- 100 N. Nishimitsu and M. Yamada, Jap. Pat. No.15.862(60) (21.10.1960) Takeda Pharmaceutical Industries Ltd.
- 101 R. Marbet, Ger. Offen. No. 2.061.507 (8.7.1971) Hoffmann-La Roche.
- 102 H. Pommer, Angew. Chem. 72, 811 (1960).
- H. Freyschlag, H. Grassner, A. Nürrenbach, H. Pommer, W. Reif and W. Sarnecki, Angew. Chem. 77, 277 (1965).
- W. Reif and H. Grassner, Chemie-Ing.-Techn. 45, 646 (1973).
- 105 H. Pommer and A. Nürrenbach, Pure appl. Chem. 43, 527
- 106 H. König, K. Lämmerhirt, J. Paust, C.H. Pich and H. Schumacher, Arzneimittel-Forsch. 24, 1184 (1974)
- 107 W. Stilz and H. Pommer, Ger. Pat. No.1.109.671 (1962) BASF.
- 108 G. Pattenden and B.C.L. Weedon, J. chem. Soc. C 1968, 1984.
- 109 H. Pommer and W. Arend, U.S. Pat. No.2.831.884 (1958); C. A. 53, 226 (1959) BASF.
- S.M. Makin, Russ. Chem. Rev. (Engl. transl.) 38, 237 (1969).
- O. Isler, H. Lindlar, M. Montavon, R. Rüegg and P. Zeller, Helv. chim. Acta 39, 249 (1956). 111
- R. Marbet, unpublished results.
- For the synthesis of further C₅-building units in this series see also J. Paust, W. Reif and H. Schumacher, Liebigs Ann. Chem. 1976, 2194.
- M. Klaus and H. Mayer, unpublished results.
- R. Rüegg, R. Marbet and P. Müller, unpublished results.
- R. Rüegg and P. Müller, unpublished results.
- P.E. Dunagin, R.D. Zachman and J.A. Olson, Science 148, 86 (1965).
- M.H. Zile, R.J. Emerick and H.F. DeLuca, Biochim. biophys. Acta 141, 639 (1967).
- H.F. DeLuca and M. Zile, Acta derm. vener. 55, suppl. 74. Proc. Int. Symp. Therapeutic Use of Vitamin A Acid, Flims, Switzerland, 1975, p. 25.
- 120 P. Rietz, O. Wiss and F. Weber, Vitamins and Hormones, Advances and Applications, vol. 32, p. 237. Academic Press, New York and London 1974.

- 121 R. Hänni, F. Bigler, W. Meister and G. Englert, Helv. chim. Acta 59, 2221 (1976).
- 122 R. Hänni and F. Bigler, Helv. chim. Acta 60, 881 (1977).
- 123 R. Hänni, F. Bigler, W. Vetter, G. Englert and P. Loeliger, Helv. chim. Acta 60, 2309 (1977).
- 124 H. Wolff, E. Christophers and O. Braun-Falco, Arch. klin. exp. Derm. 237, 774 (1970).
- L. Prutkin, J. Invest. Derm. 49, 165 (1967).
- 126 I. Lasnitzki, Natl Cancer Inst. Monogr. 12, 381 (1963).
- M. Frigg and J. Torhorst, J. natl Cancer Inst. 58, 1365 (1977). 127
- A. Matter and W. Bollag, Eur. J. Cancer 13, 831 (1977). 128
- L. DeLuca, N. Maestri, F. Bonanni and D. Nelson, Cancer 30, 1326 (1972).
- 130 S.S. Levinson and G. Wolf, Cancer Res. 32, 2248 (1972).
- G.L. Floersheim and W. Bollag, Transplantation 15, 564 131
- M. Jurin and J.F. Tannock, Immunology 23, 283 (1972).
- J.F. Tannock, H.D. Suit and N. Marshall, J. natl Cancer Inst. 48, 731 (1972). 133
- E. Seiffer, M. Zisblatt, N. Levine and G. Rettura, Life Sci. 13, 945 (1973).
- 135 M.S. Meltzer and B.E. Cohen, J. natl Cancer Inst. 53, 585 (1974).
- 136 E.L. Felix, B. Loyd and M.H. Cohen, Science 189, 886 (1975)
- 137 D.E. Ong, D.L. Page and F. Chytil, Science 190, 60 (1975).
- 138 D.E. Ong and F. Chytil, Nature 255, 74 (1975).
- F. Chytil and D.E. Ong, Nature 260, 49 (1976)
- B. P. Sani and D. L. Hill, Cancer Res. 36, 409 (1976). 140
- A. Scherrer and F. Ott, Revue suisse méd. 65, 453 (1976) 141
- F. Ott and W. Bollag, Schweiz. med. Wschr. 105, 439 (1975). A. Schimpf, Hautarzt 51, 265 (1976). 142
- 143
- F. Ott, Schweiz. med. Wschr. 107, 144 (1977). F. Ott, unpublished results. 144
- 145
- H. Koch, Quintessenz 6, 133 (1976). 146
- 147 U. Fisch, personal communication.
- T. Spreng, personal communication.

SPECIALIA

The editors do not hold themselves responsible for the opinions expressed in the authors' brief reports. - Les auteurs sont seuls responsables des opinions exprimées dans ces brèves communications. - Für die Kurzmitteilungen ist ausschliesslich der Autor verantwortlich. – Per le brevi comunicazioni è responsabile solo l'autore. – Ответственность за короткие сообщения несёт исключительно автор. - Solo los autores son responsables de las opiniones expresadas en estas comunicationes breves.

Attraction of Scolytus scolytus (F.) to the components of Multilure, the aggregation pheromone of S. multistriatus (Marsham) (Coleoptera: Scolytidae)1

Margaret M. Blight, C.J. King², L.J. Wadhams and M.J. Wenham

Agricultural Research Council, Unit of Invertebrate Chemistry and Physiology, University of Sussex, Falmer, Brighton BN1 9RQ (Sussex, England) and Forestry Commission Research Station, Alice Holt Lodge, Farnham GU10 4LH (Surrey, England), 9 February 1978

Summary. The attraction of S. scolytus to the components of Multilure is described. 4-Methyl-3-heptanol is an attractant which is synergised by a-cubebene. Multistriatin appears to be an inhibitor. A combination of 4-methyl-3-heptanol and cubeb oil is more effective as a bait for S. scolytus than Multilure.

In the United Kingdom a major vector of Ceratocystis ulmi (Buism.) C. Moreau, the causal fungus of Dutch elm disease, is the larger European elm bark beetle, Scolvtus scolytus. When unmated beetles bore into English elm, Ulmus procera Salis., the volatiles produced include threo and erythro 4-methyl-3-heptanol I, a-multistriatin II and a-cubebene III^{3,4}. (-)-Threo-I, (-)-II and (-)-III have been identified as components of the aggregation pheromone of $S.multistriatus^{5-7}$. In both species I and II are beetleassociated whilst III is a host metabolite.

In S. scolytus the male produces the secondary attractant⁸. There is also a differential production of I and II between the sexes. a-Multistriatin is produced mainly by females whilst males produce 4-methyl-3-heptanol⁴. This is in contrast to S. multistriatus where the components, I and II, of the aggregation pheromone are produced by the female A mixture, Multilure, of synthetic isomers of 4-methyl-3heptanol and multistriatin, and distilled cubeb oil (70% acubebene) is effective in trapping large numbers of S. mul-tistriatus in the USA⁹, but does not appear to attract large numbers of S. scolytus in Europe¹⁰. We report on field tests designed to indicate the relative attraction of the Multilure components to S. scolytus.

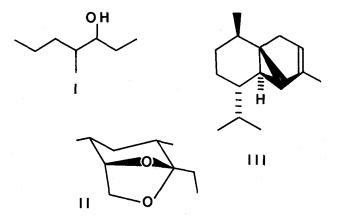
Materials and methods. Field tests were carried out on Sussex farmland between 13 and 29 July 1977. Traps consisting of a 45 cm × 20 cm cylinder of 8-mm metal mesh coated with 'Stikem Special' (Michel and Pelton, Manufacturing Chemists, Emeryville, California) were placed on 1.8 m high 2.5-cm dowels set at least 25 m apart close to hedgerows containing diseased and healthy U. procera.

The Multilure materials used in the trial were: A) 99% 4methyl-3-heptanol (threo:erythro, 2:1), B) multistriatin mixed isomers (34.7% α -isomer), and C) distilled cubeb oil (51.6% α -cubebene). Traps were baited with 1 mg each of A and B and 2 mg of C. Dispensers of the vial within a vial type were used to release the materials. Each component, in 5 ml of pentane, was placed in a separate 4-dram glass vial with a hole (1.7-mm diameter) drilled in the cap. The vials were placed in inverted aluminium containers 11.5 cm×6 cm with 9 holes (6-mm diameter) bored through the lid. The dispensers were positioned at mid-trap height.

The experimental design was a randomised block replicated 3 times (table). To reduce the positional effect of traps the treatments were randomised within blocks a total of 5 times during the experiment. Prior to each randomisation beetles were picked off the traps, immersed in xylene to remove the Stikem and sexed in the laboratory. Data were transformed to $\sqrt{x+0.5}$ and subjected to analysis of variance.

Results and discussion. The release rates of the materials from the dispensers were not constant. Laboratory tests showed that after evaporation of the solvent (i.e. after 5-6 days in the field) the release rates were approximately 300 µg/day for each of the components and thereafter declined exponentially. The ratio of I to II released (approximately 3:1) was relatively constant although the ratio of I to III and II to III was not.

The low catches obtained in these tests (table) were influenced by several factors. The weather conditions, mainly



Response of S. scolytus to the Multilure components

Treatment	Total no. of S. scolytus caught		
	Male	Female	Total
4-methyl-3-heptanol A	43	36	79
Multistriatin B	13	3	16
Cubeb oil C	9	6	15
A+C	60	43	103
A+B	13	15	28
B+C	5	5	10
A+B+C	30	18	48
Control	24	14	38

windy and unseasonally cold, were unfavourable to beetle flight. Additionally there was probably competition between the *U. procera* hedgerows and the adjacent traps. Another disadvantage of placing traps close to hedgerows is that trap silhouette is obscured. Lanier et al. have shown that trap placement influences the catch in S. multistriatus and that visually obscured traps may fail to catch beetles attracted to the immediate vicinity.

Despite the limitations in the experimental design significant data on the attraction of S. scolytus to the Multilure components was obtained. Of the materials tested only 4methyl-3-heptanol showed any attraction in the field (p=0.001). Since I is only produced in appreciable quantities by male beetles the results suggest that 4-methyl-3heptanol forms part of the male-produced aggregation pheromone in S. scolytus.

The attraction to 4-methyl-3-heptanol is enhanced by the addition of cubeb oil (p = 0.05). a-Cubebene was the only major component of the cubeb oil mixture to elicit an increased response when tested in a laboratory bioassay with 4-methyl-3-heptanol⁴. Thus the enhancement of trap catch associated with cubeb oil is probably derived from acubebene, which acts as a host-produced synergist for both S. scolytus and S. multistriatus.

The situation regarding multistriatin is more complex. In laboratory bioassays the response to the mixed isomers used in the field trials is not greatly different from that elicited by a-multistriatin alone. δ -Multistriatin, the major component is inactive⁴. Thus the inhibition shown in the field by the mixed isomers (p=0.01) is probably mediated largely by α -multistriatin.

In a separate experiment using traps baited with S. scolytus infested logs Borden and King⁸ obtained significant catches with males, whereas logs baited with females or equal numbers of males and females elicited low reponses. This effect could be due to the cessation of production of the aggregation pheromone by the males or to an inhibitor produced by the females. Our results favour the latter explanation since in S. scolytus the production of a-multistriatin is mainly associated with females boring into

Further work is in progress to determine the role of the geometric and optical isomers of I, II and III in the chemically mediated behaviour of S. scolytus.

- We thank Mr A.K. Hughes and Mr J. Boswell for their cooperation in allowing us to conduct experiments on Parham Estate; Mr D. Mobbs and Mr C. Thorne for the statistical analyses; Dr J.W. Peacock for samples of mixed isomers of multistriatin and distilled cubeb oil; Mrs J. Allsop and Mr N.J. Fielding for technical assistance. We are grateful to Mr D. Bevan, Dr J.H. Borden, Dr J.F. Grove and Prof. A.W. Johnson for their interest and encouragement.
- Forestry Commission Research Station, Alice Holt Lodge, Farnham GU10 4LH, Surrey, England.
- M. M. Blight, F. A. Mellon, L. J. Wadhams and M. J. Wenham, Experientia 33, 845 (1977).
- M.M. Blight, L.J. Wadhams and M.J. Wenham, Insect Biochem. 8, 135 (1978).
- G.T. Pearce, W.E. Gore, R.M. Silverstein, J.W. Peacock, R.A. Cuthbert, G.N. Lanier and J.B. Simeone, J. chem. Ecol. *I*, 115 (1975).
- G.T. Pearce, W.E. Gore and R.M. Silverstein, J. org. Chem. 41, 2797 (1976).
- K. Mori, Tetrahedron 33, 289 (1977).
- J.H. Borden and C.J. King, For. Commn. Res. Development
- paper U.K., No. 118 (1977). G.N. Lanier, R.M. Silverstein and J.W. Peacock, in: Perspectives in Forest Entomology, p. 149. Ed. J.F. Anderson and H.K. Kaya. Academic Press, 1976.
- J.P. Vité, R. Lühl, B. Gerken and G.N. Lanier, Z. PflKrankh. PflSchutz 83, 166 (1976).