Synthesis of a Highly Potent Gypsy Moth Sex Attractant

Sir:

The gypsy moth (Porthetria dispar L.) is one of the most serious pests of fruit, shade, and woodland trees in New England and eastern New York State, causing extensive loss by defoliation. The male is attracted to the virgin female by means of a substance secreted by her abdominal glands, and the use of traps baited with a crude extract of these glands is the best known means of detecting infestations of the insect.¹ Collection of the necessary insects and preparation of the extract are extremely costly and a practical, efficient synthetic attractant is needed as a substitute. 12-Acetoxy-1-hydroxycis-9-octadecene (I), prepared as a model compound for oxidation studies during the chemical investigation of the natural lure,² has now been found to be a highly potent attractant for the male gypsy moth.

$$CH_{3}(CH_{2})_{5}CHCH_{2}CH=CH(CH_{2})_{7}CH_{2}OH \qquad I$$

Lithium aluminum hydride reduction of ricinoleic acid (Kahlbaum) gave a quantitative yield of rincinoleyl alcohol [b.p. 175°/0.5 mm., n_D^{25} 1.4704, $[\alpha]_D^{30}$ +5.3° (chloroform); reported³ b.p. 178°/0.5 mm., n_D^{25} 1.4700, $[\alpha]_D^{24}$ +5.7° (undiluted). Anal. Found: C, 75.83; H, 12.67], which was acetylated in 62% yield with acetyl chloride in refluxing benzene (containing pyridine) to the 1,12-diacetate [b.p. 180°/1.3 mm., n_D^{25} 1.4519, $[\alpha]_D^{30}$ +8.7° (chloroform). Anal. Found: C, 71.52; H, 11.06].

Saponification with refluxing ethanolic potassium hydroxide removed only the primary acetyl group,⁴ giving a 90% yield of I [b.p. 182°/0.5 mm., n_D^{25} 1.4607, $[\alpha]_D^{30}$ +7.4° (chloroform). Anal. Found: C, 73.36; H, 11.70]. The compound shows blue fluorescence in ultraviolet light, is remarkably stable to heat, and does not appear to decompose on storage at room temperature.

Male gypsy moths in large numbers were lured to field traps containing as little as one microgram of I, 5.6 and the compound was attractive at one ten-millionth of a microgram in laboratory bioassay tests.⁷ These figures compare very favorably with the activity of the natural attractant. The use of the synthetic lure in U. S. Department of Agriculture survey traps should result in substantial monetary savings in the conduct of current programs, and the product may provide a new means of control.

The effect of isomerization of the double bond of I and its optical isomers on activity is being investigated.

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(4) The secondary acetyl group was extremely resistant to saponification with refluxing ethanolic alkali, and it was necessary to use diethylene glycol-potassium hydroxide mixture at 120° to break this linkage.

(5) Field tests were carried out as described by J. M. Corliss, *Yearbook of Agriculture (Insects)*, 694 (1952). The assistance of Mr. E. C. Paszek, U. S. Department of Agriculture, Nashua, N. H., in carrying out these tests is gratefully acknowledged.

(6) The only lures previously reported, 1,2-epoxyhexadecane and 1,2-hexadecanediol [cf. M. Jacobson, U. S. Patent 2,900,756 (Aug. 25, 1959)] were considerably less attractive in the field when tested at 0.5 g. per trap.

(7) Bioassay tests were carried out by the method of B. C. Block, J. Econ. Entomol., 53, 172 (1960).

⁽¹⁾ F. Acree, Jr., M. Beroza, R. F. Holbrook, and H. L. Haller, J. Econ. Entomol., 52, 82 (1959).

⁽²⁾ M. Jacobson, M. Beroza, and W. A. Jones, Science, October 1960.

⁽³⁾ S. P. Ligthelm, E. von Rudloff, and D. A. Sutton, J. Chem. Soc., 3187 (1950).