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Isolation and Identification of the Sex Attractant of the American Cockroach

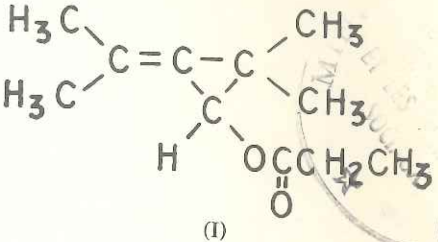
Abstract. *The highly potent sex attractant of the female American cockroach,* Periplaneta americana *(L.), has been isolated in pure form and identified as 2,2-dimethyl-3-isopropylidenecyclopropyl propionate. The hydrogenated form of the attractant has been synthesized.*

The virgin female American cockroach, *Periplaneta americana* (L.), emits a powerful attractant which elicits intense excitement and characteristic wing-raising in the males of this species (*1*). Wharton *et al.* (*2*) showed that filter paper over which these females had crawled was highly attractive to males, and these investigators have very recently reported that they obtained from such paper 28 μg of a pure attractant which they were not able to identify (*3*). As the result of an independent investigation, we report the successful isolation and identification of the natural sex attractant.

Extraction of filter papers with which virgin female roaches had been in contact gave extremely small amounts of an attractive mixture from which the abundant contaminants were very difficult to separate. Much larger amounts of fairly pure attractant were obtained by passing air continuously over many virgin females in metal containers, condensing the vapors in a dry ice cooled flask containing a little 0.1-percent hydrochloric acid (*4*), and extracting the condensate with distilled hexane (*5*). The hexane solution was washed with water, dried over sodium sulfate, and freed of solvent at 20 mm-Hg pressure (bath below 40°C). The residual yellow semisolid was chromatographed on a column of silicic acid [Bio Rad Laboratories, Richmond, Calif., specially treated to conform with that described by Hirsch and Ahrens (*6*)] by successive elution with spectral-grade hexane and 3 percent ether in hexane; elution with 10 percent ether in hexane then removed a highly active yellow liquid from which the pure attractant was obtained by steam distillation. In this way there was obtained, from the equivalent of approximately 10,000 females "milked" continuously over a 9-month period, 12.2 mg of the pure attractant as a yellow liquid with a characteristic odor; it elicits a response from males at levels below 10^{-14} μg.

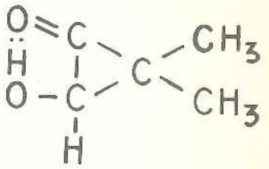
Gas chromatography of the attractant on a 4-foot Chromosorb W column (80 to 100 mesh) coated with 5-percent Apiezon M, under conditions identical with those reported by Wharton *et al.* (*3*), gave a single peak with an elution time of 6 minutes as contrasted with 105 or 145 minutes reported by them. In a single determination it analyzed for $C_{11}H_{18}O_2$, showed no optical rotation at a concentration of 1.8 percent ($CHCl_3$), and was free of absorption in the ultraviolet range. Its infrared spectrum showed it to be an ester, which was supported by its inactivation through refluxing with dilute alkali or concentrated hydrochloric acid; the presence of an isopropylidene group at 12.5 μ was also indicated (*7*). Catalytic hydrogenation of 2.2 mg of the attractant with platinum oxide catalyst resulted in an uptake of hydrogen sufficient for 1.1 double bonds, giving a colorless, inactive oil whose infrared spectrum lacked isopropylidene absorption and showed splitting at 7.25 μ characteristic of an isopropyl group. Hydrogenolytic chromatography of the attractant by the method of Beroza (*8*) gave ethane and 2,2,4-trimethylpentane. A nuclear magnetic resonance spectrum at 60 mcy/sec on the limited amount of attractant in deuterochloroform showed no hydrogen attached to a double bond and disclosed, among other features, two sharp prominent peaks: one at 75.5 cy/sec from internal tetramethylsilane was roughly equivalent to six hydrogen atoms (two methyl groups) and one at 140.5 cy/sec was equivalent to one hydrogen atom. Alkaline saponification of 2.2 mg of the saturated compound showed a saponification equivalent of 182, yielding 1.5 mg of a liquid alcohol, whose infrared spectrum showed a secondary hydroxyl group, and 0.85 mg of an acid identified by paper chromatography and its infrared spectrum as propionic acid. Oxidation of 4 mg of the attractant with periodate-permanganate reagent (*9*) gave propionic acid (identified by infrared spectrum and paper chromatography), acetone [2,4-dinitrophenylhydrazone, mp 127°C, undepressed by an authentic sample, λ_{max} 349 mμ (EtOH)], and 2.2 mg of a neutral substance that formed colorless crystals, mp 55°C (from ethyl acetate), λ_{max} 277 mμ (EtOH), whose 2,4-dinitrophenylhydrazone melted at 232°C, λ_{max} 355, 358 mμ ($CHCl_3$). The infrared spectrum of this substance indicated the presence of a chelated hydroxyl and showed two carbonyl bands. Further oxidation with periodic acid converted the neutral substance to a crystalline acid, mp 197° to 198°C, identified as dimethylmalonic acid by paper chromatography, infrared spectrum, and mixed melting point with a pure synthetic sample.

The only structure for the attractant consistent with the foregoing data is 2,2-dimethyl-3-isopropylidenecyclopropyl propionate (I).



(I)

The neutral substance formed on oxidation probably possesses the structure shown in (II).



(II)

That the attractant does indeed possess structure I was proved by synthesizing its hydrogenation product according to the following procedure. The reaction of 2,4-dimethyl-2-pentene with diazoacetic ester in the presence of copper powder (*10*) gave ethyl 2,2-dimethyl-3-isopropylcyclopropanecarboxylate (54 percent; bp 95° to 100°C at 20 mm-Hg; n_D^{25} 1.4315), which was saponified with ethanolic potassium hydroxide to the corresponding acid (66 percent), a colorless, viscous oil. The undistilled acid was decarboxylated with lead tetraacetate and iodine (*11*) to give 2,2-dimethyl-1-iodo-3-isopropylcyclopropane (66 percent; bp 52°C at 20 mm-Hg). Reaction of the iodide with silver propionate in dry benzene gave 2,2-dimethyl-3-isopropylcyclopropyl propionate (35 percent; bp 112°C at 20 mm-Hg; n_D^{25} 1.4352; analyzed exactly for $C_{11}H_{20}O_2$), whose infrared spectrum and elution time (5.9 minutes) by the previously cited gas chromatographic procedure were identical with those of the hydrogenated attractant.

MARTIN JACOBSON
MORTON BEROZA
ROBERT T. YAMAMOTO
Entomology Research Division, U.S. Department of Agriculture, Beltsville, Maryland

References and Notes

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