

METHYLBUTYNOL EFFECTIVELY REPLACES
METHYLBUTENOL, A PHEROMONE COMPONENT OF
Ips typographus (L.) (COLEOPTERA: SCOLYTIDAE)

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Abstract—In field experiments in Sweden, the constituent 2-methyl-3-buten-2-ol of the aggregation pheromone of the spruce bark beetle *Ips typographus* (L.) was effectively replaced by 2-methyl-3-buten-2-ol.

Key Words—*Ips typographus*, spruce bark beetle, Coleoptera, Scolytidae, pheromones, aggregation pheromone, methylbutenol, methylbutynol, (*S*)-*cis*-verbenol, ipsdienol, traps.

I. INTRODUCTION

Bark beetle pheromones may contain several components. One or several constituents are necessary and considered to be irreplaceable; others may contribute more or less to the overall attractive effect and are not essential. Little is known about the specific behavioral functions of the individual constituents of bark beetle pheromones.

The spruce bark beetle *Ips typographus* (L.) produces a number of substances in varying proportions (Birgersson et al., 1984). (*S*)-*cis*-Verbenol and

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2-methyl-3-buten-2-ol are claimed to be essential for eliciting aggregation response (Bakke, 1976; Bakke et al., 1977). Varying results have been obtained by the addition of ipsdienol to the essential compounds to increase attraction (Bakke et al., 1983; Schlyter, 1985; Regnander, personal communication).

Recent studies in Czechoslovakia have indicated that it is possible to replace 2-methyl-3-buten-2-ol with another substance, and patent applications for effective blends have been filed (Konečný et al., 1984, 1985). It has been claimed (Ozols et al., 1982) that methylbutenol as well as ipsdienol can be replaced by other substances, but the identity of those substances has not been revealed. To our knowledge, until now there are no documented cases in which essential bark beetle-produced pheromone components have been effectively replaced by a compound of different structure.

In this paper we present evidence from field experiments conducted in Sweden in 1985 that 2-methyl-3-butyn-2-ol can effectively replace 2-methyl-3-buten-2-ol in baits for trapping *Ips typographus*.

METHODS AND MATERIALS

Chemicals. As standards for the field experiments, commercially available Celamerck plastic bag dispensers containing 1500 mg 2-methyl-3-buten-2-ol, 70 mg (*S*)-*cis*-verbenol, and 15 mg ipsdienol were used. The release rate of the blend was expected to be about 50 mg/day, but it was ca. 30 mg/day in the experiments.

The experimental blends of the following substances were prepared in the laboratory: 2-methyl-3-buten-2-ol (ME), 2-methyl-3-butyn-2-ol (MY), (*S*)-*cis*-verbenol (CV), and ipsdienol (ID).

ME and MY were purchased from Fluka A.G. The identity of the compounds was checked by NMR and the purity by GC. None of these alcohols contained any detectable trace of the other compound (secured detection level 1/1000), either at the start or at the end of the experiments. MY gave only one peak in the GC trace, while ME contained 22% of an impurity most probably consisting of 2-methyl-3-butan-2-ol, which appears to be a by-product formed in the manufacturing process. Racemic ID was synthesized according to Baeckström et al. (1983). The CV was a gift from Borregaard (95% ee) and was purified by liquid chromatography to >99% chemical purity. The main impurity removed was verbenone.

Immediately before the field tests, special glass dispensers of our own design were prepared with the experimental blends. All blends contained CV combined with either ME or MY, in some blends ID was also added. The substances were used in the following proportions by weight: ME and MY 100, CV 5, and ID 1.

Sufficient chemical (5 ml or more) was added to each dispenser to last the

duration of the experiments. Release rates were determined gravimetrically. In three- to five-week experiments release rates varied between 34 and 79 mg/day (two faulty dispensers released 115 and 202 mg/day). The mean release rate was 56 mg/day ($N = 18$). In the long-term experiment (see below) the mean release rate was 35 mg/day, and the dispensers were still effective after more than three months.

Field Experiments. The attractiveness of the chemicals was tested in two experiments of similar design, one 18-day experiment (replacement) in which ME was replaced by MY and another three-month experiment (long-term) in which the long-term attractiveness of MY + CV was studied. In the replacement experiment, 1979 model Swedish traps with collecting funnel were used; in the long-term experiment, 1979 model Norwegian traps without funnel were used (cf Regnander and Solbreck, 1981).

The traps were placed in fresh clear-cuts 35 km north of Uppsala which contained slash and stumps of predominantly Norway spruce. The traps were set up in groups of three with distances of 6 m between traps and 50 m between groups. Each trap in a group was baited with one of three treatments (see below). All traps were placed in a single row strung parallel to the southern forest edge of the clear-cuts at a distance of 50–75 m from the forest.

The replacement experiment was conducted for 18 days. The treatments (baits) were: Commercial lure, MY + CV, and ME + CV. Five groups with three traps in each were used. The catches were collected when a nearby monitoring trap indicated that there had been sufficient flight activity. After each collection, the positions of the traps within each group were interchanged randomly. The catches were collected five times. The five groups and the five trapping periods yielded a total of 25 replicates.

The long-term experiment, at a distance of 5 km from the replacement experiment, was conducted for 102 days. The treatments were: Commercial lure, MY + CV, and ME + CV + ID. A randomized block design with 10 replicates (groups) was used. The treatments within each block remained in the same position during the entire experimental period. The catches were collected at various intervals.

RESULTS

Replacement of Methylbutenol with Methylbutynol. A total of 40,630 *Ips typographus* was caught in this experiment. Table 1 summarizes the results of the comparison between the methylbutynol blend and blends containing methylbutenol. A two-way analysis of variance (3 treatments, 25 blocks) confirmed that there were no significant differences in catch efficiency between the three pheromone blends ($F = 0.98$).

The results show that methylbutynol can effectively replace methylbutenol

TABLE 1. COMPARISON OF ATTRACTIVENESS OF THREE PHEROMONE BLENDS: MEAN CATCHES OF *Ips typographyus* PER REPLICATE FOR SUCCESSIVE TRAPPING PERIODS ($N = 5$) AND ENTIRE EXPERIMENTAL PERIOD ($N = 25$).

Trapping period 1985	No. of beetles		
	Commercial lure (ME + CV + ID)	MY + CV	ME + CV
May 15-19	538.4	439.0	400.8
May 20-27	519.2	441.0	661.8
May 28	631.4	604.6	597.4
May 29	799.0	747.0	721.0
May 30-June 2	376.6	303.4	336.4
Mean catch \pm SD (25 replicates)	572.9 \pm 224.4	507.0 \pm 234.1	543.5 \pm 275.6

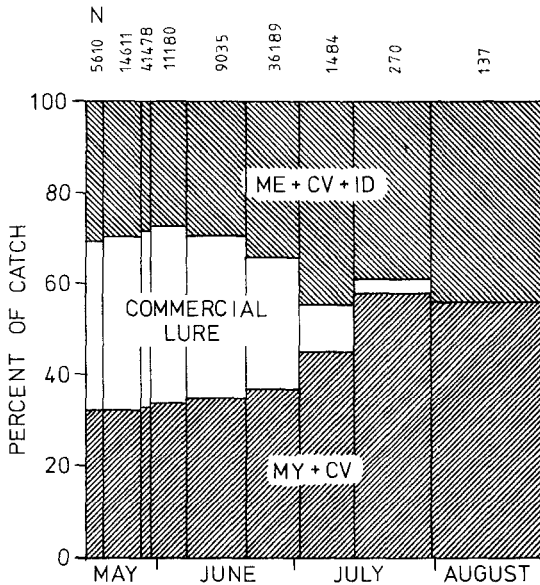


FIG. 1. Relative trap catches of *Ips typographyus* in three treatments with different pheromone blends during successive trapping periods. The catches are given as each treatment's percentage of the total catch during each period (N on top of figure = total number of beetles in period = 100%).

in the attraction of *I. typographus*. The commercial lure was not significantly more attractive than the other blends, despite the addition of ipsdienol.

Long-Term Performance of Methylbutynol. A total of 119,994 *Ips typographus* was trapped between mid-May and late August, giving a mean of 4000 beetles per trap. After one and a half months of the experimental period, the trap catches decreased sharply (Figure 1, N).

The attractiveness of the three treatments to *I. typographus* differed towards the end of the experimental period (Figure 1). Higher catches for the traps baited with commercial lure were recorded during the initial three to four weeks. However, two-way analysis of variance did not reveal any significant differences between the three treatments for trap catches up to 35 days. Later, attractiveness of the commercial dispensers decreased strongly, while the experimental glass dispensers remained attractive until the end of the experiment. MY with CV was at least as attractive as the blend containing ME, CV, and ID over a 102-day period.

The results indicate that 2-methyl-3-butyn-2-ol can effectively replace 2-methyl-3-buten-2-ol in blends for trapping *Ips typographus* over long time periods. Ipsdienol was obviously not required for effective trapping in late season.

DISCUSSION

The experiments show that 2-methyl-3-buten-2-ol can be replaced by 2-methyl-3-butyn-2-ol. We are, however, aware of the impurity of the methylbutenol used (see Methods and Materials).

Several thorough studies have been made on substances produced by *Ips typographus*. It is unlikely that 2-methyl-3-butyn-2-ol would have been overlooked. In any case, it can hardly be expected to be released in nature by the beetles in such amounts that it may act as an effective component in combination with (*S*)-*cis*-verbenol to attract the beetles. A possible release of 2-methyl-3-butyn-2-ol by the host plant has not been studied, but such release is improbable.

In the replacement experiment, no significant differences in catches were found between the three mixtures containing methylbutynol or methylbutenol. In the long-term experiment, MY plus CV was not less attractive than the blend ME + CV + ID. Thus, the usefulness of adding ipsdienol to baits for *I. typographus* can be questioned, particularly since it is so attractive for clerid beetles which prey upon *I. typographus* (e.g., Bakke and Kvamme, 1981; Schlyter, 1985).

The release rate of our glass dispensers was adjusted to the expected release rate of the commercial lure used as the standard. In the experiments the actual release rates of the standards were, on average, lower than those of our glass dispensers. According to studies by Sauerwein (1981), Bakke et al. (1983),

and Regnander (personal communication), this difference in release rates is not expected to significantly affect trap catches. This appears confirmed by the first 35 days of the long-term experiment, during which similar blends in the two types of dispenser gave similar catches, while the drop in catch of the commercial dispensers after these 35 days seems to signify a drastic drop in release and attraction.

Interaction between neighboring treatments could be a source of experimental error in trapping experiments, in our case an overestimation of the least attractive treatment. However, the results of Schlyter (1985) indicate low interaction at a 6-m trap distance.

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REFERENCES

- BAECKSTRÖM, P., BJÖRLING, F., HÖGBERG, H.-E., and NORIN, T. 1983. New three-step syntheses of racemic and optically active ipsdienol from myrcene. *Acta Chem. Scand. B* 37 : 1–5.
- BAKKE, A. 1976. Spruce bark beetle, *Ips typographus*, pheromone production and field response to synthetic pheromones. *Naturwissenschaften* 63 : 92.
- BAKKE, A., and KVAMME, T. 1981. Kairomone response of *Thanasimus* predators to pheromone components of *Ips typographus*. *J. Chem. Ecol.* 7 : 305–312.
- BAKKE, A., FRÖYEN, P., and SKATTEBÖL, L. 1977. Field response to a new pheromonal compound isolated from *Ips typographus*. *Naturwissenschaften* 64 : 98–99.
- BAKKE, A., SAETHER, T., and KVAMME, T. 1983. Mass trapping of the spruce bark beetle *Ips typographus*. Pheromone and trap technology. *Medd. Nor. Inst. Skogsforsk.* 38 : 1–35.
- BIRGERSSON, G., SCHLYTER, F., LÖFQVIST, J., and BERGSTRÖM, G. 1984. Quantitative variation of pheromone components in the spruce bark beetle *Ips typographus* from different attack phases. *J. Chem. Ecol.* 10 : 43–69.
- KONEČNÝ, K., KRIŠTIN, A., ROMAŇUK, M., VARKONDA, Š., and VRKOČ, J. 1984. Czechoslovak Author's Certificate AO 238 949.
- KONEČNÝ, K., KONEČNÝ, V., KRIŠTIN, A., KURÚC, L., ROMAŇUK, M., VARKONDA, Š., and VRKOČ, J. 1985. Czechoslovak Patent Application PV 5988-85.
- OZOLS, G., BIČEVSKIS, M., MENNIKIS, E., GAVELIS, V., JAKAITIS, D., MIHKELSON, S., and ŪNAP, H. 1982. (Results of a study of the application of the synthetic pheromone for the spruce bark beetle in the Baltic area in 1981). *Acta Commun. Univ. Tartu* 616: 7–16 (Russian, English summary).
- REGNANDER, J., and SOLBRECK, C. 1981. Effectiveness of different types of pheromone traps used against *Ips typographus* (L.) (Col., Scolytidae) in Sweden. *Anz. Schaedlängsk. Pflanz., Umweltschutz* 54 : 104–108.
- SAUERWEIN, P. 1981. Untersuchungen zur Wirksamkeit von Pheromonfallen in der Überwachung und Bekämpfung der "Buchdrucker" *Ips typographus* und *Ips amitinus*. Dissertation Hochschulverlag, Freiburg.
- SCHLYTER, F. 1985. Aggregation pheromone system in the spruce bark beetle *Ips typographus*. Dissertation University of Lund, Sweden.