IDENTIFICATION OF ADDITIONAL COMPONENTS OF THE SEX PHEROMONE OF Dendrolimus pini

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The sex pheromone of the pine moth Dendrolimus pini L. (Lepidoptera: Lasiocampidae) has been identified previously as dodeca-cis-5,trans-7-dienal (I) [1-3]. In view of the multicomponent nature of the sex pheromones of the genus Dendrolimus [4], we have continued to study the composition of the sex pheromone of females of this species.

Because of the small amount of biomaterial, as the method of study we chose chromatomass fragmentography, in which the full ion current is recorded by scanning several definite fairly intense and characteristic masses. This approach ensures a high sensitivity and informativeness of the method. In the present case, we selected the ions with m/z 224 (M^+) and 61 $(CH_3COOH_2)^+$ to characterize the acetates of dodecadienols, 182 (M^+) and 164 ($M^+ - 18$) for dodecadienols, 180 (M^+) for dodecadienals, 166 ($M^+ - CH_3COOH$) and 61 $(CH_3COOH_2)^+$ for dodecenyl acetates, and 166 ($M^+ - 18$) for dodecenols. The choice of these ions was based on our own and literature [5] mass-spectrometric results.

The presence of (I) as a component of the sex pheromone of D. pini was confirmed by the appearance of an ion with m/z 180 (M^+) with a retention time (13.152 min) agreeing well with that for the same ion on the chromatography of an authentic sample of dodeca-cis-5, trans-7-dienal (13.130 min), synthesized according to [6].

We did not detect the ions with m/z 224 (M^+) and 61 $(CH_3COOH_2)^+$ with the same retention time corresponding to that for these ions from an authentic sample of dodeca-cis-5,trans-7-dien-1-ol (11.320 min). The same fact excluded the presence of any dodecadien-1-yl acetate as a component of the sex pheromone of D. pini.

At the same time, the presence of ions with m/z 182 (M^+) and 164 ($M^+ - 18$) with retention times coinciding with those for authentic dodeca-cis-5,trans-7-dien-1-ol synthesized according to [6] (15.872 min) showed that this compound was present in the extract of the sex pheromone of pine moth females.

The appearance in the mass spectrum of ions with m/z 166 ($M^+ - CH_3COOH$) and 61 $(CH_3COOH_2)^+$ (retention time 15.381 min) showed the presence of the acetate of a monoenic dodecen-1-ol, presumably that of dodec-cis-5- or -trans-7-en-1-ol.

Thus, in addition to compound (I), identified previously, we have established the presence in an extract of the sex pheromone of pine moth females of another two components: dodeca-cis-5,trans-7-dien-1-ol (II) and the presumable acetate of dodec-cis-5- or -trans-7-en-en-1-ol.

Field trials of biological activity that we have conducted in plantations of the Veshenskaya leskhoz [forestry farm], rostov province, and in the Khashuri leskhoz, Georgia, have shown that compound (II) affects the behavior of D. pini males, substantially increasing the attractive effect (Table 1).

Chromato-mass fragmentography was conducted on a HP 5890 chromatograph with splitless injection fitted with a mass-selective detector from the same firm, HP 5970, and a HP data-processing system.

Separation was achieved on a 0.25 mm × 30 m DB-WAX quartz column.

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TABLE 1. Attractiveness of Mixture of Dodeca-cis-5,trans-7-dienal with Dodeca-cis-5,trans-7-dien-1-ol (dose 1 mg)

Substances and their ratio, %		Number of pine moth males trapped	
5Z,7E-12-al	5Z,7E-12 OH	total in six traps	average per trap
100	0	14	2.33
80	20	39	6.50
60	40	57	9.50

Chromatographic conditions: initial temperature 50°C; after the injection of the sample, this temperature was maintained for two minutes and was then raised at the rate of 10°C/min to the final temperature of 190°C.

To prepare the extract of the sex pheromone the abdominal tips of recently (2-3 h) hatched females that were in the attractive attitude were cut off and extracted with n-hexane at 20-25°C for 8-10 min. The amount of hexane used was 10 µl per gland. The extract was separated from the abdominal tips with a fine capillary, evaporated to 2-3 µl, and used in the investigation. Usually the extract from 7-8 pheromone glands was injected into the chromatograph.

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