Short Communication

Identification of the Female Sex Pheromone of the Pine Moth

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The application of the electroantennogram (EAG) technique¹⁾ has suggested that the sex pheromone of the pine moth, *Dendrolimus spectabilis* Butler (Lepidoptera: Lasiocampidae), one of the most harmful defoliators of the pine tree, is 5, 7-dodecadien-1-ol, and three of four geometrical isomers of this compound synthesized stereo-selectively *via* acetylenic compounds have been shown to strongly stimulate the male antenna of the pine moth.²⁾ This paper deals with the confirmation of the presence of the diene alcohol in the female extract and a preliminary field trial with the synthetic compounds.

About 2000 female pupae were collected from the pine stands in Ibaraki-prefecture. Immersing the abdominal tips of the virgin females for a few hours in *n*-hexane gave 174 mg of the crude extract, which was successively purified by a preparative TLC (silica gel) to afford 38 mg of the alcohol fraction with strong EAG-activity. GC of this fraction on a nonpolar column (OV-1 1%, 0.3×200 cm, 100–170°C, 10°C/min) showed a peak at 6.4 min corresponding to the retention time (*Rt*) of 5, 7-dodecadien-1-ol. And analysis with a polar column (PEG 20 M 2%,

0.3×200 cm, 135°C) suggested the presence of (Z)-5, (E)-7-isomer (*Rt* 13.3 min) and (E)-5, (E)-7-isomer (*Rt* 15.6 min) in the ratio of *ca.* 5:1, while no peaks were observed at *Rt* of (E)-5, (Z)-7-isomer (*Rt* 13.8 min) and (Z)-5, (Z)-7-isomer (*Rt* 14.5 min). Further purification with a preparative TLC using a silica gel plate impregnated with 20% AgNO₃ gave 5 mg of EAG-active fraction. GC-MS of this fraction was scanned every six seconds for eleven minutes (column: PEG 20M 2%, column temperature was kept at 130°C for 2 min at first and raised by 7.5°C/min). The mass spectrum of one major peak at 5.6 min, which corresponded to *Rt* of (Z)-5, (E)-7-dodecadien-1-ol, was identical with that of synthetic 5, 7-dodecadien-1-ol (Fig. 1), and that of a minor peak at 6.0 min, which corresponded to *Rt* of (E)-5, (E)-7-isomer, was also similar to that of the authentic alcohol. The mass chromatographic analysis of this GC-MS measurement conducted on five ions (*m/e* 182, 164, 135, 121 and 107) indicated that a little amount of another isomer flowed out at 6.0 min separately from a major peak of (Z)-5, (E)-7-isomer of the diene alcohol (*Rt* 5.6 min), as shown in Fig. 2.

To examine the possibility for the occurrence of other pheromone-like compounds such as straight chain (C₁₀–C₁₈) alcohols in this fraction, mass chromatographic analyses were conducted on the following ions: saturated and monoene alcohols; M⁺-18, M⁺-46, M⁺-74, M⁺-88 and M⁺-102, diene alcohols; M⁺, M⁺-18, M⁺-47, M⁺-61 and M⁺-75, and the presence of two monoene alcohols, tetradecen-1-ol and hexadecen-1-ol, was indicated, while no saturated and diene alcohols could be noticed except the above dodecadiene-1-ol. Although the fractions on preparative GC, which contained these monoene alcohols, have slight but non-negligible EAG-activities, a series of synthetic mono-unsaturated 14- and 16-carbon alcohols failed to show appreciable EAG-activities.

Field attractiveness of each isomer of synthetic 5, 7-dodecadien-1-ol was tested as a single source in July 1979 in Ibaraki-prefec-

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FIG. 1. Mass Spectrum of (Z)-5, (E)-7-Dodecadien-1-ol.

The mass spectra of the other geometrical isomers of 5, 7-dodecadien-1-ol are quite similar to this spectrum.

FIG. 2. Mass Chromatography of the Alcohol Fraction from the Female Extract of the Pine Moth.

Five selected ions (m/e 182, 164, 135, 121 and 107) were monitored for eleven minutes. This figure shows that a large amount of (Z), (E)-isomer of 5, 7-dodecadien-1-ol flowed out from 5.4 min to 5.7 min and a small amount of (E), (E)-isomer at 6.0 min, while none at 5.8 min. As some part of (E), (E)-isomer was lost by the purification of a preparative TLC using a silica gel plate impregnated with AgNO_3 , the quantity of the two isomers determined by this mass chromatography was different from that by GC. Appearance of a peak at 5.9 min monitored by m/e 164 and 121 may be due to a impurity.

ture, using sticky type traps (Takeda pheromone trap^{*1}). Despite a low field population of the pine moth, it was observed that only the traps baited with (Z)-5, (E)-7-isomer could catch appreciable number of male moths. Thus it is concluded that the main component of the female sex pheromone of the pine moth is (Z)-5, (E)-7-dodecadien-1-ol. This compound is the first one identified from insects as a sex pheromone.

Recently, bombykol ((E)-10, (Z)-12-hexadecadien-1-ol), the sex pheromone of the

silkworm, was shown to be contaminated with a small amount of (E), (E)-isomer.⁸⁾ We could also reveal the presence of (E), (E)-isomer as a minor component of 5, 7-dodecadien-1-ol in the extract of the pine moth. The experiments to clarify the role of the (E), (E)-isomer on the seriated sex behavior, particularly examination of the synergistic effect of this isomer in the field attraction, are in progress.

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