

Syntheses of (*Z,E*)-5,7-Dodecadienol and (*E,Z*)-10,12-Hexadecadienol, Lepidoptera Pheromone Components, via Zinc Reduction of Enyne Precursors. Test of Pheromone Efficacy against the Siberian Moth

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Efficient syntheses of (*Z,E*)-5,7-dodecadienol, a pheromone component of the Siberian moth, *Dendrolimus superans sibiricus*, and (*E,Z*)-10,12-hexadecadienol, a pheromone component of various Lepidoptera pheromones, were accomplished by cis reduction of the corresponding enynols with activated zinc. The most energetic reagent was zinc galvanized with copper and silver (Zn/Cu/Ag) that achieved rapid and high-yield reduction in methanol–water. The stereoselectivity of semi-hydrogenation was $\geq 98\%$. A process whereby zinc dust was continuously activated throughout the reduction with an acid was also satisfactory (95–98% cis). Field evaluation of the 1:1 mixture of (*Z,E*)-5,7-dodecadienol and (*Z,E*)-5,7-dodecadienal with the Siberian moth in Russia showed that the rubber septa pretreated with compound and stored at $-80\text{ }^{\circ}\text{C}$ were as effective as freshly treated septa. Moth responses to septa aged in open air indicated that lure effectiveness declined significantly after 2 weeks of aging. Thus, if rubber septa are used as pheromone dispensers in Siberian moth traps monitoring, they should be replaced biweekly with fresh septa for optimal trap effectiveness.

KEYWORDS: (*Z,E*)-5,7-Dodecadienol; Siberian moth; *Dendrolimus superans sibiricus*; (*E,Z*)-10,12-hexadecadienol; pheromone; zinc reduction

INTRODUCTION

The Siberian moth, *Dendrolimus superans sibiricus* Tschetverikov, is a destructive defoliator of conifer forests throughout northern Asia. Recent outbreaks caused severe damage to more than 8 million hectares of fir and larch forests in Siberia and the Far East, Russia. This species does not currently occur in North America, but the moth is a potential threat to U.S. forests (1). Should the Siberian moth become established in North America, it could have an adverse impact on forest environmental quality and production, resulting in economic damage from restrictive internal and external quarantines on trade.

The capability to monitor potentially damaging exotic insect populations is critical to preventing the accidental establishment of invasive insects at ports of entry.

A semiochemical-based monitoring for this species was recently established with the discovery by Klun et al. (2) that a 1:1 blend of (*Z,E*)-5,7-dodecadien-1-ol (*Z5,E7*-12:OH) and (*Z,E*)-5,7-dodecadienal (*Z5,E7*-12:Ald) was as attractive to Siberian moth males as virgin females in field trapping experiments conducted in 1998. A Russian group subsequently identified *Z5,E7*-12:OH and *Z5,E7*-12:Ald in the volatiles produced by Siberian moth females and reported their attractiveness to males in laboratory studies (3). Finally, Chinese scientists confirmed that the same two compounds are the major pheromone components of *D. superans* (4). *Z5,E7*-12:OH and *Z5,E7*-12:Ald and their geometric isomers have also been found in other *Dendrolimus* spp. (5).

Because the composition of a Siberian moth pheromone had been positively identified, we decided that it would be appropriate to develop a reliable and easy to scale-up synthetic methodology for producing large amounts of pheromone for population monitoring in regions threatened by invasion and possibly for mass trapping and mating disruption.

Z5,E7-12:OH was synthesized in the literature using different approaches including cis reduction of an enyne precursor with

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a stereodefined trans double bond. This route seemed attractive due to the availability of starting (*E*)-7-dodecen-5-yn-1-ol through the palladium-catalyzed alkylation of tetrahydro-2-(5-hexynyloxy)-2*H*-pyran with (*E*)-1-iodo-1-hexene (6). Ando et al. (6) reported that Lindlar reduction of (*E*)-7-dodecen-5-yn-1-ol lacked selectivity, providing a mixture of (*Z,E*)-diene and monoene compounds from which the desired product was isolated by chromatography on silica impregnated with silver nitrate. Stille and Simpson (7) used hydroboration of the protected (*E*)-7-dodecen-5-yn-1-ol to achieve high yield and purity of the pheromone. In the present study, we applied an activated zinc hydrogenation technique to synthesize (*Z,E*)-5,7-dodecadien-1-ol from (*E*)-7-dodecen-5-yn-1-ol. This method was selected over other cis-reduction techniques because of its simplicity and propensity to furnish conjugated dienes, including insect sex pheromones, without significant side reactions (8–13). In particular, zinc activated with copper and silver had been the reagent of choice in cis reduction of the conjugated trienes (10). To our knowledge, there were no reports on the use of Zn/Cu/Ag reagent in pheromone synthesis. We also discuss the application of Zn reduction to the synthesis of (*E,Z*)-10,12-hexadecadienol (*E10,Z12-16:OH*, or bombykol), a sex pheromone component of *Bombyx mori* (L.) (14) that had been previously synthesized through hydroboration of an enyne precursor (15). *E10,Z12-16:OH* and *E10,Z12-16:Ald* are also known as pheromone components of several other insects (15, 16 and references therein) including the pests pickleworm, *Diaphania nitidalis* (Stoll) (17), and melonworm, *Diaphania hyalinata* (L.) (18).

MATERIALS AND METHODS

Chemical Analytical Methods. ¹H NMR spectra were recorded in CDCl₃ with TMS as an internal standard on a Bruker QE-300 spectrometer. ¹H NMR coupling constants are reported in Hz. GC was performed on a Shimadzu 17A gas chromatograph using a 60 m × 0.25 mm RTX-1701 column (Restek Corp.) or a 60 m × 0.25 mm DB Waxter column (J&W Scientific). Hydrogen was used as a carrier gas. EI mass spectra (70 eV) were obtained with a Hewlett-Packard 5971 GC-MS equipped with 30 m × 0.25 mm DB-5 (J&W Scientific) column. Flash chromatography was carried out with 230–400 mesh silica gel (Whatman). Reagents and solvents were purchased from Aldrich unless otherwise specified. Tetrahydrofuran (THF) was dried by distillation from sodium–benzophenone ketyl under N₂. Mention of a proprietary company or product does not imply endorsement by the U.S. Department of Agriculture.

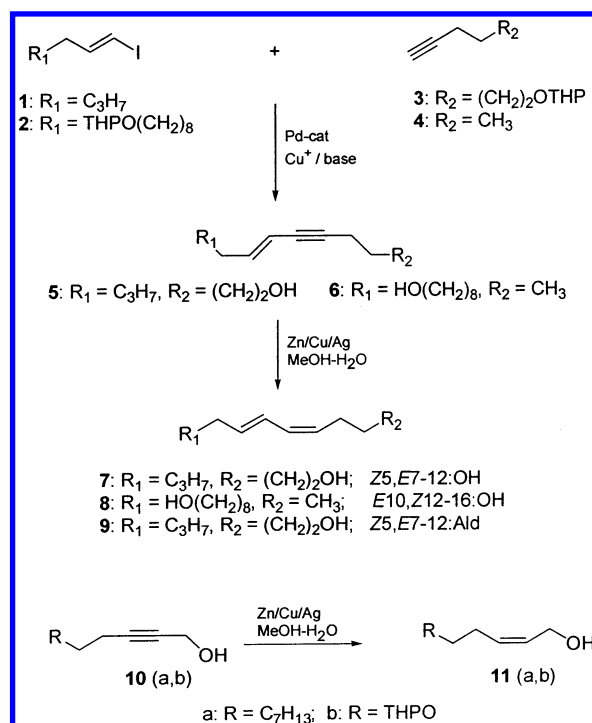
Syntheses. The syntheses of the pheromones are outlined in Scheme 1.

(*E*)-1-Iodo-1-hexene (**1**) was prepared according to Stille and Simpson (7) by hydroalumination–iodinolysis of 1-hexyne. (*E*)-Tetrahydro-2-[(11-iodo-10-undecenyl)oxy]-2*H*-pyran (**2**) was synthesized by hydrozirconation–iodinolysis of the corresponding tetrahydro-2-[(10-undecynyl)oxy]pyran (7). The crude product containing ~10% tetrahydro-2-[(10-undecynyl)oxy]-2*H*-pyran was carried on to the next step. (*E*)-Tetrahydro-2-[(5-hexynyloxy)-2*H*-pyran (**3**) was made by a standard procedure from the commercially available 5-hexyn-1-ol and 3,4-dihydro-2*H*-pyran.

(*E*)-7-Dodecen-5-yn-1-ol (**5**) was obtained by the coupling of compounds **1** and **3** as described in Klun et al. (2) followed by deprotection of the (*E*)-tetrahydro-2-[(7-dodecen-5-ynyl)oxy]-2*H*-pyran. The compound of 99% purity was used in the reduction step.

(*E*)-10-Hexadecen-12-yn-1-ol (**6**). The synthesis was accomplished by coupling of **2** with 1-pentyne (**4**) according to a procedure described by McElfresh and Millar (15) for the unprotected (*E*)-11-iodo-10-undecen-1-ol (**2**, R₁ = HO(CH₂)₈). To a slurry of *trans*-dichlorobis-(triphenylphosphine)palladium(II) (263 mg, 0.375 mmol, Strem Chemicals) in dry THF (5 mL) were added sequentially a solution of **2** (3.072 g, 8.1 mmol) in THF (20 mL), CuI (263 mg, 1.377 mmol), and

Scheme 1



1-pentyne (1.311 g, 19.28 mmol). The mixture was cooled to 5–10 °C, and diisopropylamine (4.16 mL) was added dropwise. After a brown precipitate formed, the mixture was stirred for 1.5 h and poured into hexane (100 mL). The mixture was filtered through Celite 521. The brown solution was washed with saturated aqueous NH₄Cl, dried with Na₂SO₄, and concentrated. The crude product (2.98 g) was refluxed in methanol (20 mL) with a few crystals of *p*-toluenesulfonic acid monohydrate to remove the THP group. The mixture was worked up by addition of ~1 g of NaHCO₃, removal of most of the MeOH by rotary evaporation, and partitioning the residue between water and hexane/ether 1:1. The organic extract was washed with brine, dried, concentrated, and purified by flash chromatography (hexane/ethyl acetate, 7:3), yielding **6** (1.510 g). The product was further purified by chromatography on SiO₂–AgNO₃ (hexane/ethyl acetate, 7:3) to give (*E*)-10-hexadecen-12-yn-1-ol (1.0 g) of ≥95% purity by GC.

(Z,E)-5,7-Dodecadien-1-ol (7, Table 1, Entry 4). Zinc dust (11.16 g, 279 mmol) from a freshly opened bottle was treated with 25–30 mL of 3% HCl for 1–2 min, and then the liquid was decanted. This was repeated two more times, after which the zinc slurry was rinsed repeatedly with distilled water to remove traces of acid. A solution of copper(II) acetate hydrate (1.556 g, 7.78 mmol) in 20 mL of hot water was added slowly to the zinc slurry while cooling in an ice bath. The mixture was stirred for 10–15 min, and a solution of silver nitrate (1.852 g, 10.87 mmol) in 20 mL of water was added likewise. The resulting mixture was filtered, and the active zinc reagent was suspended in a mixture of 20 mL of MeOH and 30 mL of water. A solution of (*E*)-7-dodecen-5-yn-1-ol (1.989 g, 11.11 mmol) in 10 mL of MeOH was added at once, and the mixture was stirred at 50–60 °C for 11 h under an N₂ atmosphere. Upon completion of the reaction (GC on RTX-1701), the unreacted Zn/Cu/Ag was filtered off on a glass filter and washed with 10 mL of MeOH and then with a mixture of 40 mL of MeOH and 5 mL of 10% HCl. The filtrate was concentrated to remove most of the MeOH and extracted with 1:1 ether/hexane (5 × 50 mL). The extract was washed with NH₄Cl solution, dried with Na₂SO₄, and evaporated to leave (*Z,E*)-5,7-dodecadien-1-ol (**7**) (1.75 g, 87% yield, purity 98%). The isomer distributions in the reduction products were found by acetylation (AcCl, Py) and GC analysis on DB-Waxter column.

¹H NMR: 0.90 (t, *J* = 6.5, H-12), 1.20–1.70 (m, 8H, H-2,3,10,11), 2.10 (dt, *J*₁ ≈ *J*₂ = 7.5, H-4), 2.20 (dt, *J*₁ = *J*₂ = 7.0, H-9), 3.65 (t, *J* = 6.5, H-1), 5.29 (dt, *J*₁ = 11.0, *J*₂ = 7.5, H-5), 5.67 (dt, *J*₁ = 15.0, *J*₂ = 7.5, H-8), 5.96 (dd, *J*₁ = *J*₂ = 10.5, H-6), 6.29 (dd, H-7). MS:

Table 1. Cis-Reduction of Acetylenic Alcohols with Zinc

entry	starting compd (mmol)	reagent			solvent/ <i>T</i> (°C)	time (h)	conversion (%)	stereomeric purity ^a (%)	product (isolated yield, %)
		Zn (mmol)	Cu (mmol)	Ag (mmol)					
1	5 0.27	13.8	0.4	0.5	MeOH–H ₂ O, 1:1, 60–65	5.5	99	98	7
2	5 0.27	6.8	0.2	0.3	MeOH–H ₂ O, 1:1, 50	14	81	98	7
3	5 5.56	138.0	2.2	2.7	MeOH–H ₂ O, 1:1, 65–75	7	100	99	7 (74)
4	5 11.11	277.8	7.8	10.9	MeOH–H ₂ O, 1:1, 50–60	11	100	99	7 (87)
5	5 0.29	7.0	0.2	0.3	MeOH, 60	5.5	1		
6	5 0.28	7.0	0.2		MeOH–H ₂ O, 1:1, 65	5.5	77	97	7
7	5 0.16	4.1 ^b			MeOH–H ₂ O, 1:1, 60–65	15	99	98	7
8	5 5.6	138.0 ^c			MeOH–H ₂ O, 1:1, 60–65	18	100	95	7 (80)
9	5 0.27	6.9	0.2		dioxane–H ₂ O, 1:1, 80	5.5	92	99	7
10	6 1.31	65.0	2.9	3.3	MeOH–H ₂ O, 2:1, 60–70	6.5	100	97	8 (90)
11	10a 27.9	688.5	19.3	26.2	MeOH–H ₂ O, 1:1, 60–70	2	99	98	11a (93)
12	10b 0.27	6.9	0.2	0.3	MeOH–H ₂ O, 1:1, 60–70	5	99	99	11b

^a GC analyses of the acetates on DB-Waxter. ^b Activated with 100 μ L of 10% HCl after 10 h. ^c 2 mL of 10% HCl was slowly added throughout the run.

182 (M⁺, 2), 164 (5), 135 (3), 121 (8), 97 (13), 93 (28), 79 (96), 67 (100), 55 (44), 41 (73).

(Z,E)-10,12-Hexadecadien-1-ol (8). The reduction was run according to Table 1, entry 10. After the workup described above, compound **8** of 97% purity was isolated by flash chromatography (hexane/ethyl acetate, 7:3) in 90% yield. ¹H NMR: 0.90 (t, *J* = 6.5, H-16), 1.10–1.70 (m, 16H), 2.03–2.18 (m, 4H, H-9, H-14), 3.62 (t, *J* = 6.5, H-1), 5.29 (dt, *J*₁ = 10.5, *J*₂ = 7.5, H-13), 5.64 (dt, *J*₁ = 15.0, *J*₂ = 7.5, H-10), 5.94 (dd, *J*₁ = *J*₂ = 11.0, H-12), 6.29 (dd, H-11). MS (acetate, *m/z*): 280 (M⁺, 18), 237 (1), 220 (4), 177 (3), 163 (5), 149 (11), 135 (21), 121 (29), 109 (23), 96 (50), 81 (66), 67 (100), 55 (29), 43 (50).

(Z,E)-5,7-Dodecadienal (9). (Z,E)-5,7-Dodecadien-1-ol (592 mg, 3.29 mmol) was oxidized with pyridinium chlorochromate (1.862 g, 8.64 mmol) in the presence of sodium acetate (803.6 mg, 9.8 mmol) in dry methylene chloride (40 mL) at 0 °C, following the procedure by Corey and Suggs (19) to provide (Z,E)-5,7-dodecadienal (285 mg, 48% yield) after flash chromatography (hexane/ethyl acetate, 95:5). MS: 180 (M⁺, 15), 151 (7), 136 (20), 79 (100). Purity: 99% by GC.

(Z)-2-Dodecen-1-ol (11a) was synthesized according to Table 1, entry 11, by reduction of 2-dodecyn-1-ol with Zn/Cu/Ag as a reducing agent. ¹H NMR: 0.88 (t, *J* = 7.0, H-12), 1.27 (m, H-5 through H-11, 14 H), 2.08 (dt, *J*₁ = *J*₂ = 7.0, H-4), 4.20 (d, *J* = 5.5, H-1), 5.55 (m, H-2,3).

(Z)-5-[(Tetrahydro-2H-pyran-2-yl)oxy]-2-penten-1-ol (11b) was prepared by reduction of 5-[(tetrahydro-2H-pyran-2-yl)oxy]-2-pentyn-1-ol with Zn/Cu/Ag (Table 1, entry 12).

¹H NMR: 1.30–1.85 (m, 6H), 2.42 (dt, *J*₁ = *J*₂ = 7.0, H-4), 3.47 (m, 2H), 3.80 (m, 2H), 4.14 (d, *J* = 6.5, H-1), 4.60 (m, 1H), 5.60 (m, H-2 or H-3), 5.84 (m, H-2 or H-3). The NMR data are in agreement with literature values (20).

Insect Trapping. Gray rubber septa (No. 10600275, The West Co., Kearney, NE) were extracted with acetone in a Soxhlet extractor prior to use. Five sets of 10 septa were numbered 1–5 and positioned large end up on a plastic sheet with double sticky tape. Each septum was treated with 12.2 μ L of a solution containing 164 μ g of a 1:1 mixture of Z5,E7-12:OH and Z5,E7-12:Ald per 1 μ L of heptane (2 mg of sex attractant/septum). The solution was stored at –80 °C when not in use. Septa (treatments 1–5) were aged in the laboratory (ca. 22 °C) for 0, 14, 28, 53, and 90 days, respectively. At the end of each aging period, septa were transferred to a screw-cap liquid scintillation vial, purged with nitrogen, sealed, and held at –80 °C until they were shipped to

Russia. On the day the vials were shipped, 10 additional septa (treatment 6) were freshly treated with 2 mg of sex attractant and sealed in a nitrogen-purged vial.

Trapping studies were conducted in the larch (*Larix sibirica*, Ledeb.) forest in the south-eastern foothills of Kuznetskiy Alatau mountains (Shira region of the Khakass Republic, South Siberia, Russia). We used standard gypsy moth milk-carton traps (21) with wide (2.5 × 3.0 cm) entrance holes. A replicate consisted of six traps sequentially baited with treatments 1–6, and the study consisted of 10 replicates. The traps were positioned ca. 1.5 m from the ground on the periphery of larch tree crowns in line with 200–250 m between them along a logging road through the forest. Moths entering the traps were killed by an insecticidal (4 cm × 1.3 cm Vapona) strip placed in the bottom of the trap. Siberian moth population density was low at the location of the experiment. A standard sampling procedure (22) used in late May for estimating overwintering 3–4 instar larval density of the species indicated only 0.08 larvae per tree.

Traps were placed on July 5, 2001, and then checked on July 6, 7, 9, 11, 13, 15, and 17. After being checked, each trap was moved to the next trap location. Temperature data were collected at 4-h intervals using two HOBO temperature loggers (ONSET Computer Corp., Bourne, MA), positioned in the larch crowns. The average night temperatures were calculated as an average of four temperature readings from 8:00 p.m. to 8:00 a.m. During the course of the trapping, the temperature ranged from 18 to 24 °C, and there were no rainy days.

Statistical Methods. Counts of trapped male moths in each replicate were summed over a 6-day period (July 6–11). Moth captures declined after July 11, 2001, and these were not included in the analysis. A square root transformation of the summed counts was taken to stabilize the variances. The transformed counts were analyzed using Proc Mixed in SAS (23), which can estimate mixed linear models, with treatment as the fixed independent variable and replicate as the random independent variable. A multiple comparison of all pairs of treatments was conducted using the Tukey–Kramer *p*-value adjustment.

RESULTS AND DISCUSSION

The results of the zinc reductions of enyne alcohols **5** and **6** are summarized in Table 1. The active Zn reagent prepared by treatment of Zn with Cu(OAc)₂ and AgNO₃ (10) easily and stereoselectively reduced the enynol **5** in methanol–water

Table 2. Mean Male Siberian Moth Captures and Their Standard Errors of the Square Root of Summed Counts of Moths Trapped over a 6 Day Period, with Different Letters Indicating Statistically Distinguishable Groups

treatment no.	septom age (days)	mean captures/trap
1	0	3.77 (0.27) a
6	0 (fresh)	3.31 (0.27) ab
2	14	2.43 (0.27) bc
3	28	2.03 (0.27) c
4	53	0.87 (0.27) d
5	90	0.48 (0.27) d

(Table 1, entries 1 and 2). Apparently, (Z,E)-5,7-dodecadien-1-ol (**7**) has high affinity for Zn/Cu/Ag reagent and could be efficiently recovered only after extensive washing of the slurry with methanol acidified with aqueous HCl (Table 1, entry 4, compare with methanol only, entry 3). Importantly, the reduction was very clean, and further purification of **7** was not necessary. Several reduction procedures involving a Zn/Cu reagent have been reported using an alcohol as solvent (11, 24). However, the reduction of **5** with Zn/Cu/Ag in pure MeOH was totally inefficient (Table 1, entry 5). A Zn/Cu reagent was found effective if the reduction was run in a dioxane–water mixture (Table 1, entry 9), apparently because of higher reaction temperature (9). Interestingly, with Zn powder taken from a fresh bottle and activated with acid before use, the reduction of (E)-7-dodecen-5-yn-1-ol stalled at about 20% conversion but was driven nearly to completion by adding some aq HCl to the mixture (Table 1, entry 7). On a larger scale, adding 10% HCl slowly throughout the run allowed the reduction to go to completion with reasonably good stereochemistry (Table 1, entry 8). Mäeorg and Timoteus (9) reported that the most vigorous cis reduction of the triple bond with Zn/Cu occurred at pH ~6 and below. It appears that not only the reduction rate but also the stereochemistry may be dependent on the amount of acid added. Thus, an optimum pH could possibly be found to promote the reaction but not to significantly decrease cis stereoselectivity. Zn/Cu/Ag reagent was also very efficient in the semi-hydrogenation of enynol **6** providing E10,Z12-16:OH (**8**) in 90% yield (Table 1, entry 10). The last two entries in Table 1 demonstrate the applicability of the Zn/Cu/Ag reagent to the rapid and highly stereoselective cis reductions of propargylic alcohols. The resulting allylic alcohols are useful intermediates in pheromone syntheses. (Z,E)-5,7-Dodecadien-1-ol (**7**) was oxidized with pyridinium chlorochromate to (Z,E)-5,7-dodecadienal (**9**). The 1:1 (w/w) blend of the alcohol and the aldehyde was loaded on rubber septa at the 2 mg dose (see above).

Results of the trapping experiment in Russia are shown in Table 2. Clearly, the 1:1 mixture of Z5,E7-12:OH and Z5,E7-12:Ald was biologically effective. There were significant differences among treatments, with longer-aged lures attracting fewer moths. Since treatments 1 and 2 (with a lure age difference of 2 weeks) were significantly different, these results indicate that it is necessary to replace the lures at intervals of less than 2 weeks to best monitor Siberian moth populations. There was no significant difference between treatments 1 and 6, demonstrating that the compounds store well for at least a 90-day period on the gray rubber septa in a nitrogen atmosphere at –80 °C.

In conclusion, activated zinc reduction was efficiently applied in preparation of the two dienic sex pheromones from the corresponding enynes. The results on formulation and trapping the Siberian moth with the synthetic pheromone mixture could

be used by regulatory agencies (such as APHIS) in their operational program of monitoring this potentially invasive species in the U.S.

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