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Chemistry

Characterization and synthesis of volatile compounds from the defensive secretions of some "daddy longlegs" (Arachnida: Opiliones: *Leiobunum* spp.)*

(arthropods/integumental glands/acyclic alcohols, aldehydes, and ketones)

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ABSTRACT **Analyses of the chief volatile constituents of the defensive secretions of three oplionids were carried out. *Leiobunum nigripalpi* produces three closely related C_7 compounds: *E*-4-methyl-4-hexen-3-one(I), 4-methylhexan-3-one(II), and 4-methylhexan-3-ol(III), along with *E*-4-methyl-4-hepten-3-one(IV), *E,E*-2,4-dimethylhexa-2,4-dienal(IX), and a minor, unidentified component. *L. leiopenis* secretion contains *E*-4-methyl-4-hepten-3-one(IV), 4-methylheptan-3-one(V), *E,E*-2,4-dimethylhexa-2,4-dien-1-ol(VII), and *E,E*-2,4-dimethylhepta-2,4-dien-1-ol(VIII). *L. calcar* yields chiefly *E*-4,6-dimethyl-6-octen-3-one(VI) and *E,E*-2,4-dimethylhexa-2,4-dien-1-ol(VII). Six of these compounds are new natural products. The structures of these compounds, which can be regarded either as polyketide-derived or as modified isoprenoids, raise interesting biosynthetic questions.**

Recent studies of the defensive secretions of arachnids of the order Opiliones have led to the characterization of a small family of volatile, acyclic ketones from seven species within the suborder Palpatores (1–3). We have now carried out a study of the defensive compounds from three members of the genus *Leiobunum* within this suborder. Each of the species examined produces a mixture of at least three to five volatile organic components. These all proved to be based on *n*-hexane, *n*-heptane, or *n*-octane skeletons bearing one or two methyl substituents, and incorporating zero, one, or two double bonds, along with a single oxygen function either as a carbonyl group or as an hydroxyl group.

Our findings are summarized in Table 1, which gives the structures of the nine compounds characterized, along with the relative amounts of these compounds in the secretions.

Because of the small quantities of secretion available for study, our chief analytical tool was the computer-controlled gas chromatography/mass spectra (GC/MS). In three cases (II, V, and VI), the observed mass spectra served to identify a given component directly; comparison with authentic samples confirmed these identifications. In the six remaining instances (I, III, IV, VII, VIII, and IX), the mass spectra were only suggestive. Structures could be guessed, however, based on these spectral data considered along with the results of some simple chemical transformations, and were confirmed by direct comparisons with independently synthesized materials. The experimental details are given in the section that follows.

EXPERIMENTAL

Gas chromatographic analyses were carried out on a Varian model 2100 gas chromatograph using a 2.5 m × 2 mm column packed with 5% OV-1 on Gas-Chrom Q(column A), OV-225 on Gas-Chrom Q(column B), or a 1.5 m × 2 mm column packed with 3% FFAP on Chromosorb W(column C). Mass spectra (MS) were obtained by using column *A* or *B* in a Finnigan 3300 GC/MS coupled with a System Industries model 150 computer. Infrared spectra were determined from the neat liquids with a Perkin-Elmer model 237 recording spectrophotometer. Nuclear magnetic resonance (NMR) spectra were determined at 60 MHz on a Varian A-60A instrument.

Abbreviations: GC, gas chromatograph; MS, mass spectrometer; NMR, nuclear magnetic resonance spectroscopy; IR, infrared spectroscopy.

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RESULTS

L. nigripalpi

The secretion obtained from individuals of both sexes of *L. nigripalpi* was collected directly in glass capillaries and examined by GC and by GC/MS. Five components were characterized. The mass spectra of *E*-4-methyl-4-hexen-3-one(I), 4-methylhexan-3-one(II), 4-methylhexan-3-ol(III), *E*-4-methyl-4-hepten-3-one(IV), and *E,E*-2,4-dimethylhexa-2,4-dienal(IX) were identical with those obtained from the synthetic compounds (*vide infra*), and the GC retention times of these components were indistinguishable from those of the synthetic compounds on column A. There is an additional minor component in this mixture which could not be identified because of the small amount of secretion available.

4-Methyl-4-hexen-3-one(I). This ketone was prepared by dehydration of the aldol condensation product obtained from 3-pentanone and acetaldehyde as described previously by Heilmann *et al.* (4). Its NMR spectrum was identical to that reported (5); in its MS it had the following key peaks: *m/e* 112(33), 83(93), and 55(100). A small amount of the Z isomer was present in this product. It had a shorter GC retention time (column A), but an identical mass spectrum.

4-Methylhexan-3-one(II). A solution containing 12.2 g of *E*-4-methyl-4-hexen-3-one(I, 0.11 mol) in 150 ml of ethanol was hydrogenated over 1.0 g of 10% Pd/C catalyst at atmospheric pressure. After the mixture had taken up the theoretical amount of hydrogen, it was filtered and distilled to give 9.7 g (78%) of II as a colorless liquid, boiling point 135–138° [literature (6) 135–136°]; infrared (IR) peak absorption 1710 cm^{-1}; NMR δ2.38 (2 protons, quartet, J = 7.5 Hz, CH_3CH_2CO), 1.36 (1 proton, broad quintet, J $\simeq$ 8 Hz, $CHCO$), and 1.09–0.95 (11 protons, complex multiplet); MS, (*m/e*) 114(17), 86(10), 85(15), and 57(100).

4-Methylhexan-3-ol(III). A solution containing 3.0 g (0.0263 mol) of 4-methylhexan-3-one in 5 ml of ether was added dropwise to a stirred solution containing 0.45 g of lithium aluminum hydride in 30 ml of ether. After careful workup with dilute hydrochloric acid, the ether extracts were washed with saturated aqueous sodium bicarbonate and dried over anhydrous potassium carbonate. Distillation of the concentrated solution from glass wool gave 2.7 g of III as a colorless liquid, boiling point 63–65° (23 mm Hg); IR 3350 cm^{-1} (broad); NMR

δ3.35 (1 proton, multiplet, C*H*-OH), 2.26 (1 proton, singlet, O*H* by D_2O exchange), and 1.7–0.7 (14 protons, complex multiplet); MS, *m/e* 98(1), 87(19), 69(20), 59(100), 57(12), 45(23), and 41(30).

***E*-4-Methyl-4-hepten-3-one(IV).** A solution containing 38 ml (0.53 mol) of propionaldehyde in 50 ml of 3-pentanone was added over 3 hr to a well stirred solution prepared from 1.6 g of potassium metal, 10 ml of ethanol, and 114 g of 3-pentanone, maintained at 5°. After stirring for an additional hour, the mixture was neutralized with 3.7 g of oxalic acid, filtered, and distilled at reduced pressure. The distillate was redistilled slowly from a few crystals of iodine, dried over anhydrous magnesium sulfate, and distilled a third time from glass wool to give 19.5 g (30%) of IV as a colorless liquid, boiling point 80–83°/23 mm [literature (6) 80–82°/20 mm Hg]; IR 1670 (sharp), 1640 cm^{-1}; NMR δ6.61 (1 proton, triplet quartet, J = 1.5, 7 Hz, *H*C=C), 2.67 (2 protons, quartet, J = 7.5 Hz, $COCH_2CH_3$), 2.18 (2 protons, quartet, J = 7 Hz, CH_3CH_2C=C), 1.78 (3 protons, broad singlet, CH_3C=C), and 1.07 (6 protons, broad triplet, CH_3CH_2C=C and CH_3CH_2CO); MS, *m/e* 126(32), 97(100), 69(97), and 41(90). A small amount of the Z isomer which was also formed had a shorter retention time (column A) than the predominant *E* isomer, but an identical mass spectrum.

Ethyl *E,E*-2,4-Dimethylhexa-2,4-dienoate. Ethyl α-diethylphosphonopropionate (7) (23.8 g, 0.1 mol) was added over ½ hr to a stirred suspension of 2.4 g of sodium hydride in 35 ml of benzene carefully maintained at 20° under nitrogen. After stirring an additional hour we added 8.4 g (0.1 mol) of tiglic aldehyde (8) dropwise over a 15-min interval while the temperature of the mixture was maintained at 25°. The mixture was refluxed for 15 min, and then the benzene layer was decanted. The residual solids were washed with four 50 ml-portions of hot benzene, dissolved in 10% hydrochloric acid, neutralized with saturated aqueous sodium bicarbonate, and continuously extracted with ether. The combined organic extract was dried over anhydrous magnesium sulfate, and distilled to give 9.1 g (54%) of a colorless liquid, boiling point 89–91°/8 mm Hg; IR 1710, 1625, 1250, and 1115 cm^{-1}; NMR δ7.1 (1 proton, broad singlet, *H*CH=C—CO), 5.68 (1 proton, broad quartet, J ≃ 7 Hz, CH_3CH=C), 4.19 (2 protons, quartet, J = 7.0 Hz, —OCH_2CH_3), 2.01 [3 protons, broad singlet, C=C(CH_3)CO], 1.82 [3 protons, broad singlet, C=C(CH_3)-C=C], 1.75 (3 protons, broad doublet, J ≃ 7 Hz, CH_3-CH=C), and 1.28 (3 protons, triplet, J = 7.0 Hz, OCH_2CH_3); MS, *m/e* 168(9), 153(12), 140(32), 125(30), 111(45), 109(41), 107(61), 97(21), 95(22), 93(30), 91(55), 83(35), 82(30), 81(29), 79(57), 77(47), 69(59), 67(77), 65(28), 55(100), 53(39), 43(98), and 41(79).

***E,E*-2,4-Dimethylhexa-2,4-dien-1-ol(VII).** A solution containing 8.0 g (0.048 mol) of ethyl *E,E*-2,4-dimethylhexa-2,4-dienoate in 10 ml of ether was added dropwise over a 35 min-interval to a stirred suspension of 1.1 g (0.028 mol) of lithium aluminum hydride in 50 ml of ether at 5°. After stirring for an additional 15 min, we worked up the reaction mixture by successive addition of 1.1 ml of water, 1.1 ml of 15% sodium hydroxide solution, and 3.3 ml of water. After filtration, the residue was washed with ether, and the combined ether portions were dried over anhydrous potassium carbonate. Distillation afforded 5.3 g (88%) of VII as a colorless liquid, boiling point 83–85°/8 mm Hg; IR 3300 (broad), 1650 cm^{-1}; NMR δ5.85 (1 proton, broad singlet, *H*C=C—CH_2OH), 5.38 (1 proton, broad quartet, J ≃ 7 Hz, CH_3—C*H*=C), 3.97 (2 protons, singlet, —CH_2OH), 3.31 (1 proton, singlet O*H* by D_2O exchange), 1.71 (9 protons, broad multiplet, three-CH_3); MS, *m/e* 126(30), 111(32), 109(18), 108(13), 97(34), 93(50), 91(44), 84(21), 83(34), 81(13), 79(31), 77(51), 69(46), 67(39), 65(22), 56(21), 55(100), 53(36), 51(20), 43(63), and 41(72).

***E,E*-2,4-Dimethylhexadienal(IX).** A solution containing 0.5 g (3.97 mmol) of *E,E*-2,4-dimethylhexadien-1-ol in 10 ml of methylene chloride was added dropwise to a well stirred suspension of 1.3 g (6 mmol) of pyridinium chlorochromate in 15 ml of methylene chloride at room temperature. After stirring for 2 hr, the mixture was diluted with ether, and filtered through a small amount of Florisil. Kugelrohr distillation gave 0.25 g of IX as a pale yellow liquid, boiling point 110–120°/39 mm Hg; IR 2850, 2700, 1685, 1620, 1190, and 1010 cm^{-1}; NMR δ 9.35 (1 proton, singlet, C=C—C*H*O), 6.71 (1 proton, broad singlet, C*H*=C—CHO), 5.95 (1 proton, multiplet, CH_3—C*H*=C), 2.0–1.7 (9 protons, multiplet, three CH_3—C=C); MS, *m/e* 124(7), 123(4), 110(8), 109(100), 95(4), 93(4), 91(8), 81(31), 79(25), 77(12), 67(17), 65(9), 55(13), 53(18), and 41(17).

L. leiopenis

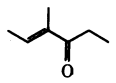
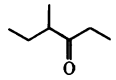
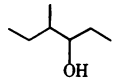
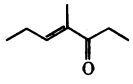
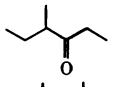
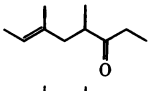
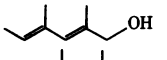
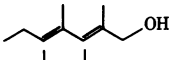
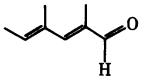
The secretion of *L. leiopenis*, also collected in glass capillaries was found to contain four components in the relative amounts shown in the table. The mass spectrum of 4-methylheptan-3-one(V) was identical to that reported (9). The mass spectra of *E*-4-methyl-4-hepten-3-one(IV), *E,E*-2,4-dimethylhexa-2,4-dien-1-ol(VII) and *E,E*-2,4-dimethylhepta-2,4-dien-1-ol(VIII) were identical with those obtained from the synthetic compounds. In addition, the GC retention times of these three components were identical to those of the synthetic compounds on columns B and C.

Ethyl *E,E*-2,4-Dimethylhepta-2,4-dienoate. This ester was prepared in exactly the same manner as ethyl *E,E*-2,4-dimethylhexa-2,4-dienoate using 9.8 g (0.1 mol) of 2-methyl-2-pentenal (10) in place of tiglic aldehyde. The product was distilled from glass wool to give 10.7 g (59%) of a colorless liquid, boiling point 98–101°/8 mm Hg; IR 1705, 1620, 1245, 1120, 1100, and 1025 cm^{-1}; NMR δ7.1 (1 proton, broad singlet, *H*C=C—CO), 5.60 (1 proton, broad triplet, J = 6.8 Hz, CH_3C*H*=C), 4.25 (2 protons, quartet, J = 7.0 Hz, CH_3CH_2O), 2.0 [3 protons, broad singlet, C=C(CH_3)CO], 2.15 (2 protons, broad quartet, J = 6.8 Hz, CH_3CH_2C=C), 1.82 [3 protons, broad singlet, C=C(CH_3)—C=C)], 1.28 (3 protons, triplet, J = 7.0 Hz, OCH_2CH_3), 0.99 (3 protons, triplet, J = 6.8 Hz, CH_3CH_2C=C); MS, *m/e* 182(17), 153(69), 137(16), 125(100), 109(53), 108(18), 93(28), 91(22), 81(17), 79(28), 77(28), 67(41), 65(15), 55(15), 53(16), 43(28), and 41(30).

***E,E*-2,4-Dimethylhepta-2,4-dien-1-ol(VIII).** This alcohol was prepared in exactly the same manner as *E,E*-2,4-dimethylhexa-2,4-dien-1-ol using 8.0 g (0.044 mol) of ethyl *E,E*-2,4-dimethylhepta-2,4-dienoate and 0.84 g (0.022 mol) of lithium aluminum hydride. The product was distilled to give 4.0 g (65%) of VIII as a colorless liquid, boiling point 96–99°/8 mm Hg; NMR δ5.85 (1 proton, broad singlet, C*H*=C—CH_2—OH), 5.29 (1 proton, broad triplet, CH_3CH_2C*H*=C), 4.0 (2 protons, singlet, CH_2OH), 2.70 (1 proton, singlet, O*H* by D_2O exchange), 2.03 (2 protons, quartet, 6.8 Hz, CH_3CH_2C=C), 1.75 (6 protons, multiplet, two CH_3—C=C), 0.97 (3 protons, triplet, J = 6.8 Hz, CH_3CH_2C=C); MS, *m/e* 140(33), 125(10), 122(3), 111(42), 109(29), 107(56), 97(23), 93(30), 91(58), 83(35), 82(26), 81(27), 79(53), 77(45), 69(58), 67(70), 65(26), 57(23), 55(100), 53(35), 43(73), and 41(83). In this case the reduction was not quite complete and the alcohol contained 10–15% of starting ester.

Manganese Dioxide Oxidation of the Secretion of *L. leiopenis*. The secretion from 34 specimens was taken up in 1 ml of ether and stirred for 1 hr with 50 mg of freshly prepared manganese dioxide. After filtration through a small plug of glass wool and removal of most of the solvent with a gentle stream of argon, the mixture was analyzed by GC/MS and shown to

Table 1. Volatile components from daddy longlegs defensive glands

Compound	Species (no. of specimens)						
	L. nigripalpi			*L. leiopenis*		*L. calcar*	
	(24)	(13)	(14)	(59)	(33)	(39)	(31)
I. 	78	80	20				
II. 	10	12	10				
III. 	3	3	3				
IV. 	1	1	1	18	8		
V. 				2	5		
VI. 						32	26
VII. 				44	47	67	65
VIII. 				35	40		
IX. 	2	2	60				

Each table entry gives the percentage of total volatile secretion represented by a given component, as determined by gas chromatographic analysis. Minor uncharacterized components account for the remainder of the secretion.

contain the following identifiable components: 4-methyl-3-heptanone, *E*-4-methyl-4-hepten-3-one, *E,E*-2,4-dimethylhexa-2,4-dienal, and *E,E*-2,4-dimethylhepta-2,4-dienal (9).

Hydrogenation of the Secretion of *L. leiopenis*. The secretion from 54 specimens was taken up in 1 ml of ether and hydrogenated in the presence of 10% Pd/C at atmospheric pressure for 15 min. After removal of the solvent with a gentle stream of argon, the mixture was analyzed by GC/MS and was found to contain the following identifiable components: 2,4-dimethylheptane (9), 4-methyl-3-heptanone, and 2,4-dimethylheptan-1-ol (9).

L. calcar

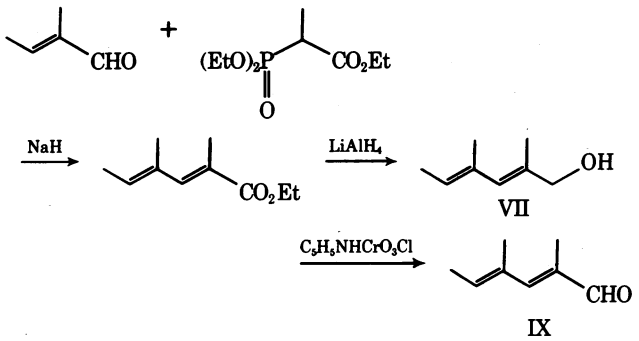
The secretion of *L. calcar* contained two major components, one of which was the previously described *E*-4,6-dimethyl-6-octen-3-one(VI) (2). The second component had a mass spectrum identical to that obtained for *E,E*-2,4-dimethylhexa-2,4-dien-1-ol(VII). This component had GC retention times identical to those of synthetic VII on columns B and C. In these samples of *L. calcar* secretion there was a third component comprising 1–8% of the mixture which could not be identified because of lack of material.

DISCUSSION OF RESULTS

The six-component secretion from *L. nigripalpi* (of which one minor component remains uncharacterized) proved particularly interesting, in that the mixture was found to contain three C_7 compounds (I, $C_7H_{12}O$; II, $C_7H_{14}O$; III, $C_7H_{16}O$) based on the same carbon skeleton in three different states of oxidation. Of these, II, the compound of intermediate oxidation state, was readily recognized on the basis of its characteristic mass spectrum as 4-methylhexan-3-one, previously isolated from ants of the genus *Manica* by Fales *et al.* (11), as well as from the defensive secretion of a staphylinid beetle (12). We suspected that the two remaining closely related compounds were 4-methyl-4-hexen-3-one(I) and 4-methylhexan-3-ol(III). An authentic sample of *E*-I, not previously found in nature, was conveniently prepared by the condensation of acetaldehyde with 3-pentanone as previously described (4).

Catalytic hydrogenation of this unsaturated ketone afforded II, which yielded III upon reduction with lithium aluminum hydride. Direct GC/MS comparison of these three synthetic samples with the three C_7 natural products confirmed these identifications.§

A fourth constituent of the *L. nigripalpi* secretion seemed from its mass spectrum to be 4-methyl-4-hepten-3-one(IV), the next higher homologue of I. This compound was prepared conveniently by the aldol condensation of propionaldehyde with 3-pentanone; the major (*E*) stereoisomer proved indistinguishable from component IV. The last substance to be identified from this species was *E,E*-2,4-dimethyl-2,4-hexadienal(IX), synthesized in three steps from tiglic aldehyde as outlined below. The stereochemistry of the terminal double bond in these compounds can be assumed to be the same as that in tiglic aldehyde itself (*E*), while the assignment of the *E* configuration to the newly formed double bond is based on the known steric course of analogous Wadsworth-Emmons condensations using the α-phosphonate ester derived from methyl propionate (13–15).

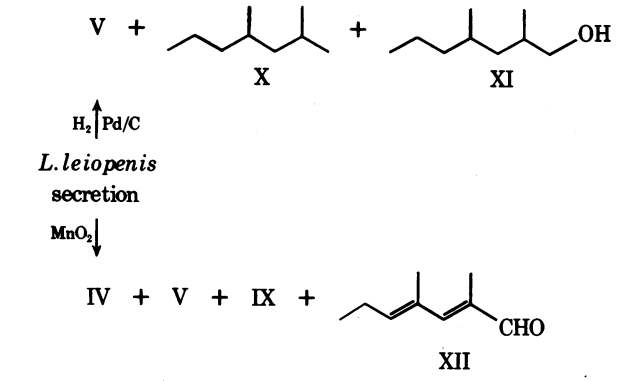


The *L. leiopenis* secretion played a central role in our study. Examination of the secretion by GC/MS showed the presence of two major and two minor volatile components. The minor consituents were most readily identified. 4-Methylheptan-3-one(V), which was easily recognized on the basis of its mass spectrum, is well known both from ants (16) and from opilionids (1–3). E-4-Methyl-4-hepten-3-one(IV), a minor constituent already found in *L. nigripalpi*, was identified by its GC/MS behavior as well as by its catalytic reduction to V.

The mass spectra of the two major components in the *L. leiopenis* secretion had strong parent ions at *m/e* 126 and 140 respectively, which along with an M-18 peak in each spectrum suggested that these compounds might be primary, allylic alcohols. That these alcohols are homologous is evident from the similarity of their mass spectral fragmentation patterns.

Catalytic hydrogenation of the *L. leiopenis* secretion led to the aforementioned V, as well as to two other known compounds, 2,4-dimethylheptane (X), and 2,4-dimethylheptan-1-ol(XI), which were identified on the basis of their published mass spectra (9). These compounds, which are clearly unrelated to the ketones IV and V, define the carbon-oxygen skeleton of the *m/e* 140 alcohol.

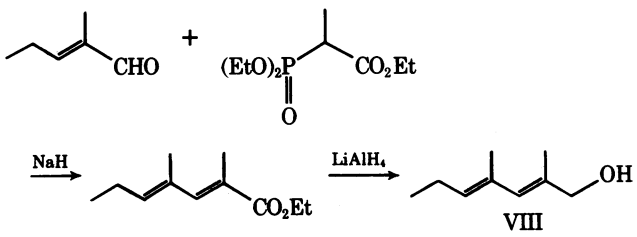
§ The diastereomers of III were not separated under our experimental conditions, so that whether natural III has the *erythro* or the *threo* configuration remains unknown.



Additional evidence for the structures of the two alcohols was obtained by manganese dioxide oxidation of the total secretion, which left ketones IV and V unchanged, but produced two conjugated aldehydes, thereby confirming the primary allylic nature of their original *m/e* 126 and 140 precursors. The aldehyde of higher molecular weight was recognized as 2,4-dimethyl-2,4-heptadienal(XII) on the basis of its published mass spectrum (9). The second aldehyde had a mass spectrum identical to that of *E,E*-2,4-dimethyl-2,4-hexadienal(IX), already encountered in *L. nigripalpi*.

These data indicated that 2,4-dimethyl-2,4-hexadien-1-ol(VII) and 2,4-dimethyl-2,4-heptadien-1-ol(VIII) were the two major components in the *L. leiopenis* secretion. A sample of *E,E*-VII, synthesized (as an intermediate in the preparation of IX) as described above, had a mass spectrum and gas chromatographic retention times on two different columns indistinguishable from those of the natural material, thus confirming both the structure and stereochemistry of this component.

In an analogous fashion, *E,E*-2,4-dimethyl-2,4-heptadien-1-ol(VIII) was synthesized in two steps from *E*-2-methyl-2-pentenal as outlined below.



Once again, the synthetic material had a mass spectrum and gas chromatographic retention times on two different columns identical to those of the natural product, which, allowed assignment of the *E,E* configuration to the defensive compound.

The *L. calcar* secretion showed two major volatile components. The first was identified on the basis of its gas chromatographic retention time and mass spectrum as *E*-4,6-dimethyl-6-octen-3-one(VI), which has been previously described (2). The second proved identical to *E,E*-2,4-dimethyl-2,4-hexadien-1-ol(VIII) on the basis of the same criteria.

The variability in composition of samples of secretion collected from different groups of specimens of the same species (see Table 1) is sometimes dramatic. For example, in *L. nigripalpi* component I comprised 78–80% of the mixture obtained from two groups of animals, but only 20% of the secretion obtained from a third group. The difference is made up by the increase in concentration of IX from about 2% to 60%. Similarly, in the *L. calcar* secretion, we had noted earlier that VI comprised about 70% of a three component mixture. Our two more recent samples from this species show only 26–32% of VI, while VII has increased in importance to 65–67%. We conclude that the proportions of these alicyclic compounds in a given defensive secretion are not fixed characteristics of each species.

Leiobunum discharge their secretion only in response to disturbance, and there can be no doubt that the fluid is defensive in all three species studied. Whether the different compounds produced by these animals are variously deterrent to predators, and whether their actions are somehow synergized by admixture, remains to be determined. In bioassays comparable to those previously employed with polyzonimine, another arthropodan defensive agent (17), 4-methylheptan-3-one, was found to be powerfully deterrent to insects: it causes instantaneous dispersal of ants (*Formica exsectoides*) and is a potent topical irritant to cockroaches and flies. Aside from their significance as new natural products, the *Leiobunum* compounds are also of interest because of questions they raise regarding their biosynthetic origin. While it seems likely that the substances arise from polyketide intermediates, it is also possible that they may be derived from mevalonic acid by a modification of the conventional isoprenoid biosynthetic pathway. Because very little is known about the biosynthetic capacities of arachnids, this area is an attractive one for further studies.

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1. Blum, M. S. & Edgar, A. L. (1971) *Insect Biochem.* **1**, 181–188.
2. Meinwald, J., Kluge, A. F., Carrel, J. E. & Eisner, T. (1971) *Proc. Natl. Acad. Sci. USA* **68**, 1467–1468.
3. Jones, T. H., Conner, W. E., Kluge, A. F., Eisner, T. & Meinwald, J. (1976) *Experientia* **32**, 1234–1235.
4. Heilmann, R., Arnaud, P. & Scheuerbrandt, G. (1961) *Bull. Soc. Chim. Fr.* 1337–1340.
5. Elguero, J. & Marzin, C. (1973) *Bull. Soc. Chim. Fr.* 3401–3406.
6. Dubois, J. E. & Luft, R. (1954) *Bull. Soc. Chim. Fr.* 1153–1156.
7. Dolby, L. J. & Riddle, G. N. (1967) *J. Org. Chem.* **32**, 3481–3485.
8. Green, M. B. & Hickinbottom, W. J. (1957) *J. Chem. Soc.* 3262–3270.
9. Stenhagen, E., Abrahamsson, S. & McLafferty, F. W. (1974) *Registry of Mass Spectral Data* (Wiley, New York), Vol. 1.
10. Hausermann, M. (1951) *Helv. Chim. Acta* **34**, 1482–1491.
11. Fales, H. M., Blum, M. S., Crewe, R. M. & Brand, J. M. (1972) *J. Insect Physiol.* **18**, 1077–1088.
12. Fish, L. J. & Pattenden, G. (1975), *J. Insect Physiol.* **21**, 741–744.
13. Sasaki, K. (1966) *Bull. Chem. Soc. Jpn.* **39**, 2703–2706.
14. Sasaki, K. (1967) *Bull. Chem. Soc. Jpn.* **40**, 2967–2968.
15. Sasaki, K. (1967) *Bull. Chem. Soc. Jpn.* **40**, 2968–2970.
16. Altman, P. L. & Dittmer, D. S. (1973) *Biology Data Book* (Federation of American Societies for Experimental Biology, Bethesda, Md.), 2nd ed., Vol. II.
17. Smolanoff, J., Kluge, A. F., Meinwald, J., McPhail, A., Miller, R. W., Hicks, K. & Eisner, T. (1975) *Science* **188**, 734–736.