

## 7-VINYLDECYL ACETATE, NOVEL INHIBITOR OF PHEROMONAL ATTRACTION IN THE FALSE CODLING MOTH, *CRYPTOPHLEBIA LEUCOTRETA*

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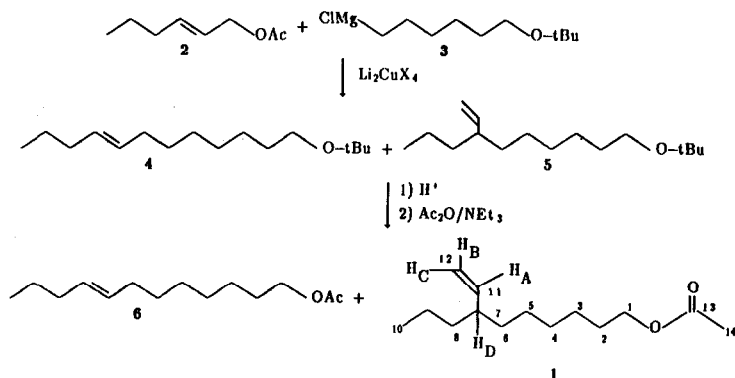
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**Summary:** It was found that 7-vinyldecyl acetate, a by-product of the synthesis of one of the constituents of the sex attractant of the false codling moth, *Cryptophlebia leucotreta*, effectively disrupts the attraction of male moths to virgin females or to synthetic lures.

Females of the false codling moth, *Cryptophlebia leucotreta*, emit a sex pheromone which attracts conspecific males and has been identified to consist of (E)- and (Z)-8-dodecenyl acetate in a 1:1 ratio<sup>1</sup>. Other ratios and the presence of dodecyl acetate in the secretion have subsequently been reported, and synthetic lures containing the two unsaturated acetates in widely varying proportions were found to attract males in field tests<sup>2-4</sup>. The erratic results that are often obtained with commercial false codling moth lures possibly contributed to sustain continuing interest in the composition of the sex pheromone of the insect and in the formulation of "competing" synthetic lures. In a study in which solventless introduction of the sex pheromone glands of the insect into the injector of a gas chromatograph was used, a wide variation in the proportion of the two acetates was, for example, found in populations from different geographical origins, while several other compounds were also identified in the glands.<sup>5</sup>

In an evaluation of differently formulated synthetic false codling moth lures, formulations in which a certain batch of (E)-8-dodecenyl acetate was used, did not attract any male moths. On closer inspection it was found that, although the major constituent of this material had the correct structure, this batch of the ester contained an impurity in a concentration of approximately 9%. A typical formulation in which (E)- and (Z)-8-dodecenyl acetate were used in a ratio of 1:1 would therefore have contained the impurity in a concentration of 4.5%. The impurity had a slightly shorter GC retention time on an apolar phase than (E)-8-dodecenyl acetate or its Z-isomer. From a comparison of mass spectral data obtained by GC/HR-MS analysis of the mixture, (E)-8-dodecenyl acetate and the impurity appeared to be structurally related, the only significant difference between the mass spectra of the two compounds being the higher relative abundance of the ions at  $m/z$  123 and 137, and the lower abundance of the ion at  $m/z$  166 in the spectrum of the impurity<sup>6</sup>. Since these differences could not be translated unequivocally into an acceptable structure, the impurity was isolated by preparative GC for NMR spectral analysis. Data obtained from the <sup>1</sup>H and <sup>13</sup>C NMR spectra<sup>7</sup>, and multiplicities determined by the APT technique, furnished conclusive evidence that the impurity was 7-vinyldecyl acetate 1. In the preparation of (E)-8-dodecenyl acetate 6 by a catalyst-induced coupling of (E)-2-hexenyl acetate 2 with the Grignard reagent 3, as shown in the following scheme, the branched-chain impurity 1 is formed by attack at the vinylogous position with a concurrent shift of the double bond<sup>8,9</sup>.

The ratio in which the isomeric esters 1 and 6 are formed, can be controlled, to a certain extent, by changing the reaction conditions. The following procedure gave a final product containing 28% of the branched-chain compound 1. The Grignard reagent 3, prepared from 1-*t*-butoxy-6-chlorohexane



(96.3 g, 0.5 mol) and Mg turnings (13.3 g, 0.55 mol) in THF (100 ml), was added dropwise at 70°C to a mixture of (E)-2-hexenyl acetate 2 (58.9 g, 0.41 mol) and the catalyst, prepared by adding CuBr (2.9 g, 0.02 mol) to LiCl (0.9 g, 0.02 mol) in THF (45 ml). After stirring the reaction mixture at 70°C for a further 15 h, crushed ice was added. The organic product, isolated in the usual manner, contained the straight- and branched-chain isomers 4 and 5 in a ratio of 72 : 28 (GC analysis). Removal of the protective group<sup>10</sup> and acetylation<sup>11</sup> gave the acetates 6 and 1 in the same ratio and in an overall yield of 60%. The branched-chain isomer 1 was isolated by careful fractionation and preparative GC.

As already mentioned, the presence of the branched-chain acetate 1 strongly reduced the attractiveness of synthetic false codling moth lures. The strong inhibition of pheromonal response in *C. leucotreta* by this compound was also illustrated in experiments in which its effect on the attractiveness of live virgin females for males of the species was determined. It was, for instance, found that whereas 370 males were caught over a period of 21 days in traps, each baited with a virgin female, not a single moth was caught in traps baited with females plus polyethylene cap dispensers containing 2  $\mu\text{l}$  of the branched-chain acetate 1. In these experiments females were exposed in small wire gauze cages suspended centrally in tube traps and were replaced with fresh females every 3–4 days. Although further research is needed to determine the inhibitory threshold of this compound, its mode of action, the activity of analogues, etc., it is clear that 7-vinyldecyl acetate acts as a strong pheromonal inhibitor in *Cryptophlebia leucotreta* and might find application in controlling this insect pest by mating disruption. These results furthermore suggest that it might be advisable to investigate the possible presence of similarly formed branched-chain by-products in other synthetic pheromones that do not elicit the expected behavioural response in the target insects.

#### REFERENCES AND NOTES

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6. EIMS:  $m/z$  166 (2,  $\text{C}_{12}\text{H}_{22}$ ), 137 (34,  $\text{C}_{10}\text{H}_{17}$ ), 123 (36,  $\text{C}_8\text{H}_{15}$ ), 109 (10,  $\text{C}_6\text{H}_{13}$ ), 95 (30,  $\text{C}_7\text{H}_{11}$ ), 81 (52,  $\text{C}_6\text{H}_9$ ), 67 (53,  $\text{C}_5\text{H}_7$ ), 61 (13), 55 (94), 43 (100), 41 (64).
7.  $^1\text{H}$  NMR (60 MHz, 30°C, benzene- $d_6$  at  $\delta$  7.20 was used as internal reference in 1.7 mm O.D. sample tube).  $\delta_{\text{H}}$ : 5.521 (m,  $\text{H}_A$ ,  $J_{AB} = 10.12$  Hz,  $J_{AC} = 17.21$  Hz,  $J_{AD} = 8.53$  Hz); 5.035 (m,  $\text{H}_B$ ,  $J_{BC} = 2.13$  Hz,  $J_{BD} = -0.27$  Hz); 5.005 (m,  $\text{H}_C$ ,  $J_{CD} = -0.59$  Hz); 4.02 (t,  $\text{OCH}_2$ ,  $J = 6.4$  Hz); 1.95 (m,  $\text{H}_D$ ); 1.74 (s,  $\text{CH}_3\text{CO}$ ); 1.1–1.65 (m,  $\text{CH}_2$ , 14 H); 0.93 (t,  $\text{CH}_3$ ,  $J = 5.9$  Hz).  $^{13}\text{C}$  NMR (20 MHz, 34°C, benzene- $d_6$  at  $\delta$  128.0 was used as internal reference and lock solvent in 1.7 mm O.D. sample tube).  $\delta_{\text{C}}$ : 169.80 (s,  $\text{C}_{13}$ ); 143.59 (d,  $\text{C}_{11}$ ); 114.20 (t,  $\text{C}_{12}$ ); 64.36 (t,  $\text{C}_1$ ); 44.23 (d,  $\text{C}_7$ ); 37.66 (t,  $\text{C}_8$ ); 35.30 (t,  $\text{C}_9$ ); 29.68 (t,  $\text{C}_4$ ); 29.01 (t,  $\text{C}_2$ ); 27.40 (t,  $\text{C}_3$ ); 26.19 (t,  $\text{C}_5$ ); 20.61 (t,  $\text{C}_6$ ); 20.49 (q,  $\text{C}_{10}$ ); 14.33 (q,  $\text{C}_{10}$ ).
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