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Possibilities to monitoring/control of the horse-chestnut leafminer (*Cameraria ohridella*) with some acetal derivatives of (8*E*,10*Z*)-tetradeca-8,10-dienal

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Abstract: This paper shows possibility of utilization ether derivatives of (8*E*,10*Z*)-tetradeca-8,10-dienal [2-((7*E*,9*Z*)-trideca-7,9-dienyl)-1,3-dioxan (**2**) and 2-((7*E*,9*Z*)-trideca-7,9-dienyl)-4-hydroxy-6-heptyl-5-hexyl-1,3-dioxan (**3**)] as potential lures for monitoring of horse-chestnut leafminer population. The both propheromones were synthesized at the Institute of Industrial Organic Chemistry (IPO) and then tested in 2006/07 on field trials at several different sites on terrain of Mazovian province.

Within the scope of these investigations, acetal **2** was checked at different doses (10, 100, 500 µg) by the pheromone trapping technique, and aldoxane **3** was used both in pheromone trapping (at the dose 50 µg) and mating disruption technique. The good attractiveness properties were obtained for both tested compounds. However, the dose of 2-((7*E*,9*Z*)-trideca-7,9-dienyl)-1,3-dioxan had to be a 10 times higher than dose of aldoxane for the same good activity.

Keywords: acetals, attractant, propheromone, *Cameraria ohridella, Aesculus hippocastanum* L., dispenser, pheromone trapping, mating disruption

INTRODUCTION

The horse-chestnut leafminer *Cameraria ohridella* Deschka et Dimić (Lep., Gracillariidae) is a small moth of unknown origin that recently invaded Europe. Males of this pest have been shown to respond in the behavioral reaction to the (8*E*,10*Z*)-tetradeca-8,10-dienal (**1**), which was isolated from virgin female by Svatos et al. [1]. Currently, this sex pheromone has been intensely investigated for use in protection of horse-chestnut trees against *C. ohridella* [2].

Two years ago, (8*E*,10*Z*)-tetradeca-8,10-dienal was synthesized at the Institute of Industrial Organic Chemistry (IPO) using a new and simple method from the readily available 5-chloro-1-pentyne [3]. 2-((7*E*,9*Z*)-Trideca-7,9-dienyl)-1,3-dioxan (**2**) obtained during the synthesis is an immediate precursor of the final pheromone. This compound can be a useful tool for controlled release of the pheromone of leafminer to the environment. 2-((7*E*,9*Z*)-Trideca-7,9-dienyl)-1,3-dioxan and another acetal 2-((7*E*,9*Z*)-trideca-7,9-dienyl)-4-hydroxy-6-heptyl-5-hexyl-1,3-dioxan (**3**) became the object of biological investigations (pheromone trapping and mating disruption technique).

The aim of this paper was to evaluate the effectiveness of both acetals in the monitoring/control of *C. ohridella* populations. These field trials were carried out in Mazovian province (Poland) during the period 2006-2007.

MATERIALS AND METHODS

Attractant: 2-((7*E*,9*Z*)-Trideca-7,9-dienyl)-1,3-dioxan (acetal **2**) and pheromone **1** (it was used in the experiments for comparison reasons) were prepared according to the method developed at IPO [3]. This route is outlined in Figure 1. Second acetal, 2-((7*E*,9*Z*)-trideca-7,9-dienyl)-4-hydroxy-6-heptyl-5-hexyl-1,3-dioxan (**3**) was synthesized by condensation of aldehyde **1** with corresponding aldol (Figure 2). This process is well-known in literature [4]. The stereoisomeric purity of the obtained attractants were ~95% (GC).

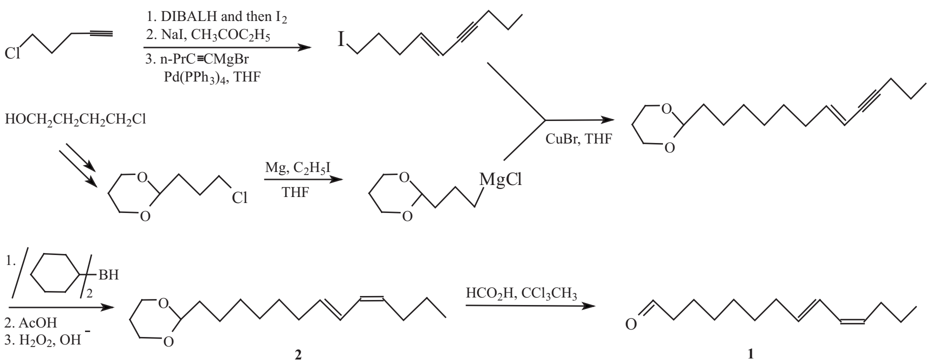

Figure 1. Synthesis of (8*E*,10*Z*)- tetradeca-8,10-dienal.

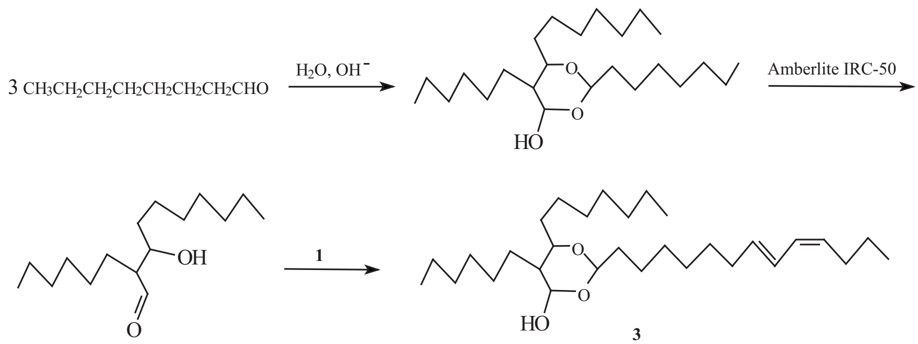

Figure 2. Synthesis of 2-((7*E*,9*Z*)-trideca-7,9-dienyl)-4-hydroxy-6-heptyl-5-hexyl-1,3-dioxan.

Trapping tests: The synthetic attractants **1-3** were dissolved in hexane and the solutions were applied to ”grey rubber caps” (commercial penicilinum vial caps LK-7/1, purchased with German-Polish Corporation “PASS-STOMIL”) at various doses. Then the dispensers were placed in traps in the area of experiments. The acetal **1** was used at doses: 10, 100 and 500 µg, while acetal **3** and pheromone **1** were applied at a dose 50 µg and 25 µg, respectively.

The delta traps with sticky insert (22 x 9.5 cm, Lunamelt PS 3199 glue) and tube traps with an insecticide inside (commercially available Italian insert with 4 mg empenthrin of the Zobele Industrie Chimiche S. PA) were employed. The field trials were done on sites in Warsaw and Falenty (region of Warsaw) in 2006 and 2007 during the *C. ohridella* flight period. The traps were suspended on branches at 4-5 m above the ground and spaced 5-10 m apart (one trap per tree). Sticky inserts were replaced as required but the lures were not renewed during experiments.

Mating disruption: Study on disruption of *C. ohridella* male orientation was carried out on the terrain of IPO. One or two trees from a few isolated groups of horse-chestnut trees (located about 100 m from each other) were sprayed with water emulsion of attractant (2% solution of acetal **3** in mineral oil with small amount of emulsifier) before the moth flight of each of the pest generations in 2007. The effect of the mating disruption was estimated by the comparison of *C. ohridella* males population density (numbers of moths trapped in tube traps) on the sprayed trees and neighboring with them control trees (unsprayed horse-chestnuts) during the flight of each generation. The tube traps with insecticide inside were baited with lures impregnated with 20 μg of the pheromone **1**.

In addition, the effectiveness of sprinkling attractant was determined by measurement of the degree of leaf blade damage in both treated and control trees after end of flight of the last generation of the pest (for inspections was taken four leaves from each horse-chestnut). Then the degree of leaf blade damage was estimated using 9 gradual scale of EPPO Guideline No. 152 [5].

The flight of the first generation of the pest was very weak (the leaves with the pupae of horse-chestnut leafminer hibernating in the mines were removed in autumn of previous season).

The data of both experiments were statistically computed using the analysis of variance (ANOVA) followed by the RIR Tukey and NIR tests.

RESULTS AND DISCUSSION

In the pheromone trapping study the males of *C. ohridella* were trapped from the start of the first generation (beginning of May) to the end of the second generation (beginning of August) in 2006 and during the second and third generation flights in 2007. The study results are presented in Figures 3-5. The effectiveness of the traps baited with 2-((7*E*,9*Z*)-trideca-7,9-dienyl)-1,3-dioxan formulated in a rubber dispenser depended on the dose of propheromone. Figures 4-5 show the effect of the propheromone dose ranging from 10 μg to 500 μg of acetal **2** on moth captures in tube trap. The attractiveness of the propheromone at the dose of 10 μg was weak (Figure 4). It was a bit higher at the dose of 100 μg and at the dose of 500 μg it was similar to the attractiveness of the standard pheromone **1** at the dose of 25 μg. The good result was also obtained for dispensers with 50 μg of acetal **3** (Figures 3-5). In case of catching *C. ohridella* in sticky traps, result of trapped moths for dispensers with attractant **2** at the dose of 100 μg (Figure 3, curve AF I) was much better during the flight of third generation in comparison with tube traps (Figure 5). It can be explained by very large density of population of the pest, and sticky traps very quickly became saturated by captured moths - more quickly than the sticky inserts were exchanged on new. This problem did not concern the tube traps which caught impressively high numbers without saturation. Therefore results for tested lures with part of tube traps are more reliable.

A relatively high difference in dose for both tested acetals (for the same good activity, the dose for acetal **2** and **3** was 500 μg and 50 μg, respectively) can resalt with their natural readiness of a break-up to aldehyde **1**. Propheromone **2** belongs to a stable enough group of acetals which very slowly hydrolyse to aldehyde under normal conditions. The acetal **3,** however, has a structure of aldoxane and can easily undergo the thermal decomposition with the emission of target pheromone. This property of aldoxanes is often used with success in cosmetic and aromas industry [4].

The traps used in our experiments retain the maximum of about 1000 moths per sticky insert and more than 30000 moths per a tube trap.

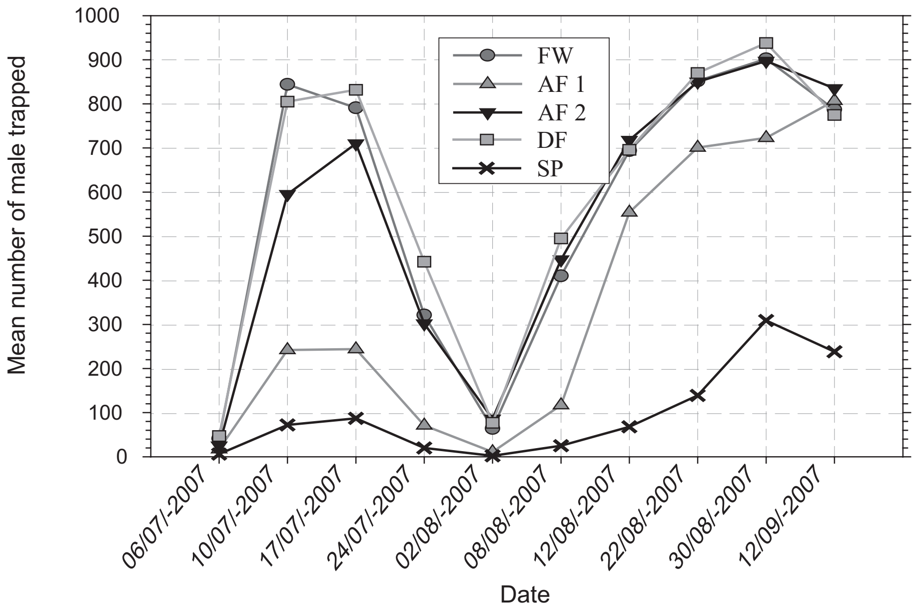

Figure 3. Mean numbers of *C. ohridella* males trapped daily in delta traps with sticky insert with various doses of active ingredient (Warsaw, July-September 2007): AF1 – acetal **2** at the dose of 100 μg, AF2 – acetal **2** at the dose of 500 μg, DF – acetal **3** at the dose of 50 μg, FW – pheromone **1** at the dose of 25 μg, SP – traps without lure.

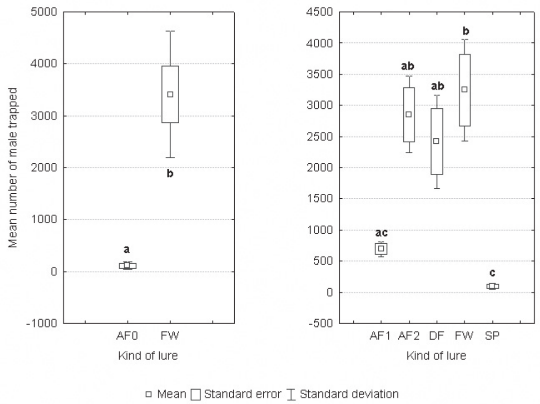

Figure 4. Catches of *C. ohridella* males in tube traps with an insecticide inside baited with various doses of active ingredient. AF0 – acetal **2** at the dose of 10 µg (Falenty, July 2 - August 5, 2006), AF1 – acetal **2** at the dose of 100 µg (Warsaw, July 6 - August 8, 2007), AF2 – acetal **2** at the dose of 500 µg (Warsaw, July 6 - August 8, 2007), DF – acetal **3** at the dose of 50 µg (Warsaw, July 6 - August 8, 2007), FW – pheromone **1** at the dose of 25 µg , SP – traps without lure.

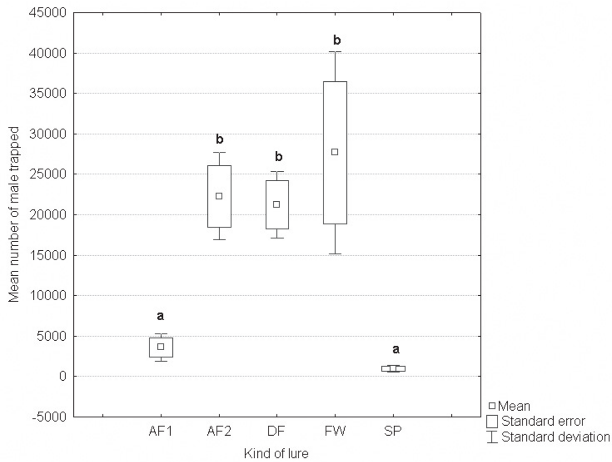

Figure 5. Catches of *C. ohridella* males in tube traps with an insecticide inside baited with various doses of active ingredient (Warsaw, August - September 2007): AF1 – acetal **2** at the dose of 100 µg, AF2 – acetal **2** at the dose of 500 µg, DF – acetal **3** at the dose of 50 µg, FW – pheromone **1** at the dose of 25 µg, SP – traps without lure.

Compound **3** was also used in the technique mating disruption (Figure 6). The first results of these studies showed noticeable difference in numbers of caught moths in traps in trees sprayed by attractant in comparison with control trees during the flight of the second and at the peak flight of the third generation (however, for the second case did not observe of a clear increase of difference in capturing of males). After the first generation of the pest, the number of captured moths were similar in both treated and control trees. This result may indicate the effect of mating disruption with this, that for the flight of the third generation, it had disappearing tendency. It can be explained by over 50 percent of population *C. ohridella* growth in the second generation (in comparison with first generation) for treated trees (Figure 6, II generation, S). Probably this fact could be main reason of disadvantageous result which was obtained after end of experiment. The infestation level of the horse chestnut trees sprayed with attractant, and the control trees showed no significant difference in autumn after vegetative period. Degree of leaf blade damage of treated and control trees was similar (Figure 7) and one was contained in range of the same scale (7 or 8) of EPPO Guideline nr. 152.

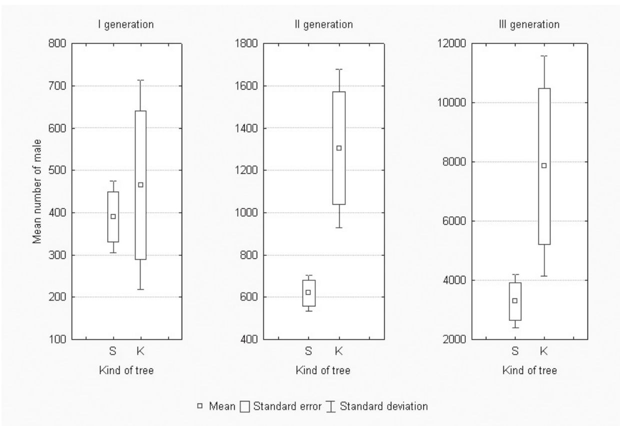

Figure 6. Effect of mating disruption on *C. ohridella* density measured by mean numbers of moths trapped in tube traps: trees sprayed by propheromone **3** (S) and control trees (K); I generation (April 27 - June 26, 2007), II generation (June 26 - August 3, 2007), III generation (August 3 - September 4, 2007).

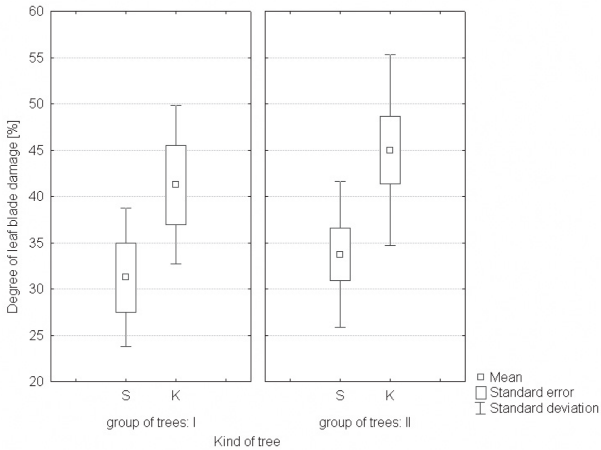

Figure 7. Degree of leaf blade damage of horse-chestnuts after end of vegetative season *C. ohridella* (October 24, 2007): trees sprayed with propheromone **3** (S) and control trees (K); the statistical significant differences were not evidenced by test.

The attractiveness properties of acetals **2-3** and others will be further examined during the next season. Within the scope of these investigations we are planning to check possibility of acceleration of natural process of the decomposition of acetal **2** to target pheromone. It would permit considerable reduction of level the effective dose of propheromone **2** in different techniques applied to control *C. ohridella*.

CONCLUSIONS

- Field study with rubber dispensers containing acetal **2** (at dose of 500 µg) and acetal **3** (at dose of 50 µg) showed their high attractiveness for *C. ohridella* male moths for the least three months, and they were similar to the attractiveness of dispensers with standard pheromone **1**.
- Increasing quantity of the synthetic propheromone **2** from 10 to 500 µg per dispenser improves significantly the effectiveness of moths caught in the traps.
- Using the acetal **3** for *C. ohridella* mating disruption resulted in the decrease of moth captures on the treated trees. However, the substantial reduction of a degree of damage of the horse-chestnut leaves was not achieved. Many

factors could have influence on results of this, especially too high increase of number of the pest during its life period (mainly at the second and third generation of *C. ohridella*).

- The acetal form of pheromone **1** (compound **2**) can be a useful tool for monitoring of *C. ohridella* population after the decrease of its effective dose. It can be obtained by the decrease of stability of the acetal **2** (for example using an acid catalyst, which can accelerate a process of hydrolysis of the acetal).

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