CHEMISTRY OF CEPHALIC SECRETION
OF FIRE BEE *Trigona (Oxytrigona) tataira*[1,2]

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Abstract—Analysis of the volatile compounds derived from cephalic glands of the fire bee *Trigona (Oxytrigona) tataira* by GC-MS was undertaken. The following compounds were readily identified: hydrocarbons: n-$C_{11}H_{24}$, n-$C_{13}H_{28}$, n-$C_{14}H_{30}$, n-$C_{15}H_{32}$, n-$C_{17}H_{36}$, n-$C_{23}H_{48}$, n-$C_{15}H_{30}$, n-$C_{17}H_{34}$, n-$C_{21}H_{42}$, and n-$C_{21}H_{44}$; carboxylic acids: palmitic acid, linoleic acid, linolenic acid, stearic acid, and oleic acid; carboxylic esters: dodecyl acetate, tetradecyl acetate, hexadecyl acetate, octadecyl acetate, and dodecyl decanoate; monoketones: 5-hepten-2-one, 3-hepten-2-one, 2-heptanone, and 5-nonen-2-one. Two major components of the mixture were identified as *E*-hepten-2,5-dione and *E*-3-nonen-2,5-dione. Structures of these novel compounds were suggested by their GC-MS behavior and the GC-MS behavior of their dimethoximes and proved by comparison with authentic synthetic samples. Trace amounts of the corresponding *Z* isomers and the saturated analogs, heptan-2,5-dione and nonan-2,5-dione, were also found. The possible functions of these glandular constituents are discussed.

Key words—Fire bee, *Trigona (Oxytrigona) tataira*, Hymenoptera, Apidae, mandibular gland secretion, enediones, monoketones, carboxylic esters, hydrocarbons, *E*-3-hepten-2,5-dione, *E*-3-nonen-2,5-dione.

INTRODUCTION

Among stingless bees in the genus *Trigona*, *T.* (*Oxytrigona*) *tataira* and its relatives are particularly noteworthy because of the unusual properties of its mandibular gland secretion. This apid successfully plunders the food reserves from the nests of other species of stingless bees. It also produces a secretion from its extensively developed mandibular gland (Kerr and Costa Cruz, 1961) that produces lesions when administered to the skin of human beings (Wille, 1961). Because of the vesicatory properties of this exudate, it is frequently referred to as the fire bee. Our recent investigations of the robbing *modus vivendi* of *T. tataira* suggest that the secretion from the capacious mandibular glands may constitute powerful allomones that effectively disrupt the defensive behavior of bees whose nests are being plundered.

One of us (T.E.R.) recently observed that workers of *T. tataira* successfully invaded the nests of honeybees (*Apis mellifera*) (Moure, 1946), which were robbed of resources in the absence of any organized resistance on the part of the host bees. During these raids, the air in the vicinity of the hives was redolent with a floral odor which was subsequently shown to be derived from the cephalic secretion of workers of *T. tataira*. In the present study, we report on the chemistry of the cephalic secretion of this bee which is characterized by the presence of several novel insect natural products.

METHODS AND MATERIALS

Bees

Workers of *T. tataira* were collected in Acarigua, Venezuela. The bees were immediately decapitated, and the heads were placed in vials containing methylene chloride. All subsequent analyses were undertaken on these extracts.

Chemical Analyses

Mass spectra and analytical gas chromatographic data were obtained on an LKB-2091 GC-MS system at 70 eV, a source temperature of 270–300°C, separator 270°C, using 50 μA ionizing current. Fused quartz capillary columns [15 m × 0.33 mm ID coated with SE-30 liquid phase (J and W Scientific Co., Rancho Cordova, California)] were used throughout. Gas chromatographic analyses of synthetic mixtures and preparative gas chromatography were carried out on a GOW-MAC model 169-150 gas chromatograph equipped with 2 m × 5 mm ID columns packed with 10% SE-30 on Chromosorb W. Infrared spectra were obtained using a Perkin-Elmer model 467 grating infrared spectrophotometer. NMR spectra were obtained at 60

MHz with a Varian A60-A instrument and at 360 MHz with a Nicolet 360 MHz FT instrument. All boiling points and melting points are uncorrected.

Heptan-2,5-dione and Nonan-2,5-dione

These 1,4-diketones were prepared according to the literature (Stetter et al., 1974) and had the following mass spectra: heptan-2,5-dione: see Figure 1a; nonan-2,5-dione MS: m/z (rel. %) 156 (1,M+·), 141(1), 128(2), 115(5), 114(76), 109(2), 99(95), 85(56), 71(70), 57(88), 55(13), 43(100), 42(9), 41(3).

Selenium Dioxide Oxidation of 1,4-Diketones

E-3-Hepten-2,5-dione. A mixture containing 5 g of heptan-2,5-dione and 4 g of selenium dioxide in 100 ml of water was heated to reflux for 5 hr (Figure 2). The mixture was steam distilled to give 200 ml of condensate which was extracted with three 70-ml portions of ether. The combined ethereal extracts were dried over anhydrous MgSO₄, filtered, and the solvent was removed in vacuo to give 2 g of an oil. Gas chromatographic analysis of the oil showed it to approximate a 1:1 mixture of the starting diketone and a single component with a longer retention time. Preparative gas chromatography provided a pure sample of this component as a waxy solid, mp 35–36°C; NMR (360 MHz): $\delta = 6.83$ (s, 2H, HC=CH), 2.69 (q, 2H, $J = 7.2$ Hz, COCH₂—), 2.63(s, 3H, CH₃CO), 1.13(t, 3H, $J = 7.2$ Hz, —CH₂CH₃); MS: see Figure 1b. A small amount (ca. 5%) of a component with an identical mass spectrum, presumed to be the Z isomer, was also discovered upon GC-MS analysis of the mixture.

E-3-Nonen-2,5-dione. A 5-g sample of nonan-2,5-dione was treated with selenium dioxide as described above. Gas chromatographic analysis of the resulting oil showed approximately a 1:1 mixture of the starting diketone and a single longer retention time component which was obtained by preparative gas chromatography as a waxy solid, mp 36–37°C; NMR (360 MHz): $\delta = 6.84$(s, 2H, HC=CH), 2.66(t, 2H, $J = 7.2$ Hz,—CH₂CO), 2.47(s, 3H, CH₃CO), 1.64(m, 2H, COCH₂CH₂), 1.35(sextet, 2H, $J = 7.2$ Hz, CH₃CH₂CH₂—), 0.92(t, 3H, $J = 7.2$ Hz, —CH₂CH₃); MS: m/z (rel. %) 154(1,M+·), 139(3), 126(2), 125(1), 112(25), 111(39), 98(12), 97(100), 85(7), 84(2), 83(2), 82(2), 71(6), 70(5), 69(17), 57(17), 55(21), 54(5), 53(3), 43(47), 41(16). As before, a minor component (ca. 5%) with an identical mass spectrum, presumed to be the Z isomer, was also observed upon GC-MS analysis of this reaction mixture.

2-Butyl-5-methylfuran. A mixture containing 3 g of nonan-2,5-dione and a small amount (ca. 0.3 g) of Dowex 50W-4X acid resin was heated to reflux under a nitrogen atmosphere (Figure 2). When the reaction was complete by gas chromatography (ca. 2 hr), the mixture was taken up in ether, dried over anhydrous K₂CO₃, filtered, and distilled to give 1.3 g (50% yield) of a
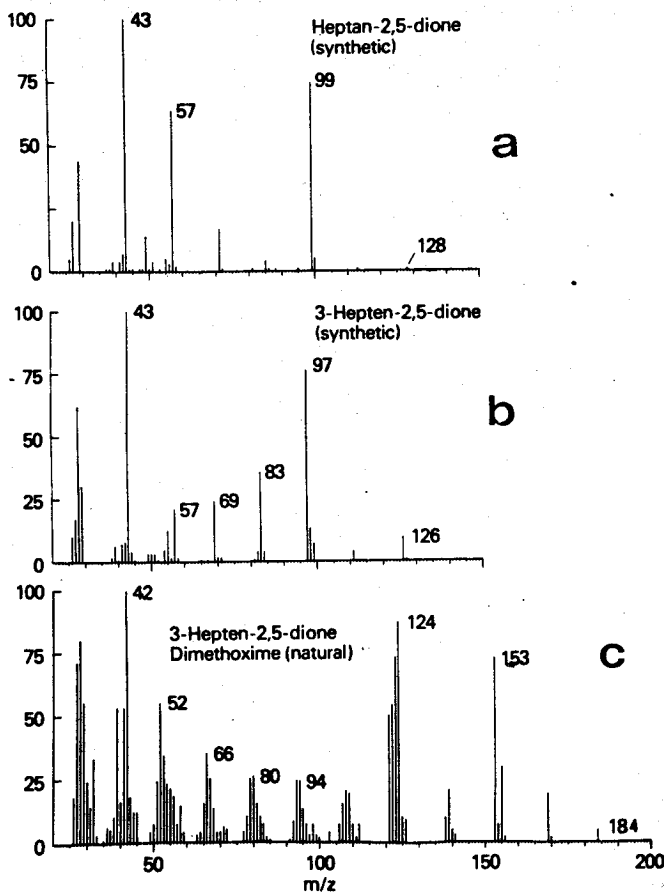
FIG. 1. Mass spectra of (a) heptan-2,5-dione (synthetic), (b) *E*-3-hepten-2,5-dione (synthetic), and (c) earliest eluting isomer (see Figure 4) of dimethoxime of *E*-3-hepten-2,5-dione (natural).

colorless, volatile liquid, bp 165° C; IR: 3052, 1220, 1015, and 770 cm⁻¹; NMR (60 MHz): δ = 5.71(s, 2H, furan 3-H and 4-H), 2.54(t, 2H, *J* = 7 Hz, furyl-CH₂), 2.20 (s, 3H, furyl-CH₃), 1.45 (m, 4H, —CH₂CH₂—), and 0.95 (t, 3H, *J* = 7.0 Hz,—CH₃).

2-Ethyl-5-methylfuran. A mixture containing 10 g of heptan-2,5-dione and a small amount of Dowex 50W-4X acid resin was distilled at atmospheric pressure. The fraction distilling between 95 and 100° C was taken up in ether, dried over anhydrous K₂CO₃, filtered, and redistilled to give 6.9 g (80% yield) of a colorless volatile liquid, bp 118° C; NMR (60 MHz): δ = 5.70 (s, 2H,
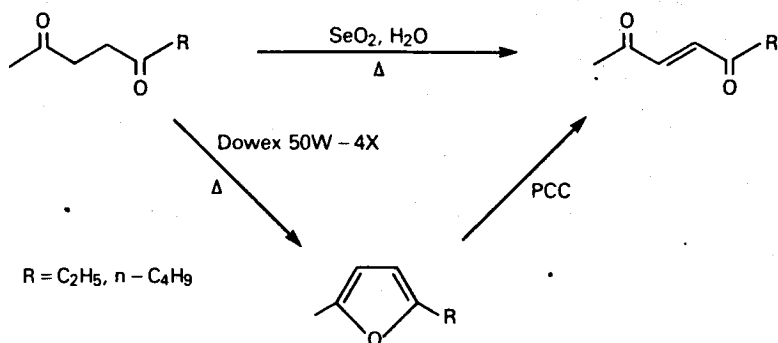
FIG. 2. Synthetic schemes for synthesis of endiones (see text).

furan 3-H and 4-H), 2.59(q, 2H, $J = 7.5$ Hz,—CH$_2$—), 2.20(s, 3H, furyl-CH$_3$), 1.18 (t, 3H, $J = 7.5$ Hz, —CH$_2$CH$_3$).

Pyridinium Chlorochromate Oxidation of 2,5-Dialkylfurans

3-Hepten-2,5-dione and 3-nonen-2,5-dione were prepared from the corresponding 2,5-dialkylfurans in 50% and 60% yield, respectively, by oxidation with pyridinium chlorochromate (Piancatelli et al., 1980). Kugelrohr distillation at 14 mm gave the solid *E*-endiones in greater than 98% purity by gas chromatographic analysis. None of the *Z* isomers were detected. These compounds were identical in all respects to the endiones prepared by selenium dioxide oxidation of the 1,4-diketones.

RESULTS

Upon GC-MS analysis of the methylene chloride extracts of *T. tataira* heads (Figure 3), the following compounds were identified from first principles and confirmed by comparison with mass spectral compilations (Heller and Milne, 1982), spectra of authentic samples, or spectra of simple homologues. Saturated hydrocarbons: n-C$_{11}$H$_{24}$, n-C$_{13}$H$_{28}$, n-C$_{14}$H$_{30}$, n-C$_{15}$H$_{32}$, n-C$_{17}$H$_{36}$, and n-C$_{23}$H$_{48}$; Olefinic hydrocarbons: n-C$_{15}$H$_{30}$, n-C$_{17}$H$_{34}$, n-C$_{21}$H$_{42}$, and n-C$_{23}$H$_{46}$; Carboxylic acids: palmitic acid, linoleic acid, linolenic acid, stearic acid, and oleic acid; Carboxylic esters: dodecyl acetate, tetradecyl acetate, hexadecyl acetate, and octadecyl acetate; Monoketones: 5-hepten-2-one, 3-hepten-2-one, and 5-nonene-2-one. Dodecyl decanoate was identified by noting intense ions at m/z 173 and m/z 168 corresponding to the $(C_9H_{19}COOH+H)^+$ and $(C_{12}H_{24})^+$ fragments expected for this substance, as well as a molecular ion at m/z 340.

Two major components of this mixture eluted at 102°C and 130°C

TRIGONA HEADS
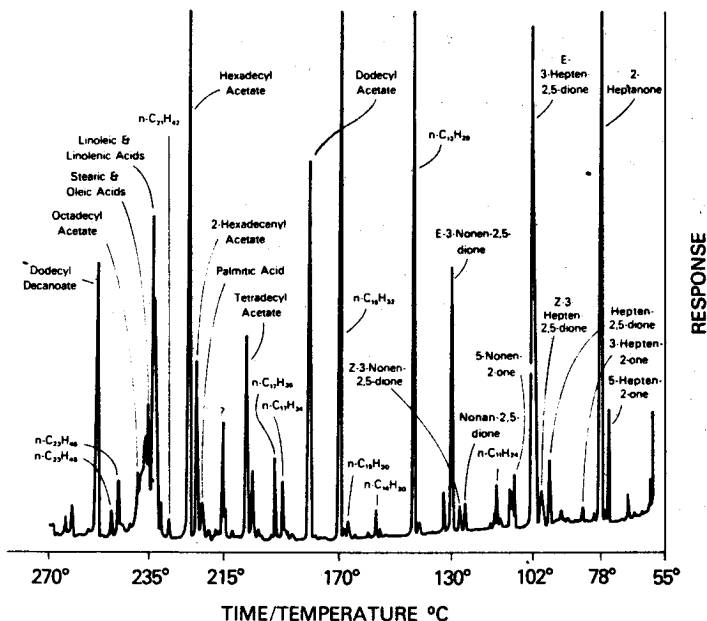10°/min, 6 ml/min
SE-30 1.5m x 0.33mm i.d.

FIG. 3. Gas chromatogram of extracts of *T. tataira* heads. Compounds identified by mass spectra.

(Figure 3). The first had a molecular ion at m/z 126 while the spectrum of the second showed many homologous ions, including a molecular ion at m/z 154, differing by two methylene units.

The structure of the substance responsible for the first peak was deduced as 3-hepten-2,5-dione from its mass spectrum alone, which showed important ions at m/z 43, 83, and 111 (CH_3CO, M-CH_3CO and M-CH_3, respectively) and m/z 57, 69, and 97 (C_2H_5CO, M-C_2H_5CO and M-C_2H_5, respectively) accounting for all of the structure except 26 mass units (C_2H_2). Two structures are possible, Ia and IIa.

I_A R = C_2H_5 II_A R = C_2H_5
I_B R = C_4H_9 II_B R = C_4H_9
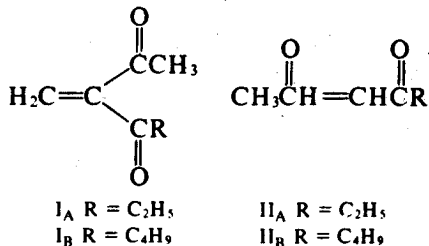
The second peak also showed ions at m/z 43, 83, and 111 for the terminal acetyl group, while ions at m/z 85, 69, and 97 represented C_4H_9CO, M-C_4H_9CO, and M-C_4H_9, respectively, indicating structures Ib or IIb. The presence in the same extract of 3-heptene-2-one, 5-heptene-2-one, and 2-heptanone as well as 5-nonene-2-one argued in favor of structures IIa and IIb while formation of dimethoximes (see below) supported the diketone function. Synthesis of the E isomers of IIa and IIb (see below) provided samples showing mass spectra and retention times identical with those of the natural products.

Upon closer examination (Figure 3), two minor components were observed which eluted before E-3-hepten-2,5-dione at 102°C. The first showed a mass spectrum and retention time identical to that of an authentic sample of heptan-2,5-dione. The second, minor, component showed a mass spectrum identical to that of E-3-hepten-2,5-dione, presumably from its Z isomer. In analogous fashion, two minor components were observed eluting just before E-3-nonen-2,5-dione and were assigned structures of nonan-2,5-dione and Z-3-nonen-2,5-dione. The retention times of all these minor components were identical to those of the synthesized samples.

Treatment of the *Trigona* extract with methoxyamine hydrochloride and pyridine followed by GC-MS analysis converted all of the ketones to syn-anti mixtures of their corresponding methoximes (Figure 4). Thus, a pair of peaks eluting at 80°C showed identical mass spectra corresponding to syn- and anti-isomers of 2-heptanone methoxime [MS: m/z (rel. %) 143 $(3, M^{+\cdot})$, 128(1), 114(6), 100(19), 87(68), 57(15), 52(14), 45(7), 43(16), 42(100), 41(31), and 39(17)]. A peak at 78°C represented the methoxime of 5-hepten-2-one (MS: $m/z = 141(M^{+\cdot})$ and 126(M-CH_3), and a peak eluting at 115°C corresponded to the methoxime of 5-nonen-2-one [MS: m/z (rel. %) 169(3, $M^{+\cdot}$), 154(2), 138(10), 127(3), 126(7), 112(15), 100(7), 87(66), 57(18), 55(30), 42(100), 41(52), 29(17)].

All four of the theoretically possible syn-anti isomers of the dimethoxime of E-3-hepten-2,5-dione were observed (Figure 4, see Figure 1c for the mass spectrum of the isomer eluting earliest), along with three from the dimethoxime of E-3-nonen-2,5-dione [MS, m/z (rel. %) 212(38, $M^{+\cdot}$), 197(8), 181(100), 170(14), 166(31), 154(28), 151(4), 140(58), 139(30), 135(22), 125(41), 124(68), 109(4), 108(71), 42(90), 29(71), and 27(65)]. Three of the possible four isomers from the dimethoxime of heptan-2,5-dione appeared between 100°C and 150°C [MS of isomer eluting second: m/z (rel. %) 186(10, $M^{+\cdot}$), 155(45), 140(100), 109(45), 100(43), 54(50), and 42(99)]. The isomeric dimethoximes had very similar mass spectral fragmentation patterns in all cases. The peak eluting before the pyridine peak was due to methoxyamine free base.

A small portion of the *Trigona* extract was hydrogenated in the presence of PtO_2 using methanol as the solvent. All of the olefinic hydrocarbon peaks
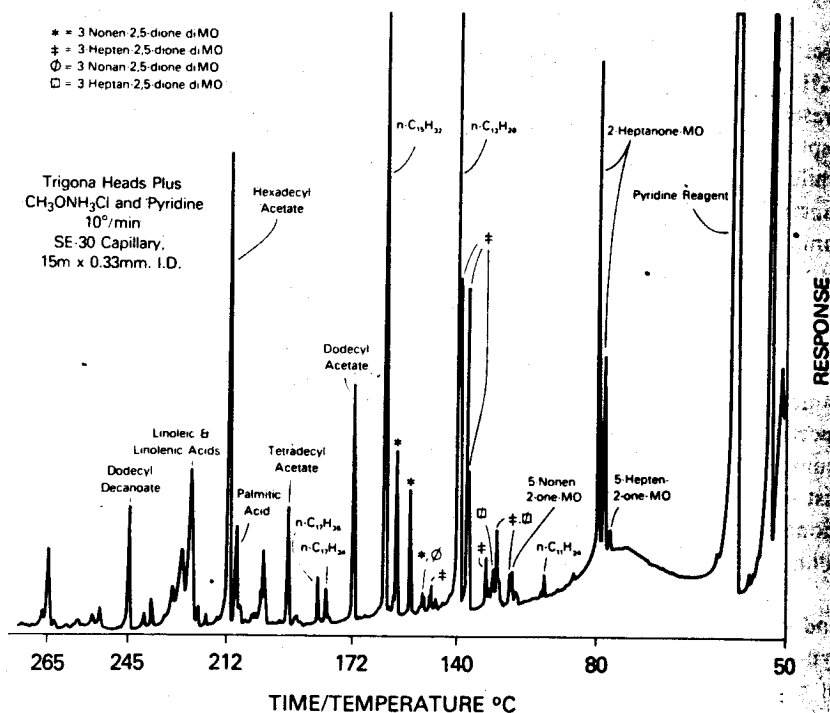
FIG. 4. Gas chromatogram of *T. tataira* heads extract treated with methoxyamine hydrochloride and pyridine. Compounds identified by mass spectra.

and olefinic monoketone peaks disappeared, presumably merging with their saturated counterparts. Likewise, the gas chromatographic peaks for 3-hepten-2,5-dione and 3-nonen-2,5-dione disappeared, and major peaks appeared whose mass spectra and retention times were identical to those of heptan-2,5-dione and nonan-2,5-dione, respectively.

The synthesis of the 3-en-2,5-diones was relatively straightforward and served to prove their structures and stereochemistry. Condensation of the appropriate aldehyde (propanal or pentanal) with methyl vinyl ketone in the presence of a thiazolium salt catalyst produced heptan-2,5-dione and nonan-2,5-dione in good yield (Stetter and Kuhlmann, 1974). Initially, the saturated 1,4-diketones were oxidized directly to the 3-en-2,5-diones with selenium dioxide (Figure 2) (Goldberg and Muller, 1938). This served to provide samples containing the starting diketones as well as both *E* and *Z* isomers of the unsaturated diketones, which were useful for GC-MS comparisons. To produce larger quantities of pure *E*-3-hepten-2,5-dione and *E*-3-nonen-2,5-dione, the two-step sequence shown in Figure 2 was found to be much more

practical. The saturated 1,4-diketones were cyclized by heating in the presence of the acid resin Dowex 50W-4X, (Scott and Naples, 1973), and the resulting 2,5-dialkylfurans were oxidized to E-3-en-2,5-diones with pyridinium chlorochromate (this oxidation is known to produce only the E-3-en-2,5-dione isomer) (Piancatelli et al., 1980). The products were purified by Kugelrohr distillation. Comparison of the natural 3-en-2,5-diones to the synthetic materials showed that the Z isomers are very minor components of the natural mixture.

DISCUSSION

The chemistry of the cephalic secretion of *Trigona* (*Oxytrigona*) *tataira* is radically different from those of *Trigona* species in other subgenera that have been subjected to similar analytical scrutiny. Indeed, only one of the oxygenated compounds detected as a cephalic product of *T. tataira* has been identified as a mandibular product of *Trigona* species in another subgenus. 2-Heptanone, a major secretory product of this bee (Figure 3), is present as one of a large series of methyl ketones which are accompanied by their corresponding carbinols in species in the subgenus *Scaptotrigona* (Luby et al., 1973). On the other hand, species in the subgenus *Geotrigona* synthesize the isomers of citral in their mandibular glands (Blum et al., 1970), whereas a species in the subgenus *Trigona* produces 2-alkanols and long-chain octyl esters in its glandular exudate (Kerr et al., 1981). Therefore, the diversity of products identified in cephalic extracts of *T. tataira* contrasts greatly with the conservatism observed with species in three other subgenera.

In a qualitative sense, workers of *T. tataira* clearly emphasize the production of ketones in their cephalic glands. The presence of 10 ketones, including both saturated and unsaturated mono- and diketones, provides the fire bee with a ketonic profile that is both distinctive and biosynthetically intriguing. The biogenetic relationship between the 2-heptanone, 3-hepten-2-one, 5-hepten-2-one, and E- and Z-3-hepten-2,5-dione on one hand and 5-nonen-2-one and E- and Z-3-nonen-2,5-dione on the other hand is particularly interesting. Are the monoketones precursors of the diketones or is the sequence reversed?

Diketones appear to be relatively rare in insects. A 1,3-diketone, 3,6-dimethylheptan-2,4-dione, has recently been discovered as a sex pheromone of the mushroom fly, *Megaselia halterata* (Wood); (Baker and Parton, 1982). Meinwald et al. (1972) and Schildknecht et al. (1972) have identified (E,E,E)-3,7-dimethyl-8,11-dioxo-2,6,9-dodecatrienal (gyrinidal, gyrinal) from gyrinid beetles.

The E-3-en-2,5-diones might be considered as a form of acyclic *p*-benzoquinone. They undergo similar Michael addition as the first step of their

reactivity toward basic nucleophiles (Piancatelli et al., 1980) and a cyclic E-3-en-2,5-dione has been reported to undergo both Lewis acid- and base-catalyzed Michael addition (Danishefsky et al., 1981). Similarly, it has been suggested that the potency of p-benzoquinones as defensive compounds may stem from their ability to function as Michael acceptors (Blum, 1981).

The saturated forms of these 1,3-diketones may also provide a clue to the formation of 2,5-dialkylpyrrolidines that are found in the unrelated ant species *Solenopsis fugax* (Blum et al., 1980). Their reductive condensation with ammonia to provide pyrrolidines has, in fact, been used extensively for their synthesis in the laboratory (Jones et al., 1980). However, pyrrolidines with side chains corresponding to those that would result from these particular diketones have not yet been encountered.

The ability of workers of *T. tataira* to plunder the nests of other species of bees with impunity may be related to their possession of a cephalic secretion that functions as a powerful chemical disruptant. Highly reactive compounds such as the endiones may constitute defensive allomones that disrupt the defensive cohesiveness of worker bees whose colonies are under attack, resulting in the pronounced disorientation that characterizes the behavior of bees being raided by the aggressive fire bees. Furthermore, the pronounced vesicatory properties of the cephalic secretion of workers presumably are also identified with specific highly reactive compounds which fortify their glandular exudates. We are now studying the effects of the compounds identified as cephalic products of *T. tataira* in order to ascertain if they are key elements of the chemical weaponry that fire bee workers direct against both honeybees and vertebrates. We also note the close relationship between IIa and 6-(2-formyl-3-methylcyclopentyl)-E-3-hepten-2,5-dione (Miller *et al.*, 1975) and its hemiacetal, gyrinidione (Wheeler *et al.*, 1972).

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