 - 2.47 (*m*, 2H); 2.11-2.15 (*m*, 2H), 1.27 - 1.85 (*m*, 18H), 0.88 (*t, J* = 7 Hz, 3H). ^{13}C NMR (125 MHz*, CDCl₃, δppm*): 98.7, 81.4, 76.7, 66.3, 62.2, 31.8, 30.6, 29.2, 29.1, 29.0, 28.9, 25.5, 22.6, 20.2, 19.4, 18.7, 14.1.

Synthesis of (Z)-3-dodecen-1-ol (**4**)

A mixture of KOH powder (0.14 g, 2.55 mmol), alkyne (**3**) (0.45 g, 1.7 mmol), and (2 % mol) catalyst of $Pd_2(dba)_3$ (37 mg, 0.04 mmol) in a pressurized Pyrex reactor, under nitrogen

atmosphere, was added to degassed DMF (3 mL). This reaction mixture was stirred (magnetic stirrer, 1000 rpm) and heated at 145 °C for 6 hrs. After cooling to *r.t*, the reaction mixture was extracted with *n*-hexane (40 mL × 3), washed with H_2O, and dried over anhydrous $MgSO_4$. The organic solution was filtered and concentrated *in vacuo* to obtain a crude product. Purification of the product by silica gel column chromatography (10 % diethyl ether/n-hexane as eluent solvent) gave (*Z*)-2-(dodec-3-en-1-yloxy)tetrahydro-2*H*-pyran (0.42 g, yield 92 %).

A solution of (*Z*)-2-(dodec-3-en-1-yloxy)tetra hydro-2*H*-pyran (0.4 g, 1.49 mmol) in MeOH (10 mL) and *p*-toluene sulfonic acid (5.4 mg, 0.028 mmol) was mixed by ultrasound (40 W power, 50 % amplitude) for 2 hrs. At the end of the reaction (monitoring by TLC), MeOH was removed, then a sat. $NaHCO_3$ solution (50 mL) was added, and the mixture was extracted with diethyl ether (40 mL × 3). The organic layer was washed with water, and brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. Purification of the crude product by silica gel column chromatography (20 % diethyl ether/*n*-hexane as eluent solvent) gave (**4**) (0.25 g, 90 % yield). Boiling point: 120-125 °C/1 mmHg. ^{1}H NMR (*500 MHz, CDCl₃, δppm*): 5.53-5.58 (*dtt, J* = 10.5 Hz, 7.5 Hz, 1.5 Hz, 1H), 5.33-5.39 (*dtt, J* = 11 Hz, 7.5 Hz, 1.5 Hz, 1H), 3.62-3.65 (*m*, 2H), 2.32-2.35 (*m*, 2H); 2.04-2.08 (*m*, 2H), 1.27 1.54 (*m*, 13H), 0.88 (*t, J* = 7 Hz, 3H). ^{13}C NMR (*125 MHz, CDCl₃, δppm*): 133.6, 124.9, 62.4, 31.9, 30.8, 29.7, 29.5, 29.3, 29.3, 27.4, 22.7, 14.1.

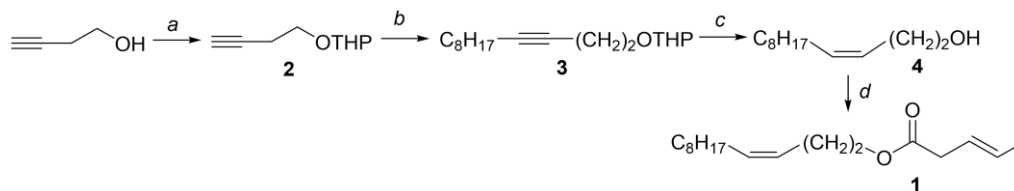*Synthesis of (Z)-3-dodecen-1-yl (E)-2-butenoate* (**1**)

A mixture of alcohol (**4**) (0.25 g, 1.36 mmol), pyridine (0.13 g, 1.7 mmol), and crotonyl chloride (0.18 g, 1.7 mmol) was stirred at 0 °C for 2 hrs, then cooled to *r.t* and stirred for another 24 hrs. After being cooled with ice, the mixture was added with 10 % HCl (20 mL) and extracted with diethyl ether (40 mL× 3). The ether layer was washed with a sat. $NaHCO_3$ solution, water, brine, and dried over anhydrous with $MgSO_4$, then filtered and concentrated *in vacuo* to give a crude product. Purification of the product by silica gel column chromatography (18 % diethyl ether/*n*-hexane as eluent solvent) gave (**1**) (0.3 g, yield 86 %). Boiling point: 104-106 °C/0.1 mmHg. ^{1}H NMR (*500 MHz, CDCl₃, δppm*): 6.93-7.00 (*dq, J* = 15.5 Hz, 7 Hz, 1H), 5.82 5.86 (*dq, J* = 15.5 Hz, 1.5 Hz, 1H), 5.48-5.53 (*dtt, J* = 11 Hz, 7 Hz, 1.5 Hz, 1H), 5.33 - 5.38 (*dtt, J* = 11 Hz, 7.5 Hz, 2 Hz), 4.12 (*t, J* = 7 Hz, 2H), 2.39 (*q, J* = 7 Hz, 2H), 2.03 (*q, J* = 7 Hz, 2H), 1.88 (*dd, J* = 7 Hz, 1.5 Hz, 3H), 1.26 1.36 (*m*, 14H), 0.88 (*t, J* = 7 Hz, 3H). ^{13}C NMR (*125 MHz, CDCl₃, δppm*): 166.6, 144.5, 132.9, 124.4, 122.8, 63.7, 31.9, 29.7, 29.6, 29.5, 29.2, 27.3, 26.9, 22.7, 17.9, 14.1.

3. RESULTS AND DISCUSSION

3.1. Synthesis results

When using the Wittig reaction to synthesize a compound (**1**), it gave a mixture of configuration isomers (*Z*)/(*E*)-alkene [5]. This product has to treat with 15 % $AgNO_3$ on column chromatography and it took more than 2 days for the processing time. So, Trost B. M., *et al.* (1989) used $Pd_2(dba)_2$/CHCl₃, Ar₃P as a catalyst system to reduce alkyne into *cis*-alkene with an efficiency of over 65 % and the selectivity of the geometric isomer was quite good [11]. However, suitable catalyst systems such as $Pd(OAc)_2$/DMF/KOH [12, 13] or PdNPs@pectin/DMF/KOH [14] using KOH/DMF as the hydrogen source could be employed to reduce alkyne to *cis*-alkene. The above two stereoselective palladium-catalyzed transfer semi-hydrogenation without using molecular hydrogen obtained a reduction yield of over 80 % and a *cis*-alkene configuration selectivity of 99 % [13, 14].

In this work, we chose to synthesize pheromone (**1**) from 3-butyn-1-ol and 1-bromooctane as starting materials (Scheme 1) and reduced an alkyne to *cis*-alkene using a catalyst system of $Pd_2(dba)_2/DMF/KOH$.

Scheme 1. Synthesis of *(Z)*-3-dodecen-1-yl *(E)*-2-butenoate (**1**) from 3-butyn-1-ol and 1-bromooctane.

Reagents. a) DHP/*p*-TSSA/CH_2Cl_2; b) 1. *n*-BuLi/THF, -78 ^{o}C; 2. KI, C_8H_{17}Br/THF, reflux 16 hrs; c) 1. $Pd_2(dba)_3$/DMF/KOH, 145 ^{o}C, 6 hrs; 2. *p*-TSA/MeOH, ultrasound; d) crotonyl chloride/Py, 0 ^{o}C, 2 hrs.

This reaction had a yield of 92 %, in which the *cis*-alkene configuration occupied almost absolute. In addition, using the *n*-BuLi agent to convert the triple bond (C≡C) between (**2**) and 1-bromooctane to (**3**) as another primary step in the scheme gave a good result. Therefore, compared with previously published results, the above reaction efficiency was also significantly improved, giving a total yield of 60 % *via* four steps calculated from 3-butyn-1-ol.

The compound (**4**) was the most important precursor of pheromone (**1**). On the ^{1}H NMR spectrum, it showed that the proton signals at δ 4.64 *ppm* (*t, J* = 4 Hz, 1H, -OC*H*O), 3.76-3.91 *ppm* (*m,* 2H, -CH$_2$C*H$_2$*O-), and 3.48-3.55 *ppm* (*m,* 2H, -C*H$_2$*OTHP) of the tetrahydropyranyl group disappeared. Next, the proton signals with chemical shift δ 1.54 *ppm* (*s,* 1H) also appeared, and δ 3.64 *ppm (t, J* = 6.5 Hz, 2H) was assigned to the proton of the -O*H* and -C*H$_2$*OH groups, contributing to the confirmation of the structure of *(Z)*-3-dodecen-1-ol. Moreover, the proton signal of the double bond (-C*H*= and =C*H*-) occurred at δ 5.33-5.39 *ppm* (*dtt, J* = 11 Hz, 7.5 Hz, 1.5 Hz, 1H), 5.53-5.58 *ppm* (*dtt, J* = 10.5 Hz, 7.5 Hz, 1.5 Hz, 1H) with a coupling constant J < 12 Hz, suitable for the *(Z)*-configuration of (**4**) (Figure 2).
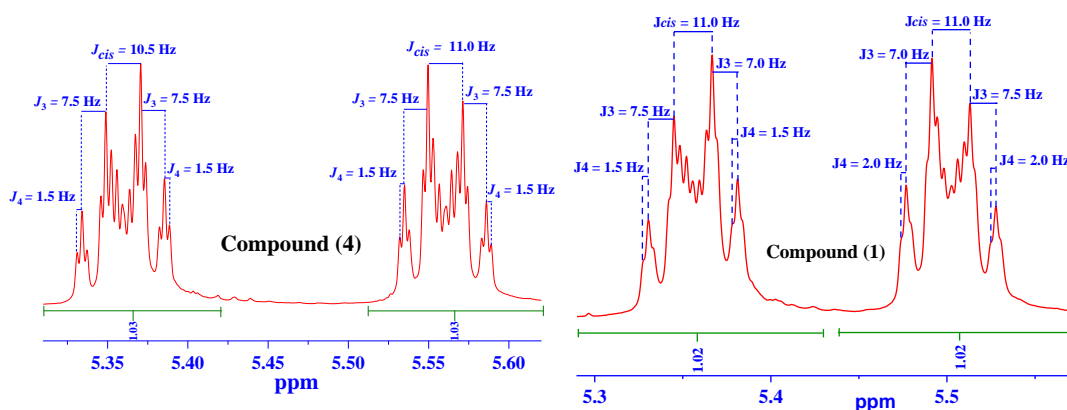

Figure 2. Two groups of signal protons *cis*-alkene of compound of (**4**) at δ_H = 5.33-5.39 *ppm* and δ_H = 5.53 - 5.58 *ppm*. Compound of (**1**) at δ_H = 5.33 - 5.38 *ppm* and δ_H = 5.48-5.85 *ppm* in $CDCl_3$.

The formation of alkenol structure was also demonstrated by the appearance of signals on the ^{13}C-NMR spectrum at positions δ_C 14.1, 62.4, 124.9, 134.6 *ppm* and assigned to carbon

positions as CH₃, C-O, and C=C, respectively. These spectral results were similar to the results in the documents [2, 4, 5, 11].

Analyzing the structure of pheromone (**1**), the results of the NMR spectrum were also consistent with the literature [2, 4, 5, 11]. On the ^{1}H NMR spectrum of (**1**), the proton signals at δ 1.54 *ppm* (*s,* 1H), 3.64 *ppm* (*t, J* = 6.5 Hz, 2H) of the -OH and -CH₂OH groups disappeared. Next, the double bond signal of the ester group with chemical shift δ 6.93-7.00 *ppm* (*dq, J* = 15.5 Hz, 7 Hz, 1H), and 5.82-5.86 *ppm* (*dq, J* = 15.5 Hz, 1.5 Hz, 1H) appeared with a coupling constant J > 15Hz, consistent with the (*E*)-configuration of the ester group. The double signal of a carbon bond with chemical shift δ 5.48-5.53 *ppm* (*dtt, J* = 11 Hz, 7 Hz, 1.5 Hz, 1H), 5.33-5.38 *ppm* (*dtt, J* = 11 Hz, 7.5 Hz, 2 Hz) also appeared with a coupling constant *J* < 12Hz, suitable for the (*Z*) configuration of the main carbon chain. Moreover, the proton signal at δ 4.12 *ppm* (*t, J* = 7 Hz, 2H), 2.39 *ppm* (*q, J* = 7 Hz, 2H), 2.03 *ppm* (*q, J* = 7 Hz, 2H), 1.87 *ppm* (*dd, J* = 7 Hz, 1.5 Hz, 3H), 1.26 1.36 *ppm* (*m,* 14H), and 0.88 *ppm* (*t, J* = 7 Hz, 3H) was assigned to proton positions as -C*H₂*O, -COC*H₂*CH=, -C*H₂*CH=, C*H₃*CH=, the 14 protons from 7 groups of -C*H₂*, and the terminal -C*H₃* group, respectively. Besides, the signal on the ^{13}C NMR spectrum at δ 166.6, 144.5, 124.4 *ppm* was assigned to carbon positions as -C=O, -C=C- of the (*Z*) configuration, and 132.9, 122.8 *ppm* as -C=C- of the (*E*)-configuration, and 63.7 *ppm* of -C-O, and 17.9, 14.1 *ppm* as the carbon from 2 groups of -CH₃, respectively.

Indeed, insect pheromones are always bioactive compounds with high specific sensitivities, so the stereoselectivity in their configuration must be represented by the efficiency in attracting weevils in the field.

3.2. Test results

3.2.1. The effect of insect attractant doses

The number of individuals entering the trap corresponding to the doses of 0.1, 0.2, 0.4, and 0.8 mg of lure was 91.3 ± 3.22, 98.3 ± 1.53, 108.3 ± 1.53, and 132 ± 3.61 individuals/trap/week, respectively, with the significance level of P < 0.05. The results showed that the number of weevils captured according to the above dosages was different (Figure 3), and the dose of 0.4 mg of lure was suitable for a trap (the average number of captured individuals was about 108.3 ± 1.53 individuals/trap/week).
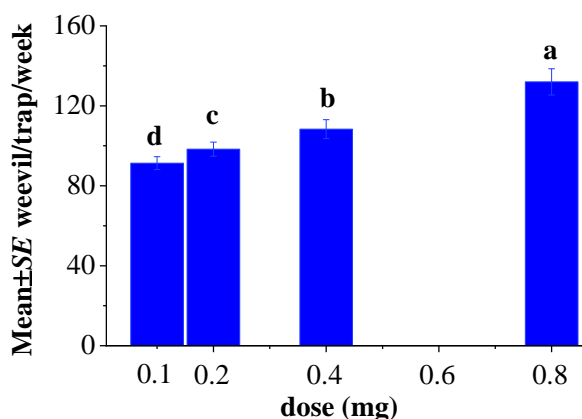

Figure 3. The field test result of sweet potato weevil with different doses.

Although further tests are needed to increase the reliability, the initial results also showed that the efficiency of using our lures was about 30 % better than the lures purchased from Can Tho University. A review of the previously published research results by a team from Can Tho University showed that with doses of 0.1, 0.3, 0.5, 0.7, and 1.0 mg of lure, the average ratio of traps was 23ab, 21.7ab, 27.3ab, 44a, and 39a individuals/trap/week, respectively, which were quite similar to the purchased lures [5]. As for the reason for the difference in attraction efficiency between our lures and the purchased lures, we assumed that these commercial lures could be partially related to the stereoselectivity of the (Z)-configuration synthesized by the Wittig reaction.

3.2.2. The effect of insect attraction time

We noticed that the weevils were very active in the afternoon on sunny days. From day 2 to day 3, the number of weevils captured increased compared to the first day (average 60 individuals/trap). And then, the weevils were less active and less mobile due to rain in the following days. The density of the weevils gradually decreased, and the number of weevils entering the trap suddenly declined on the 6th day. The above results showed that insect activity was very seriously affected by the weather. From week 1 to week 2, the number of weevils captured was reduced (average 115 individuals/trap/week) compared to the first week (141 individuals/trap/week). The number of weevils in traps continued to decrease gradually in the 3rd week (92 individuals/trap/week), and in the 4th week decreased by two times (65 individuals/trap/week) compared to the first week. Although the lures still maintained their ability to attract weevils for two consecutive weeks thereafter, there was no significant difference from the 4th week (Figure 4).
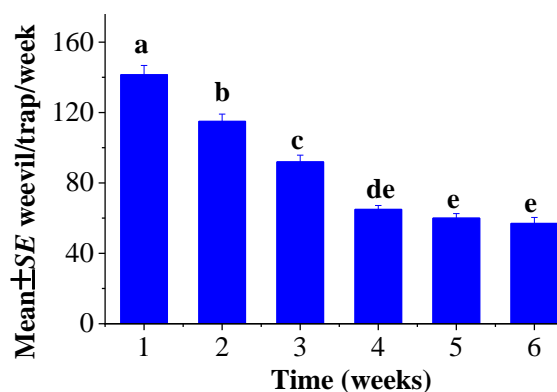

Figure 4. Evolution of the number of *Cylas formicarius* captured for six weeks at a dose of 0.4 mg/trap.

Thus, the dose of 0.4 mg of lures attracted the strongest weevils in the first two weeks and gradually decreased until the 4th week, even though the weevils entering the trap continued (65 individuals/trap/week) (Figure 4). This is important because it helps farmers determine exactly when to change lures to maintain the attractant effect on individuals in the field.

3.2.3. The effect of the window height

When changing the height of the trap window, the number of individuals captured did not have a big difference between NT1 and NT2, but there was a difference with the remaining treatments (Figure 5).
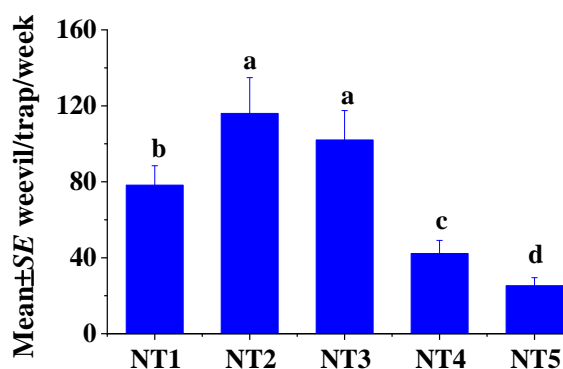
Figure 5. Results of the effect of the window height on the ability to capture individuals.

The average number of captured individuals corresponding to NT2, NT3, NT1, NT4, and NT5 was 116 ± 18, 102 ± 15, 78 ± 10, 42 ± 6, and 25 ± 4 individuals/trap/week, respectively. Therefore, the trap windows of NT2, which were placed horizontally on the surface of sweet potato leaves, were chosen afterward for the field test. This result is consistent with the previous publication of M. Dilipkumar *et al.*, according to which traps placed horizontally on potato leaves attracted the most individuals, and the number of individuals entering the trap decreased with increasing altitude [5].

3.2.4. The effect of trap material types

The effect of individuals captured among OPT, CPT (with pheromones), and the control sample (OPT-C and CPT-C without pheromones) was not significantly different for the trap material type. However, the number of individuals (Table 1) entering OPT (105 individuals/trap/week) was 1.26 times higher than CPT (83 individuals/trap/week).

Table 1. The effect of trap material types on the captured individuals.

Treatments	Dosages (mg)/trap	Medium of individuals/trap/week
OPT	0.4	105.0a
OPT-C	0.0	0.0b
CPT	0.4	83.0a
CPT-C	0.0	0.0b

Numbers in the column followed by the same letter are not significantly different at the 5 % level of Duncan's test.

These results also showed that traps made of opaque plastic-type (Figure 1A) should be selected for field testing.

4. CONCLUSIONS

The female insect pheromone of the sweet potato weevil, *Cylas formicarius*, *(Z)*-3-dodecen-1-yl *(E)*-2-butenoate (**1**) was synthesized from 3-butyn-1-ol as the starting material and gave a total yield of over 60 % of via four steps. The stereoselective reduction of alkyne to

cis-alkene using KOH/DMF as the hydrogen source in the presence of $Pd_2(dba)_3$ catalyst showed high efficiency. Therefore, the $Pd_2(dba)_3$ catalyst system in KOH/DMF was a suitable choice for the synthesis of *cis*-alkenes containing one or more double bonds with a reaction time of 6 hours.

The field test results showed that the appropriate dose was 0.4 mg/bait, and the capability of lures was maintained well for 28 days. The material traps made from opaque plastic attracted individuals more effectively than clear plastic and trap windows were suitable for catching individuals when placed across the surface of the potato leaves.

CRediT authorship contribution statement. Le Van Dung: Experiments, collecting and processing field test results, and writing drafts of the manuscript. Nguyen Cong Hao: Methodology and supervision. Nguyen Thanh Danh: Formal analysis. Ngo Le Ngoc Luong: Formal analysis. Nguyen Thuy Duong: Experimental support. Nguyen Thi My Thao: Experimental support. Dang Chi Hien: Methodology, supervision, organized research, and completed the manuscript.

Declaration of competing interest. We have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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