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# Optimization of pheromone lure and trap design for monitoring the fir coneworm, *Dioryctria abietivorella*

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## Abstract

The major components of the sex pheromone of *Dioryctria abietivorella* (Groté) (Lepidoptera: Pyralidae) were recently identified as (9Z,11E)-tetradecadien-1-yl acetate (9Z,11E-14:Ac) and a polyunsaturated, long-chain hydrocarbon (3Z,6Z,9Z,12Z,15Z)-pentacosapentaene (C25 pentaene). The optimal ratio of these components and the role of potential minor components were not fully determined in the initial short report on the pheromone's identification. We tested different ratios of the two major components loaded into grey halobutyl rubber septum dispensers, placed in sticky traps deployed in conifer breeding arboreta. The optimal ratio of the two components was 200 µg 9Z,11E-14:Ac to 2000 µg C25 pentaene. (Z)-9-Tetradecenyl acetate, which had been identified previously in female pheromone gland extracts and five other potential minor pheromone components, were tested individually as additions to the optimized two-component lure blend. None of the ternary blends were more attractive than the optimized two-component blend, at the ratios tested. Two lure adjuvants, a UV stabilizer (Sumisorb 300) and the antioxidant butylated hydroxytoluene, added individually or together, did not affect the attractiveness of the optimized lure blend. The Pherotech diamond sticky trap baited with the optimized lure blend was the most effective trap design among eight types of sticky trap and a bucket style trap that were tested. Traps baited with synthetic lures were as attractive as traps baited with virgin female moths. The optimized two-component lure blend in the Pherotech diamond trap is recommended for monitoring fir coneworm infestations. The availability of an effective synthetic pheromone opens the possibility for control tactics using mating disruption or attract-and-kill techniques.

## Introduction

The fir coneworm, *Dioryctria abietivorella* (Groté) (Lepidoptera: Pyralidae), is one of the most destructive pests of conifer seed cones across North America (Hedlin et al., 1980; Katovich et al., 1989; Moessler et al., 1992). It also attacks the terminal shoots and stems of conifers, particularly at wounds caused by other insects (Heinrich, 1956; Shu et al., 1997). This insect has been a major

problem in conifer seed orchards in British Columbia (BC), Canada (Strong, 2005), the western USA (Haverty et al., 1986; Roe et al., 2006), and eastern Canada (Turgeon et al., 2005). In 2004, it caused an estimated CDN\$ 1 million damage to seed production in BC seed orchards (Strong, 2005). Because of the internal feeding habit of *D. abietivorella* larvae, it is difficult to detect infestations until they are fairly advanced, when damage becomes visible. Consequently, it is a difficult insect to control and the small number of insecticides registered for its control exacerbates the problem. Although some aspects of the life history of this species are known (Lyons, 1957; Trudel et al., 1999), the flight phenology and other life history

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1 aspects of this species are poorly understood, because they  
 2 appear to vary between eastern and western populations,  
 3 and they have not been well documented. As a result, there  
 4 is considerable interest in developing sex pheromone  
 5 baited traps for *D. abietivorella* that would provide a useful  
 6 pest-management tool for seed orchards for detection  
 7 of infestations, for flight phenology and population  
 8 monitoring, and for timing control measures for optimal  
 9 efficacy. Sex pheromones might also be useful in direct  
 10 control of the moth through pheromone-based mating  
 11 disruption or attract-and-kill technology.

12 The major components of the *D. abietivorella* sex  
 13 pheromone were reported as (9Z,11E)-tetradecadien-1-yl  
 14 acetate (9Z,11E-14:Ac) and (3Z,6Z,9Z,12Z,15Z)-pentacos-  
 15 apentaene (C25 pentaene) in a brief rapid communication  
 16 (Millar et al., 2005). In those preliminary trials, the most  
 17 attractive ratio of the two components was 100 µg  
 18 9Z,11E-14:Ac to 500 µg C25 pentaene. However, a full  
 19 range of blend ratios and dosages of these components was  
 20 not tested and an optimum ratio was not fully established.  
 21 Moreover, (Z)-9-tetradecen-1-yl acetate (9Z-14:Ac) was  
 22 detected in female extracts, but when added to the  
 23 two-component blend, it was inhibitory at the dosages  
 24 tested. Further testing of its potential role as a pheromone  
 25 component, and of other possible minor components of  
 26 the pheromone blend, was warranted to establish the most  
 27 effective lure blend.

28 The objectives of this study were to determine the  
 29 operational details for use of pheromone-baited traps for  
 30 *D. abietivorella*. Thus, field trials were conducted to  
 31 optimize the ratio of the two major pheromone components  
 32 for *D. abietivorella*. We then evaluated the effects of 9Z-14:Ac  
 33 and related compounds found in other pyralid moths that  
 34 could potentially act as synergists or antagonists. Because  
 35 polyunsaturated compounds, such as the two main  
 36 pheromone components of the fir coneworm, are subject  
 37 to degradation by ultraviolet (UV) light and oxidation, we  
 38 also investigated whether the addition of a UV stabilizer  
 39 and an antioxidant to the lure blend would enhance lure  
 40 performance. Finally, we tested a number of different trap  
 41 designs. Hanula et al. (1984) had investigated the effects of  
 42 trap design with *Dioryctria* coneworm moths, but the variety  
 43 of designs in that study was limited. Therefore, we tested a  
 44 wider variety of commercially available sticky trap designs,  
 45 as well as a bucket style trap, to find the most suitable trap  
 46 for monitoring populations of *D. abietivorella*.

## 48 Materials and methods

### 49 Pheromone chemicals

50 (Z)-9-Tetradecen-1-ol (9Z-14:OH; >99% chemical purity,  
 51 98.7% isomeric purity), (Z)-9-tetradecen-1-yl acetate

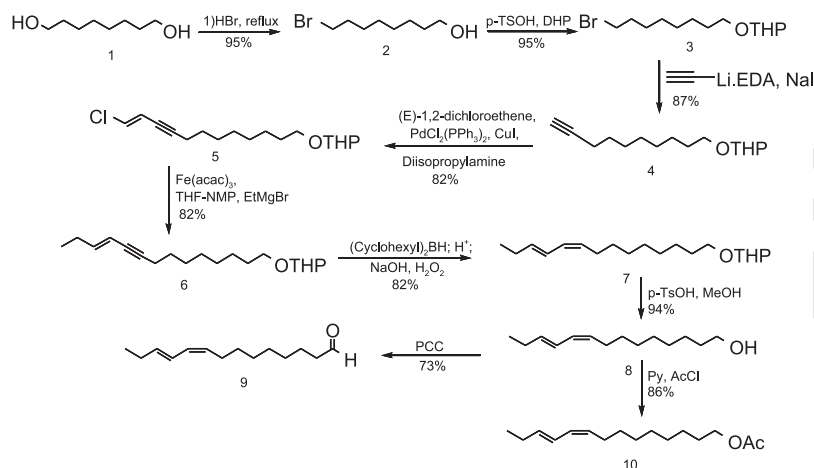
(9Z-14:Ac; >99% chemical purity, 97.5% isomeric purity),  
 (E)-11-tetradecen-1-yl acetate (11E-14:Ac; >99% chemical  
 and isomeric purity), and (9Z,12E)-tetradecadien-1-yl  
 acetate (9Z,12E-14:Ac; >98% chemical purity, >98%  
 isomeric purity) were purchased from Bedoukian  
 Research (Danbury, CT, USA). Because the *E*- and *Z*-isomers  
 of the monoenes were not separable by gas chromatography  
 (GC), the isomeric purity of the monoenes was determined  
 by epoxidizing samples with an excess of *m*-chloroperbenzoic  
 acid at room temperature in methylene chloride for 2 h.  
 The solutions were concentrated to dryness under a stream  
 of nitrogen, then taken up in hexane and washed with 1 M  
 NaOH. The resulting hexane solutions were dried over  
 anhydrous Na<sub>2</sub>SO<sub>4</sub>, and analyzed by GC-mass spectrometry  
 (MS) as described below. The epoxide derivatives from the  
*Z*- and *E*-monoenes were separated to baseline, with the  
*E*-isomers eluting first in all cases.

The C25 pentaene was synthesized in a similar manner  
 to previously described methods (Millar et al., 2005), and  
 was >99% pure by GC (DB-5MS column, see below). The  
 stabilizers 2,6-di-*tert*-butyl-4-methylphenol (= butylated  
 hydroxytoluene, BHT) and Sumisorb 300 [2-*tert*-butyl-6-  
 (5-chloro-2H-benzotriazol-2-yl)-4-methylphenol] were  
 purchased from Aldrich Chemical Co. (Milwaukee, WI,  
 USA). Commercial 9Z,11E-14:Ac obtained from Bedoukian  
 Research was found to be a mixture of positional isomers,  
 and so 9Z,11E-14:OH, 9Z,11E-14:Ac, and 9Z,11E-14:Alc  
 were synthesized as described below (Figure 1) in high  
 chemical (>99%) and isomeric (>99%) purities.

Tetrahydrofuran (THF) was purified by distillation  
 from sodium-benzophenone ketyl under argon. All  
 reactions using air- or water-sensitive reagents were carried  
 out in oven-dried glassware under argon. Unless otherwise  
 specified, solutions of crude products were dried over  
 anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated by rotary evaporation  
 under reduced pressure. Flash chromatography was  
 carried out with 230–400 mesh silica gel. Mass spectra of  
 synthetic intermediates were obtained with a Hewlett-  
 Packard 5970 mass selective detector in electron impact  
 ionization mode (70 eV), coupled to an H-P 5890 gas  
 chromatograph fitted with a 30 m × 0.25 mm ID DB-5MS  
 column (J&W Scientific, Folsom, CA, USA). Nuclear  
 magnetic resonance (NMR) spectra were obtained as  
 CDCl<sub>3</sub> solutions on a Varian INOVA-400 instrument at  
 400 and 100.5 MHz for <sup>1</sup>H and <sup>13</sup>C spectra, respectively.

### Preparation of 1-(tetrahydropyranyloxy)-9-decyne (4)

8-Bromo-octan-1-ol 2 was prepared from 1,8-octanediol 1  
 in 95% yield by treatment with 48% HBr in refluxing  
 toluene as described by Chong et al. (2000). The alcohol  
 was protected as the tetrahydropyranyl (THP) derivative by  
 reaction with dihydropyran and catalytic *p*-toluenesulphonic



**Figure 1** Synthesis of (9Z,11E)-tetradecadien-1-ol (9Z,11E)-tetradecadienal, and (9Z,11E)-tetradecadien-1-yl acetate.

acid (PTSA) (~100 mg) in  $\text{CH}_2\text{Cl}_2$  (95% yield after distillation, bp 102–106 °C, 0.6 mmHg) (Loreau et al., 2001).

Under argon, a three-necked flask was charged sequentially with lithium acetylide–ethylenediamine complex (90%, 9.42 g, 98 mmol), dry DMSO (68 ml), and NaI (1.02 g, 6.8 mmol). 1-(Tetrahydropyranyloxy)-8-bromooctane **3** (20.00 g, 68.2 mmol) was added dropwise over 40 min, keeping the temperature <25 °C. The mixture was stirred overnight at room temperature, then cooled to 0 °C and water was added dropwise. The resulting mixture was poured into water (400 ml) and extracted with hexane (5 × 100 ml). The organic phase was washed with water and brine, dried, and concentrated. The crude product was Kugelrohr distilled (82–84 °C, 0.07 mmHg), affording 14.21 g of alkyne **4** (87% yield).  $^1\text{H}$  NMR:  $\delta$  1.20–1.45 (m, 8H), 1.45–1.65 (m, 8H), 1.65–1.90 (m, 2H), 1.93 (t, 1H,  $J = 2.73$  Hz), 2.17 (td, 2H,  $J = 7.0$  and 2.73 Hz), 3.37 (dt, 1H,  $J = 9.7$  and 6.6 Hz), 3.45–3.53 (m, 1H), 3.72 (dt, 1H,  $J = 9.7$  and 6.8 Hz), 3.81–3.90 (m, 1H), and 4.56 (dd, 1H,  $J = 4.3$  and 2.7 Hz).  $^{13}\text{C}$  NMR:  $\delta$  18.60, 19.93, 25.73, 26.41, 28.68, 28.91, 29.26, 29.55, 29.94, 31.00, 62.58, 67.87, 68.29, 84.98, and 99.08. MS:  $m/z$  237 (M-1, 1), 123 (1), 121 (1), 115 (2), 109 (2), 101 (26), 95 (15), 85 (100), 81 (22), 79 (14), 67 (21), 56 (19), 55 (33), and 41 (25). Spectra were in agreement with those previously reported (Santangelo et al., 2002).

#### Preparation of 1-(tetrahydropyranyloxy)-(E)-12-chlorododec-11-en-9-yne (**5**)

Diisopropylamine (5.95 g, 59 mmol) was added dropwise to a mixture of (E)-1,2-dichloroethene (7.13 g, 73.6 mmol), 1-(tetrahydropyranyloxy)-9-decyne **4** (7.00 g, 29.4 mmol),  $(\text{PPh}_3)_2\text{PdCl}_2$  (0.73 g, 1.04 mmol), and CuI (0.73 g, 3.83 mmol) in dry THF (70 ml) at room temperature

under argon. The mixture was stirred 3 h, then poured into hexane (300 ml), stirred for 10 min, and filtered. The filtrate was washed with saturated aqueous  $\text{NH}_4\text{Cl}$  (2 × 50 ml) and brine, then dried and concentrated. The residue was purified by vacuum flash chromatography (hexane:ethyl acetate, 95:5) affording chloroenyne **5** (7.21 g, 82%).  $^1\text{H}$  NMR:  $\delta$  1.22–1.42 (m, 8H), 1.46–1.64 (m, 8H), 1.66–1.75 (m, 1H), 1.75–1.90 (m, 1H), 2.27 (tdd, 2H,  $J = 7.0, 2.34$  and 0.59 Hz), 3.37 (dt, 1H,  $J = 9.6$  and 6.8 Hz), 3.45–3.53 (m, 1H), 3.72 (dt, 1H,  $J = 9.6$  and 6.8 Hz), 3.82–3.90 (m, 1H), 4.56 (dd, 1H,  $J = 4.6$  and 2.5 Hz), 5.89 (dt, 1H,  $J = 13.7$  and 2.34 Hz), and 6.42 (d, 1H,  $J = 13.7$  Hz).  $^{13}\text{C}$  NMR:  $\delta$  19.60, 19.95, 25.72, 26.41, 28.66, 29.02, 29.26, 29.54, 29.94, 31.01, 62.60, 67.87, 75.88, 93.67, 99.10, 114.52, and 128.92. MS:  $m/z$  298 ( $\text{M}^+$ , trace), 263 (2), 178 (4), 163 (1), 149 (1), 135 (2), 119 (5), 114 (5), 105 (8), 101 (15), 91 (13), 85 (100), 79 (14), 67 (17), 57 (12), 56 (16), 55 (20), 43 (16), and 41 (35). The  $^1\text{H}$  spectrum agreed with that reported previously (Millar, 1990).

#### Preparation of 1-(tetrahydropyranyloxy)-(E)-tetradec-11-en-9-yne (**6**)

A solution of ethyl bromide (4.36 g, 40 mmol) in THF (15 ml) was added dropwise over 4 h to a suspension of Mg turnings (1.46 g, 60 mmol) in dry THF (20 ml) at room temperature under argon. After stirring for 4 h, the resulting solution of Grignard reagent was added dropwise to solution of  $\text{Fe}(\text{acac})_3$  (121 mg, 0.34 mmol), 1-methyl-2-pyrrolidinone (20.45 g, 206 mmol), and 1-(tetrahydropyranyloxy)-(E)-12-chloro-dodec-11-en-9-yne **5** (6.85 g, 22.9 mmol) in THF (35 ml) at –10 °C under argon (color changed from orange to black after the addition of a few drops). Stirring was continued for 30 min at –10 °C, by which time all the starting material had been consumed. The reaction mixture was quenched at 0 °C with saturated

aqueous  $\text{NH}_4\text{Cl}$ , and after separation of the phases, the aqueous phase was extracted with hexane ( $4 \times 50$  ml). The combined organic layers were washed with brine, dried, and concentrated. The crude product was purified by vacuum flash chromatography (hexane: $\text{Et}_2\text{O}$ , 95:5) affording 1-(tetrahydropyranyloxy)-(E)-tetradec-11-en-9-yne **6** (5.48 g, 82%).  $^1\text{H}$  NMR:  $\delta$  0.98 (t, 3H,  $J = 7.6$  Hz), 1.23–1.42 (m, 8H), 1.45–1.63 (m, 8H), 1.66–1.88 (m, 2H), 2.04–2.13 (m, 2H), 2.26 (td, 2H,  $J = 7.0$  and 1.76 Hz), 3.36 (dt, 1H,  $J = 9.6$  and 6.6 Hz), 3.45–3.53 (m, 1H), 3.71 (dt, 1H,  $J = 9.6$  and 6.8 Hz), 3.81–3.90 (m, 1H), 4.56 (dd, 1H,  $J = 4.3$  and 2.7 Hz), 5.43 (dq, 1H,  $J = 15.8$  and 1.76 Hz), and 6.07 (dt, 1H,  $J = 15.8$  and 6.6 Hz).  $^{13}\text{C}$  NMR:  $\delta$  13.30, 19.55, 19.93, 25.72, 26.23, 26.42, 29.05, 29.07, 29.32, 29.57, 29.95, 31.00, 62.57, 67.88, 79.37, 88.98, 99.07, 109.19, and 144.90. MS:  $m/z$  292 ( $\text{M}^+$ , 1), 263 (1), 233 (1), 219 (1), 208 (2), 178 (1), 163 (2), 149 (2), 135 (3), 119 (6), 107 (6), 105 (8), 101 (7), 95 (13), 94 (24), 93 (15), 91 (18), 85 (100), 79 (23), 77 (13), 67 (23), 57 (13), 55 (25), 43 (18), and 41 (36).

#### Preparation of 1-(tetrahydropyranyloxy)-(9Z,11E)-tetradecadiene (7)

A solution of cyclohexene (2.46 g, 30 mmol) in THF (10 ml) was added dropwise to a solution of  $\text{BH}_3$ -dimethylsulfide complex (2 M in THF, 7.5 ml, and 15 mmol) in THF (10 ml) at  $0^\circ\text{C}$  under argon. The mixture was stirred for 2 h between  $-10$  and  $0^\circ\text{C}$  then allowed to warm to room temperature and stirred for 1.5 h. The white slurry of dicyclohexylborane was recooled to  $0^\circ\text{C}$  and a solution of 1-(tetrahydropyranyloxy)-(E)-tetradec-11-en-9-yne **6** (2.92 g, 10 mmol) in THF (5 ml) was added dropwise over 20 min. The resulting mixture was stirred for 2 h at  $0^\circ\text{C}$  and then allowed to warm to  $20^\circ\text{C}$  and stirred an additional 2 h until all the starting material had been consumed. The mixture then was cooled to  $0^\circ\text{C}$ , glacial acetic acid (6 ml) was added, and the mixture was warmed to room temperature and stirred overnight. The solution was cooled again to  $0^\circ\text{C}$  and treated with 6 M aqueous NaOH (20 ml) followed by dropwise addition of hydrogen peroxide (exothermic! 30% wt:wt, 6 ml). The resulting mixture was stirred 30 min, then diluted with water (100 ml), and extracted with hexane ( $4 \times 30$  ml). The combined organic extracts were washed with brine, dried, concentrated, and purified by vacuum flash chromatography (hexane: $\text{Et}_2\text{O}$ , 95:5) affording (9Z,11E)-1-(tetrahydropyranyloxy)-tetradeca-9,11-diene **7** (2.38 g, 82%).  $^1\text{H}$  NMR:  $\delta$  1.01 (t, 3H,  $J = 7.4$  Hz), 1.24–1.42 (m, 10H), 1.48–1.64 (m, 6H), 1.66–1.76 (m, 1H), 1.76–1.88 (m, 1H), 1.88–2.20 (m, 4H), 3.37 (dt, 1H,  $J = 9.6$  and 6.6 Hz), 3.44–3.53 (m, 1H), 3.72 (dt, 1H,  $J = 9.6$  and 6.8 Hz), 3.81–3.91 (m, 1H), 4.56 (dd, 1H,  $J = 4.5$  and

2.5 Hz), 5.29 (dt, 1H,  $J = 10.7$  and 7.6 Hz), 5.68 (dt, 1H,  $J = 15.2$  and 6.6 Hz), 5.93 (t, 1H,  $J = 10.9$  Hz), and 6.29 (ddq, 1H,  $J = 15.2$ , 10.9 and 1.56 Hz).  $^{13}\text{C}$  NMR:  $\delta$  13.90, 19.93, 25.73, 26.11, 26.46, 27.90, 29.44, 29.67, 29.68, 29.94, 29.97, 31.01, 62.56, 67.90, 99.06, 124.91, 128.79, 130.37, and 136.34. MS:  $m/z$  294 ( $\text{M}^+$ , 91), 276 (2), 210 (1), 149 (1), 135 (1), 121 (2), 101 (6), 95 (11), 85 (100), 82 (10), 81 (13), 79 (13), 67 (34), 55 (20), 43 (12), and 41 (30). The  $^1\text{H}$  NMR spectrum was in accord with that previously reported (Bjoerkling et al., 1987).

#### Preparation of (9Z,11E)-tetradecadien-1-ol (8)

A few crystals of PTSA were added to a solution of (9Z,11E)-1-(tetrahydropyranyloxy)-tetradeca-9,11-diene **7** (2.36 g, 8 mmol) in methanol (20 ml) at room temperature and the solution was stirred overnight. After removal of the solvent under vacuum, the residue was diluted with hexane (100 ml) and washed with saturated  $\text{NaHCO}_3$  solution and brine, dried, and concentrated. The crude product was purified by vacuum flash chromatography (hexane:ethyl acetate, 9:1) followed by Kugelrohr distillation ( $94$ – $96^\circ\text{C}$ , 0.10 mmHg) affording 1.57 g (94% yield) of (9Z,11E)-tetradecadien-1-ol **8** containing ca. 5% of the monoene products from over-reduction. The impurities were removed by recrystallization of the distillate from hexane at  $-20^\circ\text{C}$ , providing dienol **8** in >99% chemical and isomeric purity.  $^1\text{H}$  NMR:  $\delta$  1.01 (t, 3H,  $J = 7.6$  Hz), 1.22–1.42 (m, 10H), 1.51–1.60 (m, 2H), 2.06–2.20 (m, 4H), 3.63 (t, 2H,  $J = 6.8$  Hz), 5.29 (dt, 1H,  $J = 10.9$  and 7.6 Hz), 5.69 (dt, 1H,  $J = 15.0$  and 6.6 Hz), 5.94 (t, 1H,  $J = 10.9$  Hz), and 6.29 (ddq, 1H,  $J = 15.0$ , 10.9, and 1.56 Hz).  $^{13}\text{C}$  NMR:  $\delta$  13.89, 25.94, 26.11, 27.89, 29.40, 29.60, 29.68, 29.92, 33.01, 63.31, 124.89, 128.81, 130.32, and 136.39. MS:  $m/z$  210 ( $\text{M}^+$ , 16), 192 (M- $\text{H}_2\text{O}$ , 1), 163 (1), 149 (2), 135 (6), 121 (11), 109 (11), 107 (11), 96 (25), 95 (61), 94 (14), 93 (26), 82 (72), 81 (50), 79 (45), 69 (13), 68 (34), 67 (100), 55 (35), and 41 (28). The  $^{13}\text{C}$  and  $^1\text{H}$  spectra were in agreement with those previously reported (Bjoerkling et al., 1987).

#### Preparation of (9Z,11E)-tetradecadienol (9)

A solution of (9Z,11E)-tetradecadien-1-ol **8** (0.100 g, 0.48 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 ml) was added dropwise to a stirred suspension of pyridinium chlorochromate (PCC, 0.135 g, 0.62 mmol) and powdered 4Å molecular sieve (0.135 g) in  $\text{CH}_2\text{Cl}_2$  (2 ml) at room temperature. The mixture was stirred 4 h, then diluted with diethyl ether (10 ml). The mixture was filtered through a plug of 1 cm Celite and 3 cm silica gel, rinsing with ether. After concentration, the crude product was Kugelrohr distilled ( $90$ – $92^\circ\text{C}$ , 0.4 mmHg) affording **9** in 73% yield (0.072 g; >99% pure).  $^1\text{H}$  NMR:  $\delta$  1.01 (t, 3H,  $J = 7.6$  Hz), 1.24–1.42 (m, 8H), 1.56–1.68 (m, 2H), 2.04–2.10 (m, 4H), 2.41

(td, 2H, J = 7.2 and 1.95 Hz), 5.29 (dt, 1H, J = 10.9 and 7.4 Hz), 5.69 (dt, 1H, J = 15.2 and 6.6 Hz), 5.94 (t, 1H, J = 11.1 Hz), 6.28 (ddq, 1H, J = 15.2, 10.9, and 1.56 Hz), and 9.76 (t, 1H, J = 1.90 Hz). <sup>13</sup>C NMR: δ 13.89, 22.28, 26.11, 27.84, 29.22, 29.33, 29.44, 29.84, 44.13, 124.85, 128.90, 130.19, 136.47, and 203.17. MS: m/z 208 (M<sup>+</sup>, 8), 179 (1), 165 (1), 151 (2), 137 (2), 135 (3), 123 (2), 121 (3), 109 (7), 95 (43), 82 (41), 81 (34), 67 (100), 55 (37), 43 (11), and 41 (56). The <sup>1</sup>H and <sup>13</sup>C spectra agreed with those previously reported (Löfstedt et al., 2004).

#### Preparation of (9Z,11E)-tetradecadien-1-yl acetate (10)

Acetyl chloride (0.05 ml, 0.71 mmol) was added to a stirred solution of (9Z,11E)-tetradecadien-1-ol **8** (0.100 g, 0.48 mmol) and pyridine (0.076 g, 0.96 mmol) in dry diethyl ether (5 ml) at room temperature under argon. The mixture was stirred overnight, then quenched with water and extracted with hexane. The hexane extract was washed with saturated aqueous NaHCO<sub>3</sub>, 1 M HCl, saturated NaHCO<sub>3</sub> solution, and brine, then dried and concentrated. The crude product was Kugelrohr distilled (118–124 °C, 0.25 mmHg) affording acetate **10** in 86% yield (0.103 g). <sup>1</sup>H NMR: δ 1.01 (t, 3H, J = 7.4 Hz), 1.25–1.43 (m, 10H), 1.60–1.65 (m, 2H), 2.03 (s, 3H), 2.06–2.20 (m, 4H), 4.04 (t, 2H, J = 6.7 Hz), 5.29 (dt, 1H, J = 10.7 and 7.6 Hz), 5.69 (dt, 1H, J = 15.0 and 6.6 Hz), 5.94 (t, 1H, J = 10.9 Hz), and 6.29 (ddq, 1H, J = 15.0, 10.9, and 1.56 Hz). <sup>13</sup>C NMR: δ 13.89, 21.25, 26.11 (2C), 27.87, 28.81, 29.37, 29.43, 29.59, 29.90, 64.87, 124.88, 128.84, 130.30, 136.39, and 171.48. MS: m/z 253 (M + 1, 3), 252 (M<sup>+</sup>, 15), 209 (1), 192 (6), 163 (5), 149 (8), 135 (16), 121 (24), 110 (18), 109 (13), 108 (15), 107 (20), 96 (30), 95 (62), 94 (30), 93 (42), 82 (64), 81 (55), 80 (31), 79 (76), 67 (100), 55 (38), 43 (58), and 41 (30). The <sup>1</sup>H spectrum corresponded to that reported by Bjoerkling et al. (1987).

#### Field trials

All field experiments were conducted in 2005 at the Kalamalka Forestry Center, Vernon, BC, Canada (119°16'W, 50°15'N) in Douglas fir, *Pseudotsuga menziesii* Franco (Mirb.) (Pinaceae), breeding orchards, except for Experiment 2 and one test in Experiment 5, which were conducted in an Engelmann spruce, *Picea engelmannii* Parry ex Engelm. (Pinaceae), seed orchard. Trees were in a 2.5 × 4 m spacing, drip irrigated, and topped to 4 m (Douglas fir) or 8 m (Engelmann spruce). A mixed grass/forb ground cover was kept mown to below 15 cm.

Pheromone blends were prepared at the University of California-Riverside as hexane solutions. Appropriate doses of the solutions were loaded into grey halobutyl rubber septa (West Pharma Co., Lionville, PA, USA), and the solvent was allowed to evaporate in a fume hood.

Control septa were loaded with hexane only. The loaded septa were packaged in heat sealed foil pouches and shipped by courier service to the test sites in BC.

Pheromone lures were suspended with a pin inside commercial sticky traps. White wing traps (Pherotech Inc., Delta, BC, Canada) without spacers were used for Experiments 1–3. Experiment 4 used green Delta traps (Pherotech Inc.), and Experiment 5 used various commercial sticky trap designs described below. Traps were hung from branches at a height of 2–2.5 m (Douglas fir) or 4–5 m (Engelmann spruce). They were spaced 18–25 m apart in all directions, and situated at least 10 m from orchard edges.

The *D. abietivorella* moths caught were counted and removed weekly, and trap bottoms (wing traps) or entire traps were replaced as necessary, if the sticky surfaces became ineffective due to coatings of moth scales and/or dust. The sex of a subset of individuals from each experiment was determined by examining the basal portion of the antennae; males possess a series of thickened spines on the basal segments (Neunzig, 2003). Individual moths and several whole traps containing moths from Experiment 1 (trials 1 and 2) were forwarded to Amanda Roe, University of Alberta, Edmonton AB, Canada (currently at University of Minnesota) for species identification by visual assessment of wing patterns (Roe, 2006). Voucher specimens were deposited in the E. H. Strickland Entomological Museum, University of Alberta, Edmonton, AB, Canada.

All experiments except Experiment 5C were randomized complete blocks with blocks being rows of trees, and with treatments randomized along the rows. Experiment 5C was a 4 × 4 Latin Square design with two squares (Steel & Torrie, 1960). Statistical analysis was by general linear model (GLM) (SYSTAT, 2004) with significantly different (P = 0.05) means being separated by Fisher's least significant differences (LSD) test. Data were transformed by log(x + 1) to normalize residuals for Experiment 1 (trials 1 and 2), Experiment 2 (trial 1), Experiment 3, and Experiment 5 (trial 1); all other trials used raw data. Untransformed means are presented with standard errors.

#### Experiment 1: ratio of 9Z,11E-14:Ac to C25 pentaene.

Two trials were conducted with varying ratios of the two identified pheromone components. In the first test, 9Z,11E-14:Ac was held at constant 100 µg per lure, while the C25 pentaene dose was varied. In the second test, the C25 pentaene was held at constant 2000 µg per lure, while the 9Z,11E-14:Ac dose was varied. Treatments were replicated five times in each of the two trials. Baited traps were deployed in the orchards on 16 May and checked weekly until 8 June. Based on the results of these trials, a two-component lure blend consisting of 200 µg

9Z,11E-14:Ac and 2000 µg C25 pentaene loaded on grey halobutyl rubber septa was established as the optimized base lure for subsequent experiments.

*Experiment 2: addition of 9Z-14:Ac.* 9Z-14:Ac has been identified as the major sex pheromone component of several other *Dioryctria* species (Pherolist, 2006), and so it was reasonable to suppose that it might have either synergistic or antagonistic effects when added to the optimized lure blend for *D. abietivorella*. We conducted two trials to determine whether this compound might affect trap catch. In the first trial, doses of 0, 0.66, 2.0, 6.6, or 20.0 µg of 9Z-14:Ac were added to the optimized blend of 200 µg 9Z,11E-14:Ac and 2000 µg C25 pentaene. In the second trial, the blend was spiked with 0, 0.01, 0.033, 0.1, and 0.33 µg of 9Z-14:Ac. Five replicates of each treatment were tested in both trials. The first set of baited traps was deployed on 10 June and checked weekly until 25 July. Traps for the second test were deployed on 28 July and checked weekly until 31 August.

*Experiment 3: addition of other potential pheromone components.* Two micrograms of each of the following compounds were added individually to the optimized lure blend of 200 µg 9Z,11E-14:Ac and 2000 µg C25, to test for any synergistic or antagonistic effects based on their chemical similarity to the diene pheromone component or their presence in pheromones of related pyralid species: (9Z,11E)-tetradecadienal (9Z,11E-14:Ald), (E)-11-tetradecen-1-yl acetate (11E-14:Ac), (Z)-9-tetradecen-1-ol (9Z-14:OH), and (9Z,12E)-tetradecadien-1-yl acetate (9Z,12E-14:Ac). Five replicates of each treatment, including a hexane-treated control, were tested. Baited traps were deployed on 10 June and checked weekly until 25 July.

*Experiment 4: addition of stabilizers to lure blends.* Five replicates of four lure treatments were tested: the optimized lure blend with no stabilizers, the lure blend plus 200 µg of the UV stabilizer Sumisorb 300, the lure blend plus 200 µg of the antioxidant BHT, and the lure blend plus 200 µg each of both stabilizers. Baited traps were deployed on 28 July and checked weekly until 28 September. Statistical analysis was conducted on overall mean trap catches, as well as on mean trap catches for each trapping session.

*Experiment 5: trap designs.* Three trials were conducted to determine the most effective trap design baited with the optimized lure blend. The first trial (19 May–23 June) included three types of sticky traps (white diamond trap, green delta trap, and white wing trap) and a green bucket type trap (Unitrap), all supplied by Pherotech Inc.. The

second trial (4 July–25 August) included Pherocon IIB and IIC traps (white, diamond-shaped sticky traps; Trécé, Adair, OK, USA), white diamond, green delta, and white wing sticky traps (Pherotech Inc.). The wing traps were tested with and without spacers, which increase the separation between the trap top and bottom. The first and second trials had five replicates each. The third trial (6 June–18 July) compared the diamond, delta, and wing traps (without spacers) from Pherotech, and the white Pherocon IC wing trap (without spacers) from Trécé. The third trial had two blocks of a 4 × 4 Latin Square. The first and third trials were conducted in the Douglas fir orchards, and the second trial in the Engelmann spruce orchard.

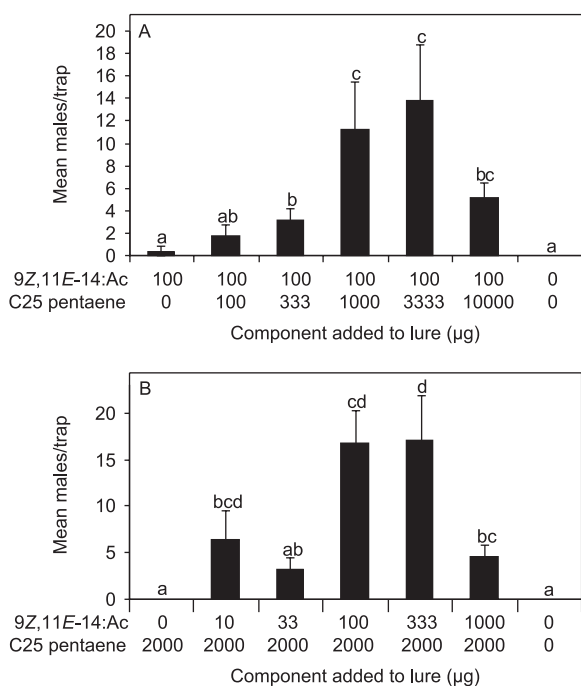
*Experiment 6: comparison of synthetic lure with virgin females.* Virgin females were reared from field-collected pupae housed individually in an eclosion vial. On eclosion, individual female moths were placed in an aluminum screen cage (30 × 30 × 40 mm), which was suspended inside a green delta trap. A 2-dram vial containing a 10% solution of sucrose in distilled water was affixed to the outside of each trap. A cotton wick (3 mm in diameter) ran from the vial through a hole in the trap wall to the caged moth to provide sustenance. Females were matured in their cages in the laboratory at 21 °C and ambient photoperiod for 48 h before being deployed in the field.

Experimental replicates were installed in the field as moths matured (14–15 September 2005). Both replicates consisted of three traps fitted with a vial of sucrose solution and an aluminum screen cage containing either a mature virgin female, the optimized lure blend (200 µg Z9,E11-14:Ac and 2000 µg C25 pentaene), or nothing (i.e., unbaited). Only two replicates were obtained because it was late in the flight season and earlier attempts to deploy female baited traps apparently failed, because females were newly eclosed instead of 2 days old, or were fed only distilled water instead of a sucrose solution.

## Results

### Synthesis of (9Z,11E)-tetradecadien-1-ol, (9Z,11E)-tetradecadienal, and (9Z,11E)-tetradecadien-1-yl acetate

The dienyl acetate pheromone component and the corresponding alcohol and aldehyde were synthesized as shown in Figure 1. Thus, 1,8-octanediol **1** was converted to bromoalcohol **2** (Chong et al., 2000), which was then protected as the THP derivative **3**. Treatment of **3** with lithium acetylide–ethylenediamine complex gave alkyne **4**, which was then coupled with (E)-1,2-dichloro-ethene with CuI and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> catalysts and diisopropylamine as a weak base, yielding chloroenyne **5**. Stereospecific substitution of the chloride with ethylmagnesium bromide



**Figure 2** Mean numbers of *Dioryctria abietivorella* moths caught in sticky traps baited with different ratios of 9Z,11E-14:Ac and C25 pentaene in rubber septum lures. (A) 9Z,11E-14:Ac dose constant at 100 µg per septum with variable doses of C25 pentaene ( $F_{6,24} = 10.69$ ,  $P < 0.001$ ); (B) C25 pentaene dose constant at 2000 µg per septum and variable doses of 9Z,11E-14:Ac ( $F_{6,24} = 10.27$ ,  $P < 0.001$ ). Bars indicate SE; columns capped by different letters are significantly different [Fisher's least significant difference (LSD) test,  $\alpha = 0.05$ ].

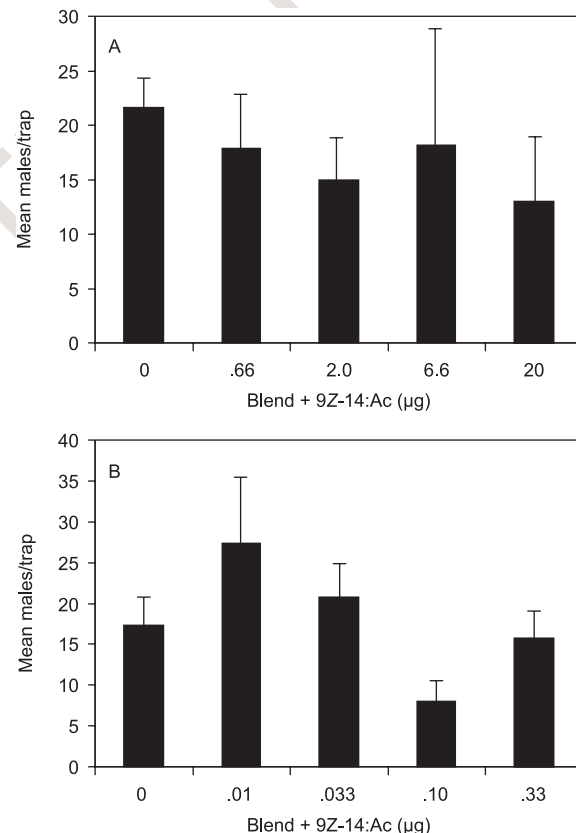
with  $\text{Fe}(\text{acac})_3$  catalyst and 1-methyl-2-pyrrolidinone (THF-NMP) as cosolvent furnished enyne **6** (Cahiez & Avedissian, 1998). Stereoselective *cis* reduction of **6** with dicyclohexylborane gave diene **7** (purity 95% by GC). Removal of the THP group in acidified methanol gave dien-1-ol **8**, which was conveniently purified to >99% chemical and isomeric purity by recrystallization from hexane at  $-20^\circ\text{C}$ . (9Z,11E)-Tetradecadienol **8** was then converted into its corresponding aldehyde **9** and acetate **10** by reaction with pyridinium chlorochromate and acetyl chloride/pyridine, respectively.

#### Field trials

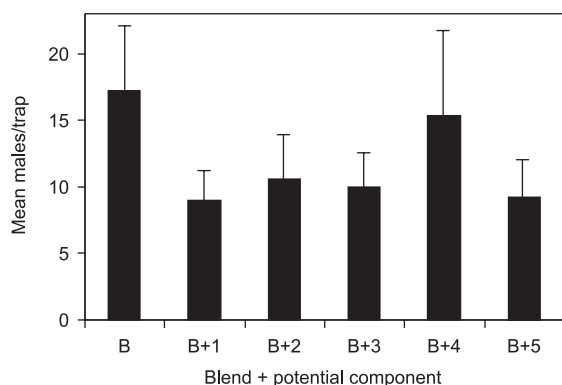
The majority of moths caught in the traps were identified as *D. abietivorella*. A few tortricid, gelechiid, crambid, and noctuid moths (all identified to family only) were caught in some traps. Of the 82 pyralid moths that were submitted for formal identification, all were confirmed to be *D. abietivorella*. All *D. abietivorella* moths ( $n = 264$ ) whose antennae were examined were identified as males.

**Experiment 1: ratio of 9Z,11E-14:Ac to C25 pentaene.** When 9Z,11E-14:Ac was held at constant 100 µg per lure, peak catches occurred with lures loaded with C25 pentaene at doses of 1000 and 3333 µg per lure (Figure 2A). Lures containing 9Z,11E-14:Ac as a single component were minimally attractive. When the C25 pentaene was held at constant 2000 µg per lure, peak catches occurred in traps baited with lures containing 100 or 333 µg 9Z,11E-14:Ac per lure (Figure 2B). The C25 pentaene as a single component was completely unattractive.

**Experiment 2: addition of 9Z-14:Ac.** The addition of 9Z-14:Ac at relatively high doses (0–10% of the amount of 9Z,11E-14:Ac) in the first trial neither increased nor decreased the attractiveness of lures (Figure 3A). At lower rates (0–0.17% of the amount of 9Z,11E-14:Ac), the



**Figure 3** Mean numbers of *Dioryctria abietivorella* caught in traps baited with the optimized lure blend (200 µg of 9Z,11E-14:Ac and 2000 µg C25 pentaene) spiked with variable doses of 9Z-14:Ac. (A) 9Z-14:Ac doses from 0–20 µg per lure [ $F_{4,16} = 1.49$ ,  $P = 0.25$ , data transformed by  $\log(x + 1)$ ]; (B) 9Z-14:Ac doses from 0–0.33 µg per lure ( $F_{4,16} = 2.77$ ,  $P = 0.06$ ; untransformed data). Bars indicate SE. There were no significant differences between treatments in either trial.



**Figure 4** Mean numbers of *Dioryctria abietivorella* caught in traps baited with the optimized lure blend (B: 200  $\mu$ g of 9Z,11E-14:Ac and 2000  $\mu$ g C25 pentaene) spiked with 2  $\mu$ g of various potential minor components. Minor components: 1, 9Z,11E-14:Ald; 2, 9Z,11E-14:OH; 3, 11E-14:Ac; 4, 9Z-14:OH; and 5, 9Z,12E-14:Ac. Bars indicate SE. There were no significant differences between any treatments ( $F_{5,20} = 0.76$ ,  $P = 0.59$ ). Data were transformed by  $\log(x + 1)$ .

addition of 9Z-14:Ac also had no significant effect on trap catches (Figure 3B).

**8** *Experiment 3: addition of other potential pheromone components.* The addition of other potential minor pheromone components to the optimized lure blend had no effect on trap catches at the ratios tested (1% of the amount of 9Z,11E-14:Ac) (Figure 3). These minor components included 9Z,11E-14:Ald, 9Z,11E-14:OH, 11E-14:Ac, 9Z-14:OH, and 9Z,12E-14:Ac.

*Experiment 4: addition of stabilizers to lure blends.* The addition of a UV stabilizer or an antioxidant alone or together to the optimized lure blend did not have a consistent effect on trap catch (Figure 5A). During this trial, trap catches decreased over time in similar fashion, regardless of treatment (Figure 5B). Statistical analysis of each count period found a significant difference between treatments in the third count only (Figure 5B), when traps baited with lures containing the antioxidant had increased catches.

*Experiment 5: trap designs.* No moths were caught in the bucket style Unitraps in the first trial (Figure 6A), so they were not investigated further. The white diamond traps were generally best, catching the most moths in all three trials, with the exception of the green delta traps in the first two trials (Figure 6A–C).

*Experiment 6: comparison of synthetic lure with virgin females.* Traps baited with 2-day-old virgin female moths

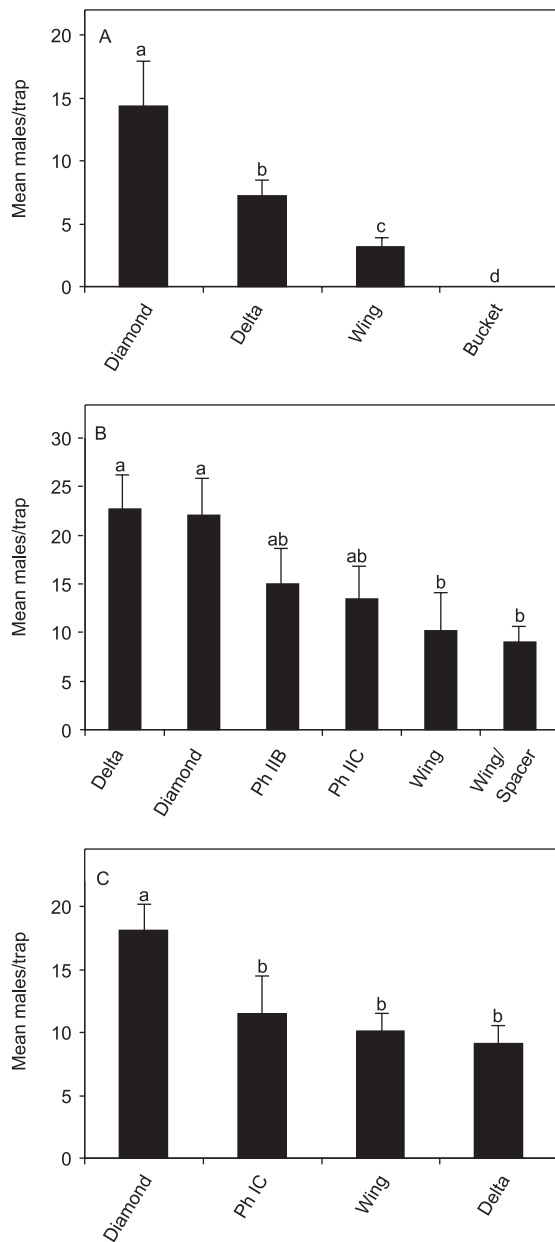
caught as many males (mean  $\pm$  SE,  $4.5 \pm 0.5$ ) as traps baited with the optimized lure blend ( $5.5 \pm 0.5$ ) over 10 trap nights, whereas empty traps caught no moths ( $F_{2,5} = 103$ ,  $P = 0.001$ ).

## Discussion

Commercially available (9Z,11E)-tetradecadien-1-yl acetate was found to consist of a mixture of dienyl acetate positional isomers, and so a new, unambiguous synthesis of this compound, and the corresponding alcohol and aldehyde, were developed. This synthetic route provided



**9** **Figure 5** Mean numbers of *Dioryctria abietivorella* caught in traps baited with the optimized lure blend (200  $\mu$ g of 9Z,11E-14:Ac and 2000  $\mu$ g C25 pentaene) formulated with no stabilizers, with the ultraviolet stabilizer Sumisorb 300 (UV), with the antioxidant butylated hydroxytoluene (BHT) (antiox), or with both stabilizers. Bars indicate SE. (A) Mean trap catches for the duration of the experiment; there were no significant differences among treatments ( $F_{3,16} = 1.68$ ,  $P = 0.22$ ); (B) Trap catches by week; there was a statistically significant difference in the third trapping session only ( $F_{3,16} = 4.28$ ,  $P = 0.02$ ). Columns within a trapping period capped by different letters are significantly different [Fisher's least significant difference (LSD) test,  $\alpha = 0.05$ ]; untransformed data used.



**Figure 6** Effect of trap design on numbers of *Dioryctria abietivorella* caught in traps baited with the optimized lure blend (200 µg of 9Z,11E-14:Ac and 2000 µg C25 pentaene) in rubber septa. Ph, Pherocon. Trial 1:  $F_{3,12} = 36.14$ ,  $P < 0.001$ ; trial 2:  $F_{5,20} = 2.87$ ,  $P = 0.04$ ; trial 3:  $F_{3,15} = 3.50$ ,  $P = 0.04$ . Bars indicate SE; bars capped by different letters in each trial are significantly different [Fisher's least significant difference (LSD) test,  $\alpha = 0.05$ ].

the target compounds more efficiently and/or in higher stereochemical purity than previous syntheses (e.g., Bjoerkling et al., 1987; Santangelo et al., 2002).

Lures containing 9Z,11E-14:Ac as a single component were minimally attractive, confirming that the C25 pentaene

is a crucial component of the blend. Optimum ratios of 9Z,11E-14:Ac to C25 pentaene ranged from 10:100 to 1:100 in the first ratio trial, and from approximately 5:100 to 17:100 in the second ratio trial. Based on these results, a lure load of 200:2000 µg of 9Z,11E-14:Ac and C25 pentaene (ratio 1:10) per septum was selected as an optimized lure blend of these components for subsequent trials.

The most effective lure blends required a higher ratio of the pentaene to the diene acetate than the 1:1 ratio found in female pheromone gland extracts (Millar et al., 2005). The long-chain C25 pentaene is a viscous oil at room temperature, with a much lower vapour pressure and volatility than 9Z,11E-14:Ac. Presumably, the ratio of the two components emitted by the rubber septum lure is similar to that released by the moth. The fact that an order of magnitude more C25 pentaene was required in the synthetic lure than was found in the pheromone gland extracts suggests that the female moths somehow enhance the volatility of this compound. Alternatively, the ratio in the pheromone gland contents may not be representative of the blend of volatiles that is actually released.

The addition of other components, including 9Z-14:Ac, 9Z,11E-14:Ald, 9Z,11E-14:OH, 11E-14:Ac, 9Z-14:OH, and 9Z,12E-14:Ac, had no discernable effect on lure attractiveness. Although small differences in the attractiveness of the various formulations might have been obscured by the high variability in trap captures within treatments, the results suggest that any effect from adding other components, either positive or negative, would likely be small.

Despite the polyunsaturated structure of both pheromone components, the addition of stabilizers did not appear to enhance or prolong the effectiveness of the pheromone blends when formulated in the grey halobutyl rubber septa. The attenuation of trap catches over time was likely due to a season-end decline in adult male population densities. In a concurrent trial, traps set out to determine *D. abietivorella* flight phenology showed a similar decline in catches, despite having lures replaced at regular intervals (WB Strong, unpubl.). Cooler end-of-season temperatures may have reduced oxidation or UV degradation of the pheromone components as well, resulting in the observed lack of apparent effect of the stabilizers. Thus, a follow-up trial may be warranted, started in spring and carried through the heavy flights and heat of summer. Under such circumstances, stabilizers may be of some value in extending lure lifetimes. Furthermore, stabilizers may afford some protection under somewhat harsher climatic conditions such as in Californian seed orchards, where sunlight is more intense and temperatures are hotter than in BC seed orchards. Whatever the case, addition of these stabilizers was not harmful, and because the stabilizers are inexpensive

1 in relation to the cost of the pheromone chemicals, routine  
2 addition of these or similar stabilizers to the pheromone  
3 formulations is probably prudent.

4 Pheromone emission rates of the *D. abietivorella* blend  
5 from grey halobutyl rubber septa have not been determined.  
6 However, our experience with hundreds of identical lures  
7 in the flight phenology trial mentioned above (WB Strong,  
8 unpubl.) suggests that lures deployed at a number of sites  
9 throughout southern BC maintained their efficacy for at  
10 least 4 weeks during summer months without noticeable  
11 loss of attractiveness. This was determined by (i) no apparent  
12 increase in catch numbers when old lures were replaced  
13 with new ones, and (ii) on several occasions, different  
14 replicates of traps at the same site that had lures replaced at  
15 different times caught similar numbers of moths. In that  
16 phenology trial, lures were left in traps no longer than  
17 6 weeks.

18 Our trap trials suggest that Pherotech delta or diamond  
19 traps should be used with *D. abietivorella*. Hanula et al.  
20 (1984) found that white Pherocon IC wing traps were  
21 more effective for *Dioryctria* coneworm species in the  
22 southern USA than a Conrel delta trap, a black Pherocon  
23 IC wing trap, or a cone trap. As a result of that study, Grant  
24 et al. (1987) used the Pherocon IC traps in further field  
25 trials of *Dioryctria* pheromones. For *D. abietivorella*, the  
26 Pherotech diamond trap is recommended, and it is also  
27 easier to assemble and use.

28 Tests attempting to use females as baits failed if females  
29 were not provided with 10% sugar water and if sexually  
30 immature females (<2 days old) were deployed in traps. As  
31 a consequence, only two replicates of the female-baited  
32 traps were successful. Despite the limited number of  
33 replicates, the optimized lure blend appeared to be as  
34 attractive as females. Thus, our two-component synthetic  
35 blend appears to be a reasonable facsimile of the natural  
36 insect-produced blend.

### 37 Conclusions

38 The diamond trap baited with our optimized lure blend of  
39 200 µg 9Z,11E-14:Ac and 2000 µg C25 pentaene dispensed  
40 from a grey halobutyl rubber septum is recommended for  
41 future detection and monitoring studies with the fir  
42 coneworm. This lure and trap combination has already  
43 been adopted as the standard operational monitoring tool  
44 for male *D. abietivorella* in British Columbian seed  
45 orchards. It is currently being used to determine the flight  
46 phenology of populations in seed orchards and natural  
47 conifer stands throughout southern BC and the  
48 northwestern USA (WB Strong, unpubl.). Its usefulness as  
49 a tool for making pest-management decisions will be  
50 contingent upon developing a relationship between  
51  
52

captured males and subsequent damage. This in turn will  
require a more detailed knowledge of the mating behavior  
of female *D. abietivorella*, and the movement of mated  
females within the landscape. An effective method of  
monitoring mated fir coneworm females (Shu et al., 1997)  
would be a useful and complimentary tool to the pheromone  
trapping system for males described in this study.

The identification of an effective pheromone for  
*D. abietivorella* may also provide new options for manage-  
ment of *D. abietivorella*. There is currently only one  
control tactic available to seed orchard managers in  
Canada, the application of dimethoate during conelet  
pollen receptivity (PMRA, 2006). This chemical is  
currently under review, and registration may be lost or  
curtailed (PMRA, 1999). The identification of the pheromone  
provides the critical information required to investigate  
the possibility of managing *D. abietivorella* with mating  
disruption or attract-and-kill tactics, as alternative control  
methods to the use of broadcast chemical pesticides.

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