

## Sex-pheromones. *cis*-Dec-5-en-1-yl 3-Methylbutanoate as the Pheromone from the Pine Emperor Moth (*Nudaurelia cytherea cytherea* Fabr.)

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**Summary** The sex-pheromone of the female pine emperor moth (*Nudaurelia cytherea cytherea* Fabr.) has been shown to be *cis*-dec-5-en-1-yl 3-methylbutanoate by g.l.c., i.r., n.m.r., and m.s.; the synthetic ester shows strong attraction in field tests.

STUDIES of the sex pheromone of the pine emperor moth (*Nudaurelia cytherea cytherea* Fabr.) which is indigenous to, and a pest in the pine plantations of, Southern Africa has resulted in the isolation from 35,000 female moths of a small quantity (300  $\mu$ g) of a pure (g.l.c.) concentrate showing strong responses on an electroantennogram (EAG) and attraction of the male moth in field tests. Early experi-

ments showed that this activity was destroyed by catalytic hydrogenation and hydrolysis and that the activity of the hydrolysate was not restored by acetylation, as in the case of the false codling moth,<sup>1</sup> or methylation. Activity was also destroyed by bromination, lithium aluminium hydride reduction, and epoxidation.

On g.l.c. the active compound showed a retention time slightly less than that of a straight chain C<sub>14</sub> methyl ester on a polar column (2% free fatty acid phase) and a retention time identical to that of the same ester on a less polar column (5% OV 25, phenyl silicone). The i.r. [ $\nu_{\max}$  (CCl<sub>4</sub>) 1735 (C=O) and 1187 (C-O) cm<sup>-1</sup>], n.m.r. [ $\tau$  (CDCl<sub>3</sub>) 9.03 (6H, d, *J* 6.3 Hz, Me<sub>2</sub>CH), ca. 9 (3H, t, aliphatic Me), 6.01

(2H, t,  $J$  6.0 Hz,  $\text{CH}_2\text{-CH}_2\text{-O}$ ), and 4.71 (2H, m,  $\text{CH}=\text{CH}$ )], and comparative g.l.c. data<sup>2</sup> of the pheromone indicated that the compound was a *cis*- $\text{C}_{15}$ -monounsaturated ester (no i.r. absorption at 970—960  $\text{cm}^{-1}$ ). The m.s.  $m/e$  240.2089 ( $M^+$ ,  $\text{C}_{15}\text{H}_{28}\text{O}_2$  requires 240.2097, 0.1%),  $m/e$  138.1408 ( $\text{C}_{16}\text{H}_{18}$  requires 138.1395, 90%), and  $m/e$  110 (100%). These spectra were indicative of *cis*-dec-5-en-1-yl 3-methylbutanoate. A synthetic sample showed identical spectra and elicited pronounced responses on the EAG and attracted male moths to traps in the field while the corresponding *trans*-5-isomer was inactive. The sex-pheromones

of the Lepidoptera so far reported as esters have all been acetates. This is the first report of a sex-pheromone as an isovalerate.

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<sup>2</sup> J. K. Hakin, *J. Chromatog.*, 1967, **26**, 17; G. R. Jamieson and E. H. Reid, *ibid.*, p. 8.