

bles the growth of *Marchantia* described by Fredericq and De Greef⁹.

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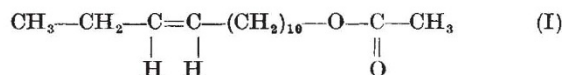
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Sex Attractant of the Red-banded Leaf Roller Moth

REPORTS on insect attractants are numerous, but few actually reveal the structure of a compound which is active outside the laboratory. We have identified the sex pheromone of the red-banded leaf roller moth, *Argyrotaenia velutinana* (Walker), to be *cis*-11-tetradecenyl acetate (I).



This compound, synthesized in two independent ways, was found to be highly attractive in apple orchards to male moths of the same species.

Abdominal tips of 40,000 female moths^{1,2} were extracted with methylene chloride and chromatographed on successive columns of 'Florilil' and silver nitrate-impregnated silica gel eluted with petroleum ether to petroleum ether-ethyl ether (50 : 50) concentration gradients. The active fractions, determined by a previously described bioassay procedure³, were combined in each case for the next purification step.

Earlier results³ obtained from saponification-acetylation, hydrogenation, and bromination of crude extract had shown the active compound to be an unsaturated acetate. Gas chromatographic analysis of the active fractions indicated the presence of only one major component, which was found to possess activity and to behave like a mono-unsaturated 14 carbon chain acetate. A comparison of retention times of the attractant compound and tetradecyl acetate gives a ratio of 1.17 on a polar column (3 per cent cyclohexanedimethanol succinate on 'Chromosorb Q') and 0.95 on a non-polar column (10 per cent JXR on 'Chromosorb Q'). Catalytic hydrogenation yields a product with the retention time of tetradecyl acetate on four different gas chromatography columns.

Collection of approximately 200 µg of attractant from the gas chromatograph enabled us to locate the double bond by ozonolysis. Reductive cleavage of the ozonide yields two products identical to propionaldehyde and 11-acetoxyundecanal by gas chromatography. An infrared spectrum of the attractant exhibits acetate absorption at 1740 and 1240 cm⁻¹, and a nuclear magnetic resonance spectrum from 128 accumulated runs appears as expected for structure I, in particular the undistorted ω-methyl triplet at 9.06τ (*J* = 7.5 Hz) which is typical for compounds containing the ω-3 double bond⁴.

To assign the geometrical configuration, we synthesized both *cis* and *trans* 11-tetradecenyl acetates. Reaction of the tetrahydropyranyl ether of 10-bromodecan-1-ol⁵ with excess lithium salt of 1-butyne in liquid ammonia and subsequent acid hydrolysis yields 11-tetradecyn 1-ol (II). Catalytic hydrogenation⁶ of II and subsequent acetylation gives *cis*-11-tetradecenyl acetate (I). Reduction of II with sodium in liquid ammonia and subsequent acetylation yields the *trans* isomer. Thin-layer chromatography on silver nitrate-impregnated silica gel with benzene-petroleum ether (80 : 20) gives *R_F* values of 0.28 and 0.48 for the *cis* and *trans* isomers, respectively. The natural attractant is identical to the *cis* isomer by thin-layer as well as gas chromatography.

An economical synthesis of I was achieved by means of a novel one-pot reaction sequence. Condensation of 11-bromoundecyl acetate and propionaldehyde was effected by a Wittig reaction^{7,8} using dimethylformamide as solvent and sodium methoxide as catalyst.

0.1 µg of the synthetic attractant elicits maximum responses in the laboratory with male red-banded leaf roller moths, while the *trans* isomer is inactive up to 100 µg. The synthetic attractant passed the ultimate test by attracting more than 3,000 male red-banded leaf roller moths to traps hung in apple orchards during a brief spring flight period. The *trans* isomer caught no moths.

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Operculum Development and the Taxonomy of Eucalypts

In eucalypts the stamens and style of the flower are covered until anthesis by a cap or operculum. Studies of the structure of the operculum have yielded valuable information about relationships within the group and materially assisted in its taxonomy. We describe here the results of further studies on the development of the operculum and show that they lead to a re-appraisal of these relationships and shed light on the evolution of the eucalypts.

We have already shown¹ that the operculum is by no means uniform in structure or development throughout the genus. There is a large group of species in which the perianth whorls are separate from each other and form two opercula which fit one over the other. Both caps are deciduous, the inner one at anthesis, the outer one before or also at anthesis. This group of di-operculate species was distinguished from a numerically smaller group (mono-operculate) in which the operculum throughout its development appeared to be a single structure, formed of the corolla only. This group includes nine species of series *Eudesmieae*² (*Eudesmieae A*) which have free sepals which surround the orifice in the flower and persist on the