Preparation of Lactam 15 from Aldehyde 14. The LDA enolate of **2** was generated as described above from *n*-BuLi (1.6 M, 2.95 mL, 4.74 mmol), diisopropylamine (0.67 mL, 4.74 mmol), and methyl *N,N*-dimethylglycinate (556 mg, 4.74 mmol) in dry THF (6 mL) at −80 °C. Aldehyde **14** (446 mg, 1.58 mmol) in THF (3 mL) and DMSO (0.35 mL, 4.93 mmol) was added, and the mixture was stirred at −80 °C for 2 h. After being warmed up to room temperature (ca. 1 h), the mixture was worked up as above. Flash chromatography (CH_2Cl_2–MeOH, 98:2) gave first 130 mg of a mixture containing mainly the starting aldehyde. Further elution (CH_2Cl_2–MeOH, 90:10) yielded 285 mg (49%) of pure lactam **15**: mp 194–195 °C (CH_2Cl_2–Et_2O); IR 3630 (OH), 2810, 2760 (Bohlmann bands), 1700 (ester C=O); ^1H NMR δ 8.56 (m, 1 H), 7.4–7.1 (m, 3 H), 4.07 (m, 1 H), 3.75 (br s, 1 H), 2.66 (s, 6 H), 0.94 (t, J = 7 Hz, 3 H); MS m/z (relative intensity) 367 (M^+, 100), 283 (38), 281 (25), 267 (13), 253 (14), 237 (12), 197 (17), 170 (15); exact mass 367.2272 (calcd for $C_{22}H_{29}N_3O_2$ 367.2260).

Preparation of Oxolactam 17. Lactam **15** (50 mg, 0.136 mmol) was dissolved in dry pyridine (3 mL). Freshly distilled acetic anhydride (0.5 mL, ca. 40 equiv) and DMAP (5 mg, 0.041 mmol) were added, and the mixture was stirred at room temperature for 30 h. Water (2 mL) was added, and stirring was continued for 10 min. The mixture was basified with aqueous $NaHCO_3$, after which it was extracted with CH_2Cl_2. Usual workup and flash chromatography (EtOAc–hexane, 50:50) gave 42 mg (96%) of oxolactam **17**: mp 152–153 °C (Et_2O) (lit.[19a] mp 156 °C); IR 1730 (ketone C=O), 1695 (lactam C=O); ^1H NMR δ 8.42 (m, 1 H), 7.45–7.25 (m, 3 H), 4.05 (br s, 1 H), 0.92 (t, J = 7.3 Hz, 3 H); MS m/z (relative intensity) 322 (M^+, 100), 321 (44), 294 (67), 293 (58), 266 (66), 265 (62), 237 (26), 197 (28), 170 (21), 169 (25); exact mass 322.1675 (calcd for $C_{20}H_{22}N_2O_2$ 322.1681).

Conversion of Oxolactam 17 to (±)-Vincamine (1) and (±)-16-Epivincamine (18). Oxolactam **17** (41 mg, 0.127 mmol) was dissolved in absolute MeOH (5 mL), and anhydrous Na_2CO_3 (135 mg, 1.27 mmol) was added. After 1 h of stirring at room temperature the solvent was evaporated, water was added, and the mixture was extracted with CH_2Cl_2. The organic phase was dried (Na_2SO_4) and evaporated to yield 43 mg of a mixture which, after flash chromatography (CH_2Cl_2–MeOH, 98:2), afforded 36 mg (78%) of (±)-vincamine (**1**), mp 224–225 °C (CH_2Cl_2–Et_2O) (lit.[13] mp 226–229 °C, lit.[19a] mp 234–236 °C). and 4.5 mg (10%) of (±)-16-epivincamine (**18**), mp 201–202 °C (MeOH) (lit.[13] mp 201 °C, lit.[19a] mp 210 °C). The IR, MS, ^1H NMR, and ^{13}C NMR data of (±)-**1** were consistent with those reported in literature.[15b,22]

Registry No. (±)-**1**, 2122-39-6; **2**, 7148-06-3; (±)-**3**, 127183-09-9; **4**, 127207-03-8; (±)-**6**, 127183-10-2; (±)-**7a**, 40179-82-6; **8**, 20717-67-9; **9**, 127183-11-3; **10**, 127183-12-4; (±)-**11**, 89240-98-2; (±)-**12a**, 89240-45-9; (±)-**12b**, 89300-54-9; (±)-**13**, 58451-76-6; (±)-**14**, 51049-28-6; (±)-**15**, 127183-13-5; (±)-**17**, 35226-35-8; (±)-**18**, 18210-81-6; CH_2=CHCHO, 107-02-8; tryptamine, 61-54-1.

Supplementary Material Available: NMR spectra for **4**, **6**, **7a**, **9**–**11**, **12a**, **14**, **15**, and **17** (11 pages). Ordering information is given on any current masthead page.

(21) We found the ^{13}C NMR signal of the carbonyl group of **14** at δ 204.8.

(22) Moldvai, I.; Szántay, Cs., Jr.; Tóth, G.; Vedres, A.; Kálmán, A.; Szántay, Cs. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 335.

Defense Mechanisms of Arthropods. 83. α- and β-Necrodol, Novel Terpenes from a Carrion Beetle (*Necrodes surinamensis*, Silphidae, Coleoptera)[1]

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The defensive secretion obtained from the rectal gland of the carrion beetle *Necrodes surinamensis* has been found to consist of a mixture of aliphatic acids and terpene alcohols. Octanoic acid, decanoic acid, (*Z*)-3-decenoic acid, (*Z*)-4-decenoic acid, hexadecanoic acid, and octadecanoic acid are the chief acidic components. The three major terpenes are lavandulol and α- and β-necrodol. The necrodols were shown to have a 1,2,2,3,4-pentamethylcyclopentane framework not previously found among natural monoterpenes. Formulas **9** and **10** are derived for α- and β-necrodol, respectively, chiefly on the basis of mass spectrometric and NMR spectroscopic analysis.

While the chemical weaponry of insects has been studied extensively, there are groups of these animals whose defenses have been largely ignored. One such neglected taxon is the beetle family Silphidae, comprising species of considerable ecological significance that are mostly carrion feeders. Silphid beetles have a single defensive gland that opens into the rectum and voids its products through the anus. Most species discharge their secretion as a liquid ooze.[2] *Necrodes surinamensis*, the so-called red-lined carrion beetle, is unusual in that it ejects its secretion as a spray, which it aims accurately in all directions by rotation of the abdominal tip.[3] In experiments with captive thrushes and ants, *Necrodes* proved highly unacceptable to such predators.[4] Initial indication that the secretion of *Necrodes* might be chemically interesting came from the odor of the spray, which combined the stench characteristic of carrion beetles with an unfamiliar fragrance.

Defensive fluid was collected for chemical analysis by causing beetles to discharge into chilled vials, or from whole glands isolated by dissection. Exploratory experiments revealed that the discharge contained a mixture of fatty acids and neutral monoterpene components. Further analysis was greatly simplified by separation of the fatty acids from the neutral components by extraction with aqueous base. The identification of the fatty acids proved

(1) For Paper 82, see: Peschke, K.; Eisner, T. *J. Comp. Physiol.* **1987**, *161*, 377.
(2) Meinwald, J.; Roach, B.; Hicks, K.; Alsop, D.; Eisner, T. *Experientia* **1985**, *41*, 516.
(3) Eisner, T.; Meinwald, J. *Psyche* **1982**, *89*, 357.
(4) Eisner, T.; Meinwald, J.; Monro, A.; Ghent, R. *J. Ins. Physiol.* **1961**, *6*, 272.

to be chemically straightforward. The neutral components, on the other hand, were found to include lavandulol, a known but uncommon terpene alcohol, along with two representatives of a new group of monoterpenes. We describe the charaterization of the acids first and then turn to the chemistry of the neutral components.

Results

Characterization of Acidic Components. The acidic components in this secretion were most easily separated and isolated by gas chromatography after conversion to the corresponding methyl esters, by treatment with diazomethane. Six esters could be resolved, and by GC/MS four of them were recognized as the methyl esters of octanoic (1), decanoic (2), hexadecanoic (3), and octadecanoic (4) acid, on the basis of a comparison of their mass spectra with literature data.[5] These identifications were confirmed by direct GC comparison of the beetle-derived esters with authentic samples.

$CH_3(CH_2)_nCO_2H$
1: $n = 6$
2: $n = 8$
3: $n = 14$
4: $n = 16$

$CH_3(CH_2)_5CH{=}CHCH_2CO_2H(Z)$ 5

$CH_3(CH_2)_4CH{=}CH(CH_2)_2CO_2H(Z)$ 6

The remaining two methyl esters gave essentially identical EI mass spectra, very similar to that reported for the methyl ester of a 3-decenoic acid of unspecified stereochemistry.[6] The two beetle-derived unsaturated esters were isolated by preparative GC and characterized as the methyl esters of (*Z*)-3-decenoic acid (5) and (*Z*)-4-decenoic acid (6) on the basis of ^1H NMR data (see Experimental Section).

Separation and Preliminary Examination of Neutral Components. Initially, the neutral components from a small number of beetles were examined by GC (OV-1). Three major peaks were observed and collected. Upon further analysis of each of these on another GC column (Carbowax 20 M), the second peak was separated into three components. Thus, five volatile constituents, designated A, B, C, D, and E, were detected. The secretion from 800 individuals was then fractionated and A, B, and E were isolated in the largest amounts (ca. 10, 3, and 1 μg per beetle, respectively). These are the only terpenes for which we obtained sufficient data to establish structures.

All five of these components appeared to have a molecular weight of 154 (EI/MS), corresponding to the molecular formula $C_{10}H_{18}O$ (confirmed by high resolution MS in the case of A). While an examination of mass spectral literature data for compounds of this molecular weight revealed similarities between several known terpenes and each of these compounds, only B, whose EI mass spectrum was almost identical with that reported for lavandulol (7),[7]

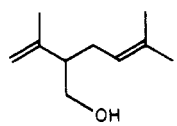

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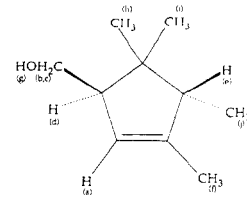
Table I. ^1H NMR Spectral Data for α-Necrodol



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resonance	H	chemical shift (δ) $CDCl_3$	chemical shift (δ) C_6D_6	$J_{x,y}$ (Hz)
a	1	5.22	5.13	$J_{a,d} = 2.0$
b	1	3.61	3.42	$J_{a,e} = 1.6$
c	1	3.56	3.36	$J_{a,f} = 1.5$
d	1	2.28	2.17	$J_{b,c} = 10.7$
e	1	2.12	2.04	$J_{b,d} = 5.5$
f	3	1.65	1.51	$J_{b,g} = 4.0$
g	1	1.2	*a*	$J_{c,d} = 5.5$
h	3	0.99	0.96	$J_{c,g} = 5.0$
i	3	0.90	0.88	$J_{d,e} = 1.8$
j	3	0.86	0.77	$J_{d,f} = 2.0$
				$J_{e,f} = 1.1$
				$J_{e,j} = 7.3$

[a] Not observed.

could be positively identified as a previously known compound. An authentic sample of 7 was prepared by a previously reported photolytic procedure[8] and was found to be indistinguishable from B on the basis of GC, MS, and ^1H NMR comparisons. The small amount of B available prevented us from determining its absolute configuration. For similar reasons, the minor components C and D were not completely characterized and remain to be reexamined when more secretion is available.

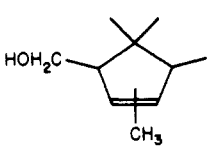
We turn now to a discussion of A and E, which we have named α-necrodol and β-necrodol.

α-Necrodol (A). While mass spectroscopic comparisons had suggested that α-necrodol, the most abundant of the neutral components, might be one of four known terpene alcohols (*cis*- or *trans*-chrysanthemol, α-terpineol, or 3-*p*-menthen-9-ol), GC comparisons with authentic samples of each of these compounds showed them all to differ in retention time from the beetle-derived compound. The EI mass spectrum of α-necrodol exhibited losses of 18 (M − H_2O, *m/z* 136, 6) and 31 (M − CH_2OH, *m/z* 123, 100), characteristic of a primary alcohol with a branched carbon skeleton capable of stabilizing the resulting positive charge.[9] Its CI mass spectrum exhibited diagnostic losses of hydride (*m/z* 153, 14) and hydroxide (*m/z* 137, 100).[10] On-column trimethylsilylation, followed by GC/MS analysis, resulted in the anticipated formation of a monotrimethylsilyl derivative (M − 15, *m/z* 211, 9).

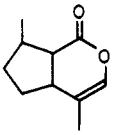
We relied chiefly on high resolution ^1H NMR experiments to deduce the structure of α-necrodol. Coupling constants were obtained from exhaustive homonuclear decoupling experiments. The free induction decays acquired to produce these spectra were resolution enhanced (double exponential weighting) prior to Fourier transformation, thus simplifying the analysis of the complex couplings observed.[11] Chemical shifts and coupling constants are summarized in Table I.

(5) The mass spectra of most terpenes, carboxylic acids, and steroids can be found in the following volumes: (a) Stenhagen, E.; Abrahamson, S.; McLafferty, F. W. *Atlas of Mass Spectral Data*; Interscience: New York, 1964. (b) Heller, S. R.; Milne, G. W. A. *NIH/EPA Mass Spectral Data Base*, U.S. Government Printing Office: Washington, DC, 1978.
(6) Von Sydow, E.; Anjou, K.; Karlsson, G. *Arch. Mass Spectrum Data* **1970**, *1*, 387–495.
(7) Von Sydow, E. *Acta Chem. Scand.* **1963**, *17*, 2506.
(8) Sadaki, T.; Eguchi, S.; Ohno, M. *J. Org. Chem.* **1970**, *3*, 790.
(9) McLafferty, F. W. *Interpretation of Mass Spectra*, 3rd ed., University Science Books: Mill Valley, CA, 1980; p 191.
(10) See ref 9, p 54, 92, 122, 123.
(11) Ernst, R. R. *Adv. Magn. Reson.* **1980**, *2*, 59.

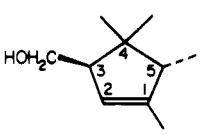
Analysis of these data led us to partial structure i, in which only the position of the vinylic methyl group and the relative stereochemistry of the hydroxymethyl group and the secondary methyl group remain to be defined. Over three decades ago, when we established the structure of nepetalactone (8, the first characterized representative



i



8



9

of the iridoid family[12]), the "isoprene rule" suggested the correct point of attachment of the methyl group on the cyclopentane ring.[13] In the case of α-necrodol, however, this rule provides no guidance, since both possible attachments lead to the same carbon skeleton, which in any case does not correspond to a head-to-tail isoprenoid. The resolution of this problem came from lanthanide induced shift (LIS) and difference nuclear Overhauser enhancement (NOE) experiments, as described below.

Using $Eu(fod)_3$ to complex with α-necrodol in deuteriochloroform, the shift induced in the single vinylic proton was much greater than that of the vinylic methyl group. On this basis, we placed the vinylic proton adjacent to the hydroxymethyl group, as shown in **9**.

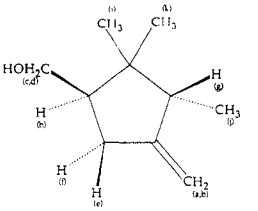
Evidence for a trans relationship between the hydroxymethyl group and the secondary methyl group was also provided by the LIS experiment, in which the C-5 allylic proton suffered a larger induced shift than did the C-5 methyl group. An examination of Dreiding molecular models suggests that this would be the expected effect only if the hydroxymethyl group were able to occupy a pseudo-axial conformation and if it were cis to the C-5 proton. Thus, the LIS experiment led to a definition of both the structure and relative stereochemistry expressed in **9** as the likely representation of α-necrodol.

Support for this assignment was obtained from NOE experiments. Unfortunately, the NOEs measured for α-necrodol by the classical technique of spectral integration were insufficiently precise for unambiguous interpretation. However, NOE difference spectra were highly informative.[14] Irradiation of the hydroxymethyl protons (δ 3.56 and 3.61 simultaneously) gave rise to an NOE in the vinyl proton, but not in the vinylic methyl group. This result confirms the placement of the vinylic methyl group at C-1, in accord with the LIS study.

The trans relationship of the C-3 and C-5 substituents was also supported by difference NOE measurements. Irradiation of the hydroxymethyl protons gave rise to a substantial NOE at the more deshielded of the C-4 methyl groups (δ 0.99). Irradiation of the C-3 allylic proton caused a greater enhancement of the more shielded C-4 methyl (δ 0.90). The configuration of these methyl groups is thus defined. Irradiation of the C-5 methine (δ 2.12) resulted in a larger NOE for the more deshielded (δ 0.99) of the C-4 methyl groups. Since irradiation of both this methine and the hydroxymethyl protons preferentially enhance the same adjacent C-4 methyl group, they must be cis to each other. Analogous experiments were carried out on the

(12) Meinwald, J. *J. Am. Chem. Soc.* **1954**, *76*, 4571.
(13) For an interesting account of the early history of the isoprene rule, see: Ruzicka, L. in *Perspectives in Organic Chemistry*; Todd, A., Ed.; Interscience Publishers: New York, 1956; pp 265–314.
(14) For details concerning NOE applications and instrumental parameters, see: Hall, L. D.; Sanders, J. K. M. *J. Chem. Soc.* **1980**, *102*, 5703.

Table II. ^1H NMR Spectral Data for β-Necrodol in $CDCl_3$



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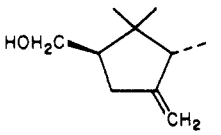
resonance	H	chemical shift (δ)	$J_{x,y}$ (Hz)
a	1	4.84	$J_{a,b}$ = 1.1
b	1	4.77	$J_{a,e} = J_{a,f} = J_{a,g}$ = 2.2
c	1	3.75	$J_{b,e} = J_{b,f} = J_{b,g}$ = 2.2
d	1	3.45	$J_{c,d}$ = 10.3
e	1	2.58	$J_{c,h}$ = 5.2
f	1	2.25	$J_{d,h}$ = 8.5
g	1	2.14	$J_{e,f}$ = 17.3
h	1	1.84	$J_{e,g}$ = 2.2
i	3	0.917	$J_{e,h}$ = 8.5
j	3	0.915	$J_{f,h}$ = 5.2
k	3	0.81	$J_{g,j}$ = 7.0

p-nitrobenzoate of α-necrodol, in which there is a larger chemical shift difference between the C-3 and C-5 methines, permitting more selective irradiation. All of these experiments support our conclusion that α-necrodol is *trans*-3-(hydroxymethyl)-1,4,4,5-tetramethylcyclopentene (**9**).

β-Necrodol (E). The EI mass spectrum of the third most abundant of the *N. surinamensis* $C_{10}H_{18}O$ isomers, β-necrodol, is strikingly similar to that of α-necrodol, except for the absence of a significant ion fragment at *m/z* 123, which we presume corresponds to the loss of CH_2OH. A GC/MS silylation experiment, however, did show β-necrodol to be an alcohol. The high resolution ^1H NMR data (Table II) made possible the assignment of structure **10** to this compound. A trans relationship between the



10

hydroxymethyl and the secondary methyl groups, as in the case of **9**, is suggested on the basis of a detailed analysis of coupling constant data. Thus, we conclude that β-necrodol is *trans*-1-(hydroxymethyl)-3-methylene-4,5,5-trimethylcyclopentane (**10**), an exocyclic double-bond isomer of **9**.

Discussion

While the structures of α- and β-necrodol seem secure on the basis of spectroscopic data, the evidence for the relative stereochemistry of β-necrodol must be regarded as somewhat speculative, and the absolute configuration of both compounds remained to be determined. Syntheses of both necrodols from precursors of known absolute configuration have now been completed and are described in the following paper.[15] This synthetic work confirms the postulated structures and their trans configuration and also shows that α-necrodol has the absolute configurations designated in expression **9**.

It is not unusual for glandular products of insects to be mixtures in which different components have different

(15) Jacobs, R.; Feutrill, G. I.; Meinwald, J. *J. Org. Chem.*, following paper in this issue.

functions. While the precise roles of the *Necrodes* spray constituents remain to be determined, there can be no question that the necrodols are defensive, since they have proven antiinsectant activity. Assays that we reported elsewhere have shown α-necrodol and β-necrodol to be topically irritating to cockroaches and flies and β-necrodol to be repellent to ants and various other insects (Coleoptera, Hemiptera).[16] Lavandulol and the aliphatic acids may themselves be repellent, although the acids could function also, as octanoic acid does in whip scorpion spray,[4] as surfactants that promote spread and penetration of secretion on target surfaces. Hexadecanoic acid and octadecanoic acid may be enteric rather than glandular constituents, added to the spray on passage of the fluid through the rectum. Neither the C16 nor the C18 acid was consistently present in extracts of the glands.

The most intriguing result of this study of the anal gland secretion of a carrion beetle has been the discovery of the 1,2,2,3,4-pentasubstituted cyclopentane ("necrodane") nucleus. To our knowledge, this highly congested C-10 skeleton has not been observed previously in nature. From a biosynthetic viewpoint, the necrodols certainly seem to be isoprenoids, although they cannot be derived from the classical terpene precursors without the intervention of a carbon skeleton rearrangement. In this context, the cooccurence of the necrodols with lavandulol (**7**), itself not previously found in the animal kingdom, is intriguing, since lavandulol also has an anomalous isoprenoid structure. The biosynthetic pathway to these novel terpenoids poses an interesting problem that merits further study.

Experimental Section

All solvents were distilled-in-glass (Burdick and Jackson). All analytical and preparative gas chromatography was carried out with a Varian 2100 chromatograph equipped with a flame ionization detector and Spectra-Physics Autolab Integrator. A column effluent splitter (9:1 ratio) was attached for preparative purposes. Analytical GC columns (2 mm × 2.5 m, Pyrex) and preparative GC columns (4 mm × 4 m, Pyrex) were prepared for on-column injection and deactivated with Sylon CT (dichlorodimethylsilane in toluene, Pierce Chem. Co.) prior to packing. Stationary phases were prepared by coating Gas-Chrom Q (100/120 mesh for analytical, 60/80 mesh for preparative, Applied Sciences) with 3% OV-1 or 3% Carbowax 20M (Pierce Chem. Co.) and then resieved before packing.

GC/MS data were recorded with a Finnigan 3300 mass spectrometer interfaced to a System Industries 150 data system. High resolution mass spectra were recorded with an AEI MS902 instrument. Electron impact mass spectra were obtained at 70-eV ionization energy. Chemical ionization mass spectra were recorded using methane as the reagent gas (500-eV ionization energy). Reported mass spectra include the 15 most intense peaks whenever possible, as well as the molecular ion and any other diagnostically important fragments.

^{1}H NMR spectra were taken with a Bruker WM-300 spectrometer, and ^{13}C NMR spectra were recorded with a Varian CFT 20 spectrometer. Chemical shifts are reported in ppm downfield from TMS. Coupling constants are in hertz. NMR solvents, with the exception of chloroform, were 99.5% deuterated and obtained in sealed ampules (0.5 mL, Merck, Sharp and Dohme). Chloroform (99.95% deuterated, Aldrich) was purified by being shaken with alumina (E. Merck), followed by passage through an alumina column onto dry, activated molecular sieves (3 Å and 4 Å, Fisher Scientific). Samples for NOE experiments were degassed (freeze, pump, thaw, 3×) and sealed under argon.

Infrared spectra were recorded with a Perkin-Elmer 299B instrument.

Sample Preparation. Initial collections of *N. surinamensis* were carried out at the Archbold Biological Station, Lake Placid, FL, by Martin Jefson and Braden Roach. Later collections, for chemical investigations, were carried out at Langmuir Laboratories, Ithaca, NY, by members of the Eisner research group.

Most of the samples used for chemical investigations were obtained by placing the beetles abdomens into a chilled vial (1 dram) and pinching the appendages with forceps, thus causing discharge of the secretions. The secretions obtained from 20 to 200 beetles were collected in a chilled vial. Methylene chloride (about 25% of the volume of the secretion) was added to each vial, and the vials were tightly sealed. These samples were stored at 0 °C until further extraction was performed.

The contents from several samples (800 individuals total) were combined in a small separatory funnel and cold water (5 mL, HPLC grade, Fisher Scientific) was added. This solution was brought to pH 11 (20% NaOH) and extracted three times with methylene chloride (15 mL total). The combined methylene chloride extracts were carefully concentrated to 1 mL with a stream of nitrogen. The remaining aqueous layer was acidified (2 N HCl) to pH 3 and extracted three times with diethyl ether (30 mL total). This ether extract was then concentrated to 2 mL with a stream of nitrogen.

Acidic Components. The acidic fraction (ether extract) was allowed to react with an excess of diazomethane for 30 min. GC analysis (OV-1, 15 mL/min N_2, 80 °C to 250 °C at 6°/min) of the reaction mixture resolved four major peaks (6.1, 9.7, 19.8, 27.0 min). The first, third, and fourth peaks were ultimately characterized as the methyl esters of acids **1**, **3**, and **4**, respectively. The remaining peak appeared as an incompletely unresolved mixture of three components using a preparative column (OV-1, 25 mL/min N_2, 130 °C). Use of a Carbowax 20M column (110° isotherm, 25 mL/min N_2) allowed resolution of this ester mixture into three components (15.0, 17.0, 18.0 min, respectively).

Spectral Data. Methyl Ester Derivatives. Component 1: EIMS *m/z* 158 (1), 129 (4), 127 (11), 155 (10), 101 (8), 87 (43), 75 (8), 74 (100), 69 (5), 59 (11), 57 (11), 55 (14). **Component 2**: EIMS *m/z* 186 (2), 155 (8), 143 (16), 129 (5), 101 (9), 88 (4), 87 (46), 75 (10), 74 (100), 73 (6), 69 (8), 59 (8), 57 (7), 43 (15), 41 (11). **Component 3**: EIMS *m/z* 270 (0.5), 227 (4), 199 (3), 185 (3), 171 (4), 143 (14), 129 (6), 101 (6), 97 (6), 88 (6), 87 (67), 83 (8), 75 (18), 74 (100), 69 (13), 59 (8), 57 (13), 55 (22), 43 (22), 41 (14). **Component 4**: EIMS 255 (2), 213 (2), 199 (5), 143 (16), 129 (6), 101 (7), 97 (6), 88 (5), 87 (70), 83 (8), 75 (22), 74 (100), 69 (13), 59 (8), 57 (16), 55 (22), 43 (24), 41 (14). **Component 5**: EIMS *m/z* 184 (2), 152 (37), 123 (18), 110 (65), 93 (37), 95 (17), 87 (21), 85 (26), 84 (46), 83 (31), 81 (39), 74 (100), 71 (21), 69 (73), 68 (37), 67 (40), 59 (58), 55 (73), 54 (47), 53 (19), 43 (33), 41 (45), 39 (16); IR ($CHCl_3$) 2960 (m), 1740 (vs), 1440 (w), 1335 (w), 1255 (w), 1165 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 5.61 (2 H, m), 3.75 (3 H, s). 3.14 (2 H, d, *J* = 5.1 Hz), 2.09 (2 H, td, *J* = 7.0, not measured), 1.5–1.2 (8 H, m), 0.93 (3 H, t, *J* = 7.0); ^{1}H NMR (C_6D_6) δ 5.81 (1 H, ttd, *J* = 7.4, 1.5, 10.7), 5.58 (1 H, ttd, *J* = 7.4, 1.5, 10.7), 3.42 (1 H, ddt, *J* = 7.4, 1.5, 1.5), 2.00 (2 H, ttdd, *J* = 7.0, 1.5, 7.4, 1.5), 1.5–1.2 (8 H, m), 0.98 (3 H, t, *J* = 7.0). **Component 6**: EIMS *m/z* 184 (4), 152 (32), 135 (13), 123 (15), 110 (53), 96 (31), 95 (15), 85 (30), 84 (37), 83 (16), 82 (22), 81 (36), 74 (100), 69 (54), 68 (36), 67 (48), 59 (28), 55 (53), 54 (37), 43 (22), 41 (34); IR ($CHCl_3$) 2960 (s), 2938 (s), 2880 (m), 1735 (vs), 1440 (w), 1365 (w), 1265 (w), 1170 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 5.46 (1 H, m), 5.40 (1 H, m), 3.73 (3 H, s), 2.41 (4 H, m), 2.09 (2 H, m), 1.5–1.2 (6 H, m), 0.95 (3 H, t); ^{1}H NMR (C_6D_6) δ 5.41 (2 H, m), 3.37 (3 H, s), 2.36 (2 H, td, *J* = 7.4), 2.19, (2 H, t, *J* = 7.4), 2.02 (2 H, td, *J* = 7.0, 7.4), 1.45–1.15 (6 H, m), 0.90 (3 H, t, *J* = 6.6); ^{1}H NMR ($CDCl_3$ + 1.0 mg of $Eu(fod)_3$) δ 6.20 (1 H, ttd, *J* = 7.4, 1.5, 11.0), 5.69 (1 H, ttd, 7.4, 1.5, 11.0), 4.88 (2 H, t, *J* = 7.4), 3.95 (2 H, td, *J* = 7.4, 7.4), 2.37 (2 H, td, *J* = 7.0, 7.4), 1.5–1.1 (6 H, m), 0.90 (3 H, t, *J* = 6.6).

Neutral Components. Initial gas chromatographic analysis (OV-1, 15 mL/min N_2, 80 °C to 250 °C at 8°/min) of the neutral fraction (methylene chloride extract) showed three major peaks (6.4, 6.9, 7.4 min, 5:1:1). Further analysis showed that two smaller peaks remained unresolved on the trailing shoulder of the center peak. Under preparative conditions (OV-1, 22 mL/min N_2, column temperature 95 °C, injector temperature 200 °C, detector temperature 125 °C), four peaks were apparent (24.0, 25.2, 26.1, 28.9 min), of which the center two were not completely resolved. Collection of three fractions gave pure samples of A (24.0 min) and E (28.9 min) and a middle fraction that was a mixture of B,

(16) Eisner, T.; Deyrup, M.; Jacobs, R.; Meinwald, J. *J. Chem. Ecol.* **1986**, *12*, 1407.

C, and D. Analysis of the middle fraction by GC on a more polar column (Carbowax 20M, 100 °C, 15 mL/min N_2) resolved these three components. Preparative GC separation using similar conditions (Carbowax 20M, 160 °C, 25 mL/min N_2) gave pure samples of B, C, and D (18.0, 19.5, 22.0 min, peak area ~3:1:1).

Spectral Data. Lavandulol (B): EIMS *m/z* 154 (1), 152 (3), 150 (1), 139 (2), 137 (5), 136 (4), 124 (20), 123 (22), 121 (17), 111 (43), 109 (26), 93 (34), 91 (21), 81 (26), 79 (20), 77 (15), 69 (100), 68 (25), 67 (37), 41 (35); ^{1}H NMR ($CDCl_3$) δ 5.06 (1 H, complex multiplet), 4.91 (1 H, mult), 4.80 (1 H, mult), 3.52 (2 H, mult), 2.26 (1 H, mult), 2.06 (2 H, mult), 1.68 (6 H, mult), 1.59 (3 H, br s). **α-Necrodol (A):** high resolution MS: *m/z* 154.1353 (calcd for $C_{10}H_{18}O$, 154.1358); EIMS *m/z* 154 (7), 139 (46), 136 (6), 123 (100), 121 (50), 107 (26), 105 (25), 95 (18), 93 (36), 91 (38), 81 (71), 79 (30), 77 (22), 69 (11), 67 (22), 65 (10), 55 (18), 53 (12), 43 (14), 41 (20), 39 (14); CIMS *m/z* 155 (0.5), 154 (2), 153 (14), 139 (15), 138 (13), 137 (100), 135 (7), 122 (8), 95 (11), 81 (10); ^{1}H NMR ($CDCl_3$) δ 5.22 (1 H, qdd, *J* = 1.5, 2.0, 1.6), 3.61 (1 H, ddd, *J* = 10.7, 5.5, 4.0), 3.56 (1 H, ddd, *J* = 10.7, 5.5, 5.0), 2.28 (1 H, qdddd, *J* = 2.0, 5.5, 5.5, 6.8, 2.0, 1.8), 2.12 (1 H, qqdd, *J* = 7.3, 1.1, 1.8, 1.6), 1.65 (3 H, ddd, *J* = 2.0, 1.5, 1.1), 1.2 (1 H, dd, *J* = 5,4), 0.99 (3 H, s), 0.90 (3 H, s), 0.86 (3 H, d, *J* = 7.3); ^{1}H NMR (C_6D_6) δ 5.13 (1 H, qdd, *J* = 1.5, 2.0, 1.6), 3.42 (1 H, ddd, *J* = 12.6, 6.8), 3.36 (1 H, ddd, *J* = 12.6, 6.8), 2.17 (1 H, qdddd, *J* = 2.0, 6.8, 6.8, 2.0, 1.8), 2.04 (1 H, qqdd, *J* = 7.3, 1.1, 1.8, 1.5), 1.51 (3 H, ddd, *J* = 2.0, 1.5, 1.8), 0.96 (3 H, s), 0.88 (3 H, s), 0.77 (3 H, d, *J* = 7.3); noise-decoupled ^{13}C NMR (C_6D_6) δ 127.8, 123.9, 62.5, 56.3, 53.4, 42.6, 24.5, 23.4, 14.7, 11.9; IR ($CHCl_3$) 3620, 2960, 2875, 1443, 1385, 1365, 1070, 1005, 950 (vw), 860 (vw) cm^{-1}.

α-Necrodol *p*-Bromobenzoate. The methylene chloride extract from the defensive spray from 140 individuals was fractionated by preparative GC (OV-1) as previously described. The first fraction, containing mostly α-necrodol, was washed from the collection tube into a 300-μL cone-shaped vial with methylene chloride (2 × 100 μL). 4-(Dimethylamino)pyridine (1 mg, Aldrich) in methylene chloride (10 μL) was added followed by *p*-bromobenzoyl chloride (3 mg, Aldrich) also in methylene chloride (50 μL). The mixture was stirred at room temperature. After 5 min, a precipitate had started to form.

When the reaction was found to be complete (TLC), a large excess of *p*-bromobenzoyl chloride remained. Addition of water (100 μL) to the reaction mixture, followed by vigorous agitation, did not result in hydrolysis of the acid chloride. Concentrated ammonium hydroxide (50 μL) was then added and resulted in the formation of an insoluble precipitate. The methylene chloride layer was examined by TLC and no acid chloride was found. This layer was removed via syringe and the remaining aqueous suspension was extracted twice with methylene chloride (50 μL). The combined methylene chloride extracts were crudely fractionated on a silica gel column (4 mm × 10 cm, hexane/ethyl acetate, 9:1 vol) and the UV-active fractions corresponding to the aromatic ester were collected. This material was then subjected to preparative high pressure liquid chromatography (9 mm × 25 cm, 10-μm Partisil, 7.5 mL/min, hexane/methylene chloride, 89:11) to give the *p*-bromobenzoate ester of α-necrodol (**11**).

Spectral Data. α-Necrodol *p*-bromobenzoate (11): EIMS *m/z* 202 (2), 200 (2), 184 (14), 183 (15), 157 (7), 155 (8), 137 (9), 136 (57), 135 (10), 123 (19), 122 (10), 121 (100), 107 (5), 105 (6), 93 (6), 81 (9), 41 (7); CIMS *m/z* 339 (4.3), 337 (5.0), 185 (0.7), 183 (0.7), 183 (0.8), 153 (0.7), 138 (11), 137 (100), 121 (5), 81 (5); IR ($CHCl_3$) 3000 (w), 1960 (s), 1715 (s), 1400 (wl), 1380 (vw), 1365 (vw), 1273 (vs), 1120 (s), 1107 (s), 1070 (s), 1013 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 7.87 (2 H, m), 7.56 (2 H, m), 5.20 (1 H, qdd, *J* = 1.5, 2.0, 1.6), 4.3 (1 H, dd, 10.8, 7.0), 4.18 (1 H, dd, *J* = 10.8, 6.8), 2.60 (1 H, qdddd, *J* = 2.0, 7.0, 6.8, 2.0, 1.8), 2.15 (1 H, qqdd, *J* = 7.3, 1.1, 1.8, 1.6), 1.65 (3 H, ddd, *J* = 2.0, 1.5, 1.1), 1.00 (3 H, s), 0.98 (3 H, s), 0.98 (3 H, s), 0.88 (3 H, d, *J* = 7.3); ^{1}H NMR (C_6D_6) δ 5.10 (1 H, qdd) 4.13 (1 H, dd), 4.27 (1 H, dd), 2.49 (1 H, qdddd), 1.95 (1 H, qqdd), 1.50 (3 H, ddd), 0.88 (6 H, s), 0.75 (3 H, d); noise-decoupled ^{13}C NMR ($CDCl_3$) δ 145.6, 131.6, 129.5, 127.8, 65.5, 42.7, 52.6, 43.1, 24.7, 24.1, 15.2, 12.4.

β-Necrodol (E): EIMS *m/z* 154 (65), 139 (63), 136 (2), 121 (100), 109 (12), 107 (16), 105 (21), 95 (17), 93 (47), 91 (31), 81 (27), 79 (34), 87 (21), 69 (23), 67 (39), 55 (25), 53 (20), 43 (23), 41 (50), 39 (26); CIMS *m/z* 153 (8), 137 (100), 121 (9), 95 (10), 81 (7); ^{1}H NMR ($CDCl_3$) δ 4.84 (1 H, dddd, *J* = 2.2, 2.2, 2.2, 1.1), 4.77 (1 H, dddd, *J* = 2.2, 2.2, 2.2, 1.1), 3.75 (1 H, ddd, *J* = 10.3, 5.2, 4.8), 3.45 (1 H, ddd, *J* = 10.3, 8.5, 4.8), 2.58 (1 H, ddddd, *J* = 8.5, 17.3, 2.2, 2.2, 2.2), 2.25 (1 H, dddd, *J* = 17.3, 5.2, 2.2, 2.2), 2.14 (1 H, qddd, *J* = 7.0, 2.2, 2.2, 2.2), 1.84 (1 H, dddd, *J* = 8.5, 8.5, 5.2, 5.2), 0.917 (3 H, s), 0.915 (3 H, d, *J* = 7.0), 0.807 (3 H, s).

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Registry No. Octanoic acid, 124-07-2; decanoic acid, 334-48-5; (*Z*)-3-decenoic acid, 2430-93-5; (*Z*)-4-decenoic acid, 505-90-8; hexadecanoic acid, 57-10-3; octadecanoic acid, 57-11-4; lavandulol, 498-16-8; α-necrodol, 104104-38-3; β-necrodol, 104086-70-6.

Defense Mechanisms of Arthropods. 84. Synthesis of (−)-α-Necrodol and (−)-β-Necrodol: Novel Cyclopentanoid Terpenes from a Carrion Beetle

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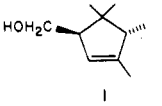
Syntheses of (−)-α-necrodol (1) and (−)-β-necrodol (2) from (+)-phenylcamphoric acid (**7a**) are described. In addition, several related compounds, (+)-*epi*-α-necrodol (**3**), (+)-*epi*-β-necrodol (**4**), and (+)-γ-necrodol (**5**), have been prepared. The absolute configuration of natural α-necrodol has been established as 3*R*,5*R* by comparison of its (+)-α-methoxy-α-(trifluoromethyl)phenylacetyl ester with the ester derived from synthetic **1**.

The defensive spray of the red-lined carrion beetle, *Necrodes surinamensis*, contains two novel C_{10} alcohols, α- and β-necrodol, for which we have proposed the structures **1** and **2**, respectively.[1] The 1,2,2,3,4-pentamethylcyclopentane (necrodane) skeleton has not been described previously for any monoterpene, nor can it be derived



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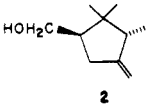

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†Deceased July 4, 1987.