VOLATILE CONSTITUENTS OF THE BRONZE ORANGE BUG, *RHOECOCORIS SULCIVENTRIS**

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Preliminary experiments in April 1960 indicated that the bronze orange bug, *Rhoecocoris sulciventris*, secretes a stinking unsaturated aldehyde of presumably defensive function, reminiscent of the occurrence of 2-hexenal in the cockroach *Eurycotis floridana* (Roth, Niegisch, and Stahl 1956). A large number of the insects were collected in January 1961 to furnish adequate material for the identification of the steam-volatile constituents. While another examination (Waterhouse, Forss, and Hackman 1961) of these odorous constituents has recently been published, our work presented here provides a more complete list of the steam-volatile constituents.

In Figure 1 are compared gas chromatograms of the oil obtained from the bugs by steam distillation and that ejected by the bugs under provocation. The steam distillate yielded in decreasing proportion, n-tridecane (78% by wt.), *trans*-2-octenal (18%), *trans*-2-octenyl acetate (2·1%), n-dodecane (1·1%), *trans*-2-decenal (0·6%), and four very minor constituents. The ejected secretion was similar but with the virtual absence of the octenyl acetate peak and the addition of another peak in the gas chromatogram at a slightly lower retention time than octenal. The absence of the ester from the ejected secretion and the report that 2-hexenyl acetate is the sex attractant of the bug *Belostoma indica* (Butenandt and Tam 1957), suggests that octenyl acetate may be a sex attractant for *R. sulciventris*. Examination of our gas chromatograms showed that 2-hexenal, reported by Waterhouse, Forss, and Hackman (1961) as a minor constituent of the steam-distilled oil, was represented only by a very small peak (*c.* 0·2% by wt.) indeed. Again in contrast to the results of Waterhouse, Forss, and Hackman our steam-distilled oil contained no significant dicarbonyl compound. The ejected secretion did however show an additional peak over the steam-distilled oil and also yielded an additional high-melting, red dinitrophenylhydrazone (m.p. >210 °C, not further investigated). The dicarbonyl compound reported by Waterhouse, Forss, and Hackman (1961) may not have withstood the higher temperatures used in our gas chromatograph.

A few specimens of another citrus inhabitant, the larger horned citrus bug (*Biprorulus bibax*), were also steam distilled to yield oil in which n-tridecane, n-dodecane, *trans*-2-decenal, and *trans*-2-decenyl acetate were indicated by gas chromatographic peaks of correct retention time.

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Experimental

Steam distillation of mature bugs of both sexes and some nymphs under an oil trap, yielded a light yellow oil (*c.* 9 μl per bug) which substantially crystallized on storage at —30 °C. The oil was fractionated in a semimicro still with 20 cm of Bower-Cooke packing under 10 mm pressure. For gas chromatography, columns (4 ft) of Apiezon M on dimethyldichlorsilane-treated Embacel were used with a flame temperature detector and Franklin's (1949) method for calculation of heats of combustion.

(*a*) trans-*2-Octenal.*—The distillate fraction (Found : C, 75·1 ; H, 11·1%. Calc. for $C_8H_{14}O$: C, 76·1 ; H, 11·2%) of b.p. 72–72·5 °C/10 mm, showed strong infrared absorption bands at 721, 975, 1650, and 1686 cm^{-1} and ultraviolet absorption maxima at 222·5 (ε=9400) and 328 mμ

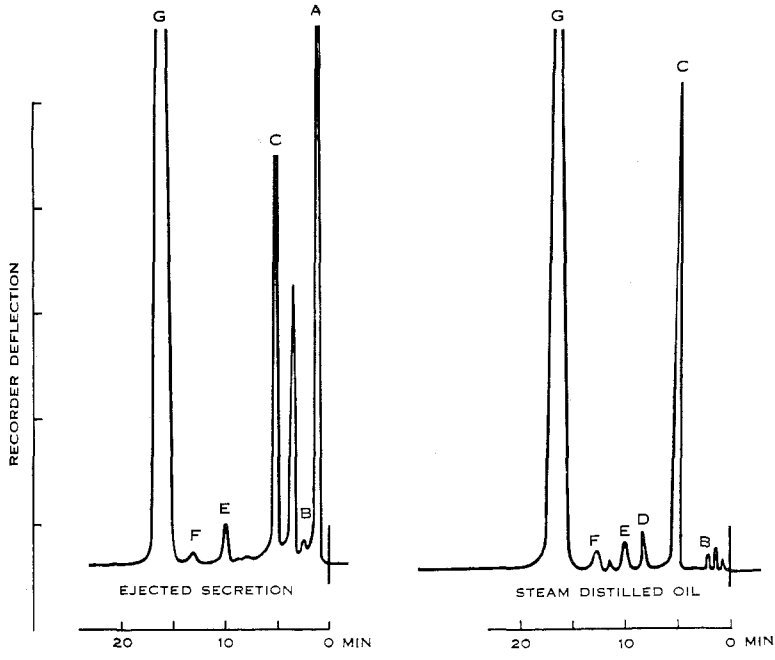

Fig. 1.—Gas chromatograms of oils from *Rhoecocoris sulciventris* on Apiezon M columns at 170 °C (at different gas flow rates). *A*, solvent ; *B*, hexenal ; *C*, octenal ; *D*, octenyl acetate ; *E*, dodecane ; *F*, decenal ; *G*, tridecane.

(ε=20). Gas chromatography showed a peak of correct retention time, contaminated by some 10% of octenyl acetate. The recrystallized dinitrophenylhydrazone (Found : C, 54·8 ; H, 6·1 ; N, 18·5%. Calc. for $C_{14}H_{18}N_4O_4$: C, 54·9 ; H, 5·9 ; N, 18·3%), m.p. 127–128 °C, showed *no* depression with a synthetic sample of m.p. 126–127 °C.

(*b*) trans-*2-Octenyl Acetate.*—The distillate fraction of b.p. 89–90 °C/10 mm was richest in octenyl acetate and after treatment with Girard's reagent P, showed only the octenyl acetate peak of correct retention time and strong paraffin peaks. This concentrate (54 mg) was ozonized in methylene chloride and the residue subjected to the usual treatment for the C-methyl determination apart from a substantial reduction in the quantity of oxidant. The neutralized distillate (1·7C-methyls) was evaporated to dryness and the salts converted to butyl esters by treatment with butanol and *p*-toluenesulphonic acid on the water-bath. Gas chromatography showed a butanol peak, a large butyl acetate peak, a small butyl propionate peak, and other peaks of increasing size attributable to butyl butyrate, valerate, and caproate. The infrared absorption spectrum showed bands consistent with the presence of *trans*-2-octenyl acetate (719, 960, 1020, 1230, 1360, 1375, 1445, 1458, 1736 cm^{-1}) contaminated with some alkane.

(*c*) *n-Dodecane.*—The distillate fraction of b.p. 86–88 °C/10 mm was treated on the water-bath with conc. H_2SO_4 to yield a resistant oil of m.p. —11 to —9 °C. The retention time of the principal peak (some tridecane also present) was identical with that predicted for n-dodecane from a log-plot of the retention times of n-undecane and n-tridecane against carbon number.

(*d*) trans-*2-Decenal.*—The distillate fraction of b.p. 90–105 °C/10 mm was treated with Girard's reagent P and the carbonyl compounds were regenerated by Teitelbaum's (1958) method. The infrared absorption bands observed at 720, 974, and 1698 cm^{-1} are consistent with the proposed structure as is the observed retention time. The recrystallized dinitrophenylhydrazone, m.p. 123–124 °C, showed no depression with an authentic sample 124–125 °C kindly supplied by Mr. D. Forss of the Dairy Research Section, C.S.I.R.O.

(*e*) *n-Tridecane.*—The distillate fraction (Found: C, 84·4; H, 15·3%. Calc. for $C_{13}H_{28}$: C, 84·7; H, 15·3%) of b.p. 105·5 °C/10 mm and m.p. —6 °C, resisted treatment with hot conc. H_2SO_4 and coincided closely in physical properties, retention time, and infrared spectrum with n-tridecane.

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