DEFENSIVE SECRETION OF A CARABID BEETLE,
*Helluomorphoides clairvillei*

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Abstract—The defensive spray of a single female of the rare carabid beetle, *Helluomorphoides clairvillei* (subfamily Cambinae, supertribe Lebiitae, tribe Helluonini), was found to contain a mixture of compounds, including carboxylic acids (formic, acetic), aliphatic esters (principally nonyl acetate), and hydrocarbons (principally decane). In a single series of discharges, the beetle ejected a total of about 1% of its body weight as formic acid (1.1 mg). Our findings demonstrate that characterization of secretory components from even minimal samples of secretion should be possible in many cases.

Key Words—Coleoptera, Carabidae, beetles, *Helluomorphoides clairvillei*, defensive secretion, formic acid, acetates, formates, hydrocarbons.

INTRODUCTION

Information is now available on the chemistry of the defensive secretion of over 300 species of carabid beetles (Blum, 1981; Weatherston and Percy, 1978; Dettner, 1987). While early characterizations had been restricted largely to major components of the mixtures, improved instrumentation, particularly capillary gas chromatography, has made possible the characterization of minor components, even from very small samples of material. We here report on the composition of the defensive spray of a rare carabid beetle, *Helluomorphoides clairvillei*, that was available to us as a single specimen only. Some years ago,
we investigated the secretions of two other species of *Helluromorphoides* and characterized only formic acid and nonyl acetate (Eisner et al., 1968). In *H. clairvillei* we were able to detect 26 components.

**METHODS AND MATERIALS**

The single female beetle (120.5 mg, 18 mm body length) was collected near Lake Placid, Highlands County, Florida, and maintained in the laboratory on water and freshly cut mealworms. The specimen is now deposited under lot label 1206 (T. Eisner) in the Cornell University insect collection.

**Collection of Secretion.** To obtain secretion for analysis, the beetle was induced to spray by pinching its legs with forceps while it was confined in a small vial. Two individual milkings were obtained in which the beetle was caused to eject several times in succession into vials (cold ether was added as solvent). After a period of three weeks, in which the beetle was kept undisturbed, it was again milked, but this time by being caused to spray only once into each of four vials, to which 100 μl of cold ether was then added.

**Chemicals.** Heptyl, octyl, nonyl, decyl, undecyl, and dodecyl acetates were purchased from Sigma Chemical Co. The formates were synthesized by heating the corresponding alcohols with 88% formic acid. The propionates and butyrates were made from the corresponding alcohols and acid anhydrides.

**Derivatization.** Pentafluorobenzyl esters of carboxylic acids and dimethyl-disulfide (DMDS) derivatives of unsaturated compounds were prepared as previously described (Attygalle and Morgan, 1986).

**Analytical Procedures.** Gas chromatography was performed on a Hewlett-Packard (HP) 5890 instrument equipped with a splitless injector, a flame ionization detector (FID), and a HP 3396A integrator. The following 25-m × 0.22-mm fused-silica columns were used: DB-1; DB-Wax; Superox-FA.

Infrared and mass spectra were obtained with a HP 5890 gas chromatograph linked in series to a HP 5965A IR detector and a HP 5970 mass selective detector (MSD). Analyses were performed using a 25-m × 0.32-mm fused-silica column coated with SE-54. Mass spectra were also obtained on a HP 5890 gas chromatograph linked to a Finnigan ion trap detector (ITD).

For quantitative determinations of acidic components (ion-trap detection) and nonacidic components (flame-ionization detection), the external standards were, respectively, formic acid (Mallinckrodt) and decyl acetate (Sigma Chemical Co.).

**RESULTS**

The pungent odor of formic acid was easily recognized when the beetle was “milked.” However, analytical determination of formic acid without prior derivatization is not entirely straightforward. Thus, the flame-ionization detector