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Short Communication

Field and Electroantennogram Responses of the Pine Sawfly, *Diprion nipponica*, to Chiral Synthetic Pheromone Candidates

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(1*S*, 2*R*, 6*RS*)-1,2,6-Trimethyldecyl propionate, a lower homolog of the sex pheromone of known sawflies, strongly attracted *Diprion nipponica*, a popular species in Japan.

Key words: pine sawfly; *Diprion nipponica*; EAD; field assay; pheromone

Pine sawflies (Hymenoptera: *Diprionidae*) are common insects in conifer forests and consist of more than 120 species. The strong sex pheromone released by the female sawfly was discovered in early 1960,[1] but its chemical identification required long-term investigations. In 1976, Jewett *et al.* found that 1,2,6-trimethyltetradecyl acetate and propionate were the pheromones of *Neodiprion lecontei* and *Diprion similis*, respectively.[2] The synthetic counterpart they prepared (a mixture of 8 possible stereoisomers), however, failed to attract male sawflies in the field. The results strongly suggested the importance of the stereochemistry of the pheromone components. Subsequent stereochemical studies from 1979 to 1990 revealed that all *Neodiprion* species so far examined in North America and Japan used (1*S*, 2*S*, 6*S*)-1,2,6-trimethyltetradecyl acetate or propionate as the main pheromone and (1*S*, 2*R*, 6*R*)-1,2,6-trimethyltetradecyl acetate or propionate as the synergist or inhibitor, while *Diprion similis* in North America used (1*S*, 2*R*, 6*R*)-1,2,6-trimethyltetradecyl propionate as the main pheromone and (1*S*, 2*S*, 6*S*)-1,2,6-trimethyltetradecyl propionate as the synergist.[3] The pheromone of *Diprion pini*, a common pine sawfly in North Europe, was recently found to use (1*S*, 2*R*, 6*R*)-1,2,6-trimethyldodecyl propionate, a lower homolog of the known pheromone, based on an intensive study of a joint Swedish and French group.[4]

We now report that a further lower homolog, (1*S*, 2*R*, 6*RS*)-1,2,6-trimethyldecyl propionate strongly attracted *Diprion nipponica*, a common species in Japan, and that either the (1*S*, 2*R*, 6*R*)- or (1*S*, 2*R*, 6*S*)-isomer could be a promising pheromone candidate.

The present study began in 1991 on the occasion of

Table I. Field Response of *D. nipponica* Males to Various Synthetic Pheromone Candidates[a]

Substance	Response of EAD	Amount baited on a cotton roll dispenser (μg)	Catch of males	Date of assay
Virgin females[b]		4 virgin females	30	July 22 to 31 1997
Unbaited			0	
(1*R**, 2*S**, 6*RS*)-1,2,6-trimethyldecyl propionate		50	7	
(1*R**, 2*R**, 6*RS*)-1,2,6-trimethyldecyl propionate		50	0	
(1*R**, 2*S**)-1,2-dimethylundecyl propionate		50	0	
(1*R**, 2*R**)-1,2-dimethylundecyl propionate		50	0	
(1*R**, 2*S**, 6*RS*)-1,2,6-trimethylundecyl propionate		50	0	
(1*R**, 2*R**, 6*RS*)-1,2,6-trimethylundecyl propionate		50	0	
(1*S*, 2*R*, 6*RS*)-1,2,6-trimethyldecyl propionate	+	10	27	August 12 to 21 1997
		50	74	
(1*R*, 2*S*, 6*RS*)-1,2,6-trimethyldecyl propionate	+	10	0	
(1*S*, 2*S*, 6*RS*)-1,2,6-trimethyldecyl propionate	+	10	0	
(1*R*, 2*R*, 6*RS*)-1,2,6-trimethyldecyl propionate	+	10	0	

[a] Field studies were carried out with an easily available cockroach trap (Earth Pharmaceutical Co.). Each compound dissolved in hexane was absorbed on a cotton-roll dispenser (1 × 4 cm, Nitiei Co.) and applied to the sticky surface of the cockroach trap. The baited traps were placed in pine trees 2 m above the ground and at least 10 m apart.

[b] Four virgin females emerging within a day were placed on the sticky surface of the cockroach trap. The females in the trap survived during the assay period (one week).

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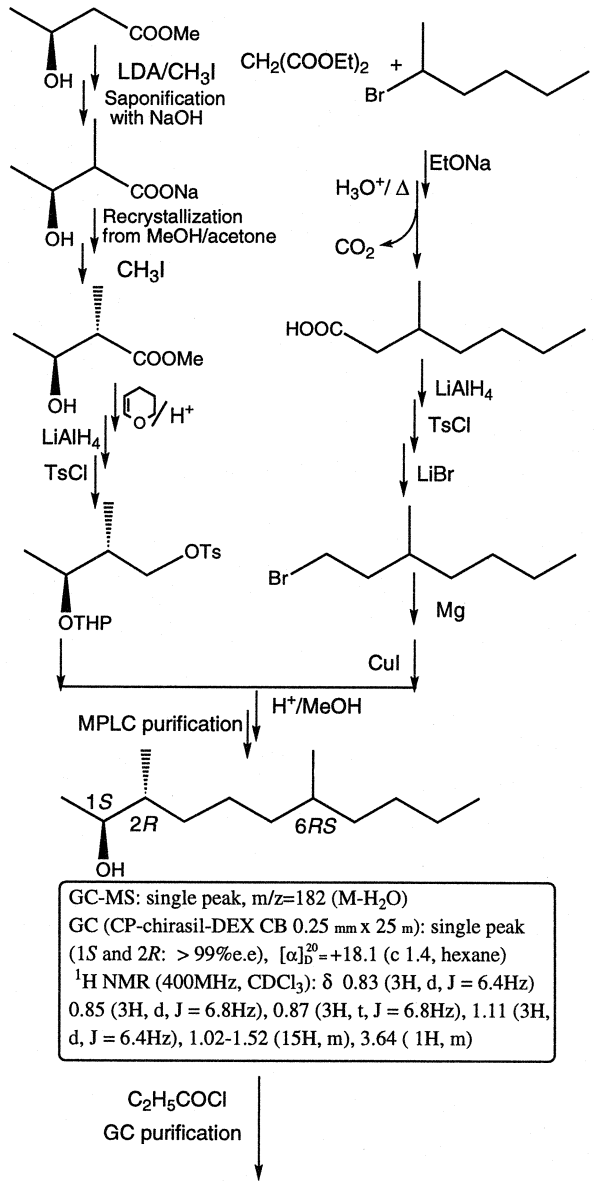
mass outbreaks of *D. nipponica* and defoliation in the pine forests of eastern Hidaka, Hokkaido. After investigating the field conditions at various locations, field attraction tests with synthetic compounds have been carried out on Apoi mountain, Hidaka, Hokkaido since 1992. The results of these studies from 1992 to 1994 indicate that none of the known pheromone components nor related compounds could attract *D. nipponica*. During this period, an indoor breeding technique for the insect was established and reared virgin females and males became available in 1996.

Based on the above-mentioned background, we started a series of analytical studies on the natural pheromone. An extract of 25 reared virgin females was subjected to an analysis by combined gas chromatographic-electroantennographic detection (GC-EAD), using an antenna of reared males, and GC-MS. The retention time of the EAD active material in the natural extract was shorter than that of 1,2,6-trimethydodecyl propionate. GC-MS data for the EAD active material indicated the acyl moiety to be propionyl, while the alcohol moiety consisted of 13 carbon atoms. Based on this information, several compounds were synthesized and subjected to a field bioassay. The results are summarized in Table 1. Only (1*R**, 2*S**, 6*RS*)- and (1*S*, 2*R*, 6*RS*)-1,2,6-trimethyldecyl propionate significantly attracted the male sawfly. The potency of the (1*S*, 2*R*, 6*RS*)-isomer to *D. nipponica* (27 males/10 μg in a cotton dispenser/in a week) was comparable to that of (1*S*, 2*S*, 6*S*)-1,2,6-trimethyltetradecyl acetate to *Neodiprion sertifer* (30 males/5 μg in a cotton dispenser)[3j] when racemic modification of the 6-position of the sample was taken into account. The results of the field bioassay also suggested that the (1*R*, 2*S*, 6*RS*)- and (1*R*, 2*R*, 6*RS*)-isomers did not inhibit the activity of the (1*S*, 2*R*, 6*RS*)-isomer.

The compounds employed in this study were similarly synthesized. As an example, the synthetic procedure for (1*S*, 2*R*, 6*RS*)-1,2,6-trimethyldecyl propionate is shown in Scheme 1.[3e,j] Details will be published elsewhere.

The synthesis of stereochemically pure (1*S*, 2*R*, 6*R*)- and (1*S*, 2*R*, 6*S*)-1,2,6-trimethyldecyl propionate to confirm the stereochemistry of the 6-position and analytical identification of the natural pheromone are currently underway.

We express our great appreciation to Earth Pharmaceutical Co. for presenting a large number of cockroach traps.



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