system used in this study. Nevertheless, a coefficient of variation of 10.5% at a level of 3.7 ppb (for NDMA) can be considered highly satisfactory.

Alternatively, one may determine average percentage recoveries of each of the volatile nitrosamines of interest and use these values (instead of NAZET recoveries) for correcting the individual results. But, since the percentage recovery of a nitrosamine may vary slightly from sample to sample (see Table II), this method of calculation would not be 100% accurate either. Therefore, the correction method suggested above (using NAZET recoveries) is a simpler and reasonable approach. It should give results within 10–15% of the true values.

In this study, the average levels of NDMA and NPYR in the first 11 cooked-out bacon fat samples (Table I) were respectively 4.8 and 21.1 ppb as compared to average levels of 6.4 ppb of NDMA and 21.9 ppb of NPYR determined in a 1978 survey (Sen et al., 1979). It appears, therefore, that the levels of volatile nitrosamines in cooked-out bacon fat have not changed appreciably during this time.

In conclusion, the liquid–liqiuid partitioning procedure is very simple and rapid and does not involve the use of any cumbersome and complicated distillation as a part of the sample preparation step. The entire procedure can be completed within 1.5–2 h. If proper fume hood and handling facilities are available, a large number (8–12) of samples can be analyzed within a working day. It is hoped the technique will be useful for rapid screening of cooked-out bacon fats for the presence of various volatile nitrosamines, mainly NDMA and NPYR.

Safety Note. Since most volatile nitrosamines are strong carcinogens, adequate precautions should be taken in handling these chemicals.

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Degradation Products (*Z*)-11-Hecadecenal and (*Z*)-9-Tetradecenal, Components of a Sex Pheromone of the Tobacco Budworm

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Degradation of two components of virelure [(*Z*)-11-hexadecenal and (*Z*)-9-tetradecenal] occurred in hexane solution in sealed tubes under air and in fluorescent light. The products were isolated by column chromatography and preparative gas–liquid chromatography and identified by a combination of gas chromatography and infrared, nuclear magnetic resonance, and mass spectrometry. Both virelure components were degraded by the same major mechanisms—oxidation to cis and trans epoxides, oxidation of the aldehyde to an acid, and subsequent decarboxylation. A total of 12 degradation products were characterized from each compound.

Two components of the pheromone of the tobacco budworm, *Heliothis virescens* (F.), were isolated, identified, synthesized, and reported to be (*Z*)-11-hexadecenal [(*Z*)-11-HDAL] and (*Z*)-9-tetradecenal [(*Z*)-9-TDAL] (Roelofs et al., 1974; Tumlinson et al., 1975). The female tobacco budworm moth contains these two compounds in the approximate ratio of 16 parts of (*Z*)-11-HDAL to one part of (*Z*)-9-TDAL, and this ratio has been used to formulate an attractant (virelure) for field trapping studies to monitor insect populations (Hendricks et al., 1977). Permeation of the air with sufficient quantities of these chemicals also has potential for preventing males from locating and orienting to individual pheromone-releasing females (Gaston et al., 1967; Shorey et al., 1967). Klun et al. (1980a) isolated and identified five additional compounds from heptane washes of ovipositors of tobacco budworms and determined that a mixture of the seven chemicals exceeded the attractiveness of four virgin females. Klun et al (1980b) also identified four chemicals from ovipositors of the corn earworm moth, *Heliothis zea*, and (*Z*)-11-HDAL comprised 90–95% of this pheromone. Preliminary observations in our laboratory suggested that

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these two chemicals are degraded under certain laboratory conditions to products of unknown identity. The present studies were initiated to identify these degradation products.

MATERIALS AND METHODS

(*Z*)-11-HDAL and (*Z*)-9-TDAL were obtained from a commercial source (Zoecon), and the specified purity of the two compounds (98.7% and 99.4%, respectively) was verified by gas–liquid chromatography (GLC) on 50-m Dexsil and Carbowax 20M capillary columns and by $AgNO_3$–silica high-performance liquid chromatography. The compounds were then stored under N_2 at −35 °C until used. Immediately prior to use, the purity of the chemicals was reconfirmed by GLC. The two chemicals were dissolved in hexane (20 mg/mL), and these solutions were sealed under air in 20-mL ampules (1 mL/ampule). These ampules were stored at room temperature in the laboratory under fluorescent lighting for a period of 4 weeks, although in final stages of isolation of sufficient quantities of acidic compounds for analysis, some samples containing 5 mg/mL (*Z*)-9-TDAL were fractionated after 14 days.

Isolation of Acidic Compounds. Solutions of (*Z*)-11-HDAL and (*Z*)-9-TDAL that had been aged were extracted with equal volumes of 0.1 N NaOH. The aqueous layer was then acidified with 0.5 N HCl and back-extracted 3 times with equal volumes of dichloromethane. The combined dichloromethane phase was washed with water to neutrality and was then dried over anhydrous sodium sulfate. This fraction was analyzed by gas–liquid chromatography (GLC) on a 1.5 m × 2 mm glass column packed with 1.5% SP2250 plus 0.95% SP2401 on 80–100-mesh Supelcoport. Conditions were as follows: column, 165 °C; injector, 220 °C; N_2 carrier gas, 40 cm^3/min; FID detector, 260 °C. The acidic fractions, isolated as indicated above, were reacted with diazomethane to form methyl esters, and the methyl esters were purified by preparative GLC on a 1.5 m × 4 mm glass column packed with the SP2250–SP2401 mixture. Parameters were those described above.

Isolation of Other Compounds. The hexane solutions of aged (*Z*)-11-HDAL and (*Z*)-9-TDAL that had been extracted with NaOH were washed with distilled water until neutral. The hexane was dried over anhydrous sodium sulfate and concentrated to near dryness on a rotary evaporator under reduced pressure. The sample was dissolved in ca. 2 mL of pentane and loaded on a silica gel column (30 cm × 1 cm) slurry packed in pentane. The column was eluted successively with 70 mL each of 0.0, 0.5, 2, 5, 10, 25, and 100% dichloromethane in pentane to provide fractionation of the residual components. All fractions were monitored on the analytical GLC columns, and compounds were purified by preparative GLC for nuclear magnetic resonance (NMR), infrared (IR), and mass spectral analysis.

In structure confirmation studies, olefins were epoxidized by addition of excess *m*-chloroperoxybenzoic acid (MCPBA) in dichloromethane (Schwartz and Blumbergs, 1964) and allowing the mixture to stand at room temperature for at least 1 h. The reaction mixture was partitioned successively with 0.1 N NaOH and distilled water until neutral. The dichloromethane solution was dried with anhydrous sodium sulfate and concentrated for purification of the synthesized epoxides by preparative GLC.

Spectral Analysis. A Varian Mat CH-7 spectrometer coupled with a Varian 2700 gas chromatograph and a 620-L Varian data system was used in GLC–mass spectral studies. The isolated compounds or fractions were injected into a 1.5 m × 2 mm i.d. glass column packed with 3% SE-30 on 80–100-mesh Gas-Chrom Q. Operating parameters for GLC–MS were as follows: injector, 190 °C; column, 125 °C for compounds eluting earlier than parent compounds and 165–180 °C for those eluting later; detector oven, separator, and inlet, 210 °C; ion source, 225 °C; helium flow, 50 mL/min; ionizing voltage, 70 eV.

^1H NMR spectra were determined in deuteriochloroform solution; a JEOL-FX-90Q spectrometer was used for these determinations. Chemical shifts are reported as parts per million downfield from tetramethylsilane.

IR spectra were obtained in CCl_4 solutions with a Beckman Acculab 8 infrared spectrophotometer equipped with a microcell and beam condenser.

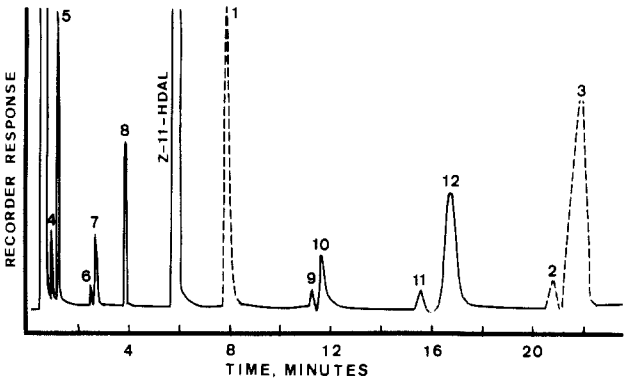


Figure 1. Composite gas chromatographic representation of (*Z*)-11-hexadecenal and its degradation products. Compounds H-1, H-2, and H-3 represent carboxylic acids that were methylated (diazomethane) before GLC analysis.

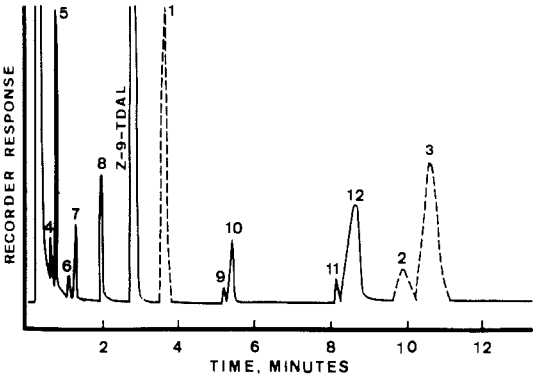


Figure 2. Composite gas chromatographic representation of (*Z*)-9-tetradecenal and its degradation products. Compounds T-1, T-2, and T-3 represent carboxylic acids that were methylated (diazomethane) before GLC analysis.

RESULTS

After methylation of the acidic fraction with diazomethane, the composite gas–liquid chromatogram of the acidic and neutral fractions of aged (*Z*)-11-HDAL and (*Z*)-9-TDAL solutions revealed the presence of 12 degradation products from each aldehyde (Figures 1 and 2). Oxidation products 1, 2, and 3 were the only compounds detected in the acidic fraction after methylation. Compounds isolated from (*Z*)-11-HDAL are designated by the prefix H (H-1, H-2, etc.), and those isolated from (*Z*)-9-TDAL are prefixed by T (T-1, T-2, etc.). The structures of the (*Z*)-9-TDAL and (*Z*)-11-HDAL degradation products identified in this study are shown in Figure 3, along with the postulated routes leading to their formation. These products were characterized as described below.

Identification of Compounds 1, 2, and 3. The GLC behavior of unmethylated H-1 and T-1 and the behavior of compounds H-1, T-1, H-2, T-2, H-3, and T-3 on silica gel columns indicated that each contained a highly polar

Table I. Mass Spectral Data for Methyl Esters of Carboxylic Acid Degradation Products of Virelure Components [(Z)-11-Hexadecenal and (Z)-9-Tetradecenal]

compound	M^+	base peak	M^+ $-OCH_3$	M^+ $-H_2O$	M^+ $-H_2O$, OCH_3	other significant ions
(Z)-11-hexadecenoic acid methyl ester (H-1)	268	55	237			194
trans-11,12-epoxyhexadecanoic acid methyl ester (H-2)	284	55	253	266	235	199, 227
cis-11,12-epoxyhexadecanoic acid methyl ester (H-3)	284	55	253	266	235	199, 227
(Z)-9-tetradecenoic acid methyl ester (T-1)	240	55	209			166
trans-9,10-epoxytetradecanoic acid methyl ester (T-2)	256	55	225	238	207	171, 199
cis-9,10-epoxytetradecanoic acid methyl ester (T-3)	256	55	225	238	207	171, 199

functional group. Because each of these compounds was extracted from a hexane or dichloromethane solution with 10% aqueous sodium bicarbonate or 0.1 N NaOH, each likely contained a carboxylic acid moiety. Therefore, the NaOH-soluble components of the (Z)-11-HDAL and (Z)-9-TDAL degradation mixtures were methylated with diazomethane (**caution**: suitable safety precautions should be used in handling diazomethane). Results of GLC–mass spectral analyses showed that the molecular ion for methylated H-1 (H-1-Me) was at m/e 268 and for T-1-Me at m/e 240 (Table I). Other significant ions for H-1-Me and T-1-Me were at m/e 237 and 209, respectively ($M^+ - OCH_3$), m/e 236 and 208 ($M^+ - OCH_3$, H), and m/e 194 and 166 ($M^+ - C_3H_6O_2$). On the basis of these data, H-1-Me was identified as methyl (Z)-11-hexadecenoate and T-1-Me was identified as methyl (Z)-9-tetradecenoate. A sample of authentic methyl (Z)-9-tetradecenoate (methyl myristoleate), obtained from commercial sources, was compared with T-1-Me from (Z)-9-TDAL. These compounds exhibited identical GLC–mass spectral behavior.

GLC–mass spectra of H-2-Me and H-3-Me revealed that both showed essentially identical mass spectra except for some minor variations in the relative intensities of certain ions. Both showed a very weak molecular ion at m/e 284 (Table I). Other significant ions were as follows: m/e 266 ($M^+ - H_2O$); m/e 253 ($M^+ - OCH_3$); m/e 235 ($M^+ - H_2O$, OCH_3); m/e 227 ($M^+ - C_4H_9$). Similarly, GLC–mass spectral analysis of T-2-Me and T-3-Me showed a weak molecular ion at m/e 256. Other significant ions were m/e 238 ($M^+ - H_2O$), m/e 225 ($M^+ - OCH_3$), m/e 207 ($M^+ - H_2O$, OCH_3), and m/e 199 ($M^+ - C_4H_9$). On the basis of their mass spectra, H-2-Me and H-3-Me from (Z)-11-HDAL were assigned as methyl *trans*- and *cis*-5,6-epoxyhexadecanoate, respectively, and T-2-Me and T-3-Me as methyl *trans*- and *cis*-5,6-epoxytetradecanoate, respectively. These structures were further substantiated by epoxidation with MCPBA. MCPBA treatment of H-1-Me from (Z)-11-HDAL gave two compounds with the same GLC–mass spectral behavior and in approximately the same ratio as H-2-Me and H-3-Me isolated from the (Z)-11-HDAL degradation mixture. Also, T-1-Me and the authentic methyl ester of myristoleic acid each gave two compounds upon epoxidation with MCPBA; these showed GLC–mass spectral behavior identical with that of T-2-Me and T-3-Me from (Z)-9-TDAL degradation mixtures.

The epoxide moiety of H-2 and T-2 was assigned the trans configuration and epoxide of H-3 and T-3 the cis configuration of the basis of NMR data. Thus, H-2-Me and T-2-Me gave partially resolved triplets at δ 2.67 and H-3-Me and T-3-Me gave partially resolved triplets at δ 2.92. These values agree with those reported by Aplin and Coles (1967) of δ 2.66 and 2.88 for the trans and cis isomers

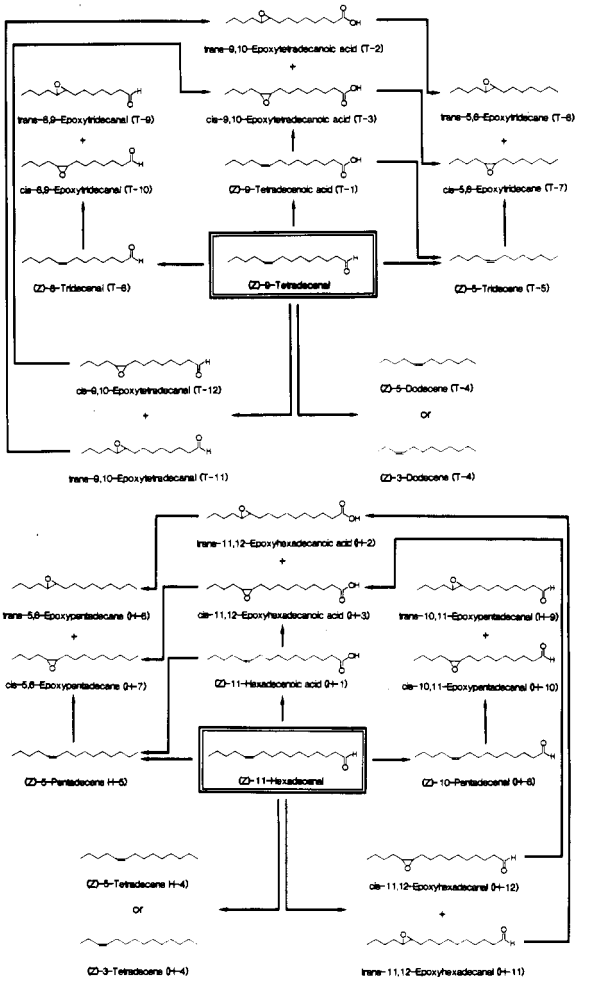
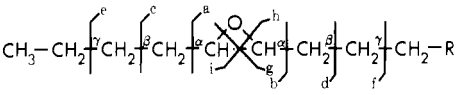


Figure 3. Schematic representation of the degradation of virelure components [(Z)-11-hexadecenal and (Z)-9-tetradecenal] as hexane solutions in the laboratory.

of fatty acid epoxides, respectively.

Identification of Compounds 4, 5, 6, and 7. Compounds H-4 and H-5 from (Z)-11-HDAL and T-4 and T-5 from (Z)-9-TDAL degradation mixtures eluted from silica gel columns with pentane and thus appeared to be hydrocarbons. H-4 and T-4 were analyzed by GLC–mass spectrometry, and each gave a spectrum characteristic of a straight-chain hydrocarbon. T-4 gave a molecular ion at m/e 168 ($C_{12}H_{24}$, dodecene) and other significant ions as follows: base peak, m/e 70; m/e 140 ($M^+ - C_2H_4$); a homologous series with decreasing intensity (m/e 83, 97, 111, 125, 139). H-4 gave a molecular ion at m/e 196 ($C_{14}H_{28}$, tetradecene) and other significant ions as follows:

Table II. Mass Spectral Data for Epoxides Isolated from Degradation Mixtures of Virelure Components [(Z)-11-Hexadecenal and (Z)-9-Tetradecenal]



compound designation	M^+	base peak	$M^+ - H_2O$	ions resulting from predicted cleavage about epoxide function								
				α		β		γ		transanular		
				a	b	c	d	e	f	g	h	i
trans-5,6-epoxypentadecane (H-6)	226	69	208	169	99	183	113	197	127	156	140	86
cis-5,6-epoxypentadecane (H-7)	226	69	208	169	99	183	113	197	127	156	140	86
trans-10,11-epoxypentadecanal (H-9)	240	69	222	183	99	196	113	211	127	170	154	86
cis-10,11-epoxypentadecanal (H-10)	240	69	222	183	99	196	113	211	127	170	154	86
trans-11,12-epoxyhexadecanal (H-11)	254[a]	69	236	197	99	211	113	225[a]	127	170	154	86
cis-11,12-epoxyhexadecanal (H-12)	254[a]	69	236	196	99	211	113	225[a]	127	170	154	86
trans-5,6-epoxytridecane (T-6)	198	69	180	141	99	155	113	169	127	128	112	86
cis-5,6-epoxytridecane (T-7)	198	69	180	141	99	155	113	169	127	128	112	86
trans-8,9-epoxytridecanal (T-9)	212	69	194	155	99	169	113	183	127	142	126	86
cis-8,9-epoxytridecanal (T-10)	212	69	194	155	99	169	113	183	127	142	126	86
trans-9,10-epoxytetradecanal (T-11)	226[a]	69	208	169	99	183	113	197[a]	127	156	140	86
cis-9,10-epoxytetradecanal (T-12)	226[a]	69	208	169	99	183	113	197[a]	127	156	140	86

[a] Ion not observed.

Table III. Relative Distribution of Degradation Products of Virelure Components [(Z)-11-Hexadecenal and (Z)-9-Tetradecenal] Formed after Exposure for 28 Days as Hexane Solution in the Laboratory

(Z)-11-hexadecenal product	%[a]	(Z)-9-tetradecenal product	%[a]
(Z)-11-hexadecenoic acid (H-1)	29.7	(Z)-9-tetradecenoic acid (T-1)	33.8
trans-11,12-epoxyhexadecanoic acid (H-2)	0.9	*trans*-9,10-epoxytetradecanoic acid (T-2)	1.3
cis-11,12-epoxyhexadecanoic acid (H-3)	17.6	*cis*-9,10-epoxytetradecanoic acid (T-3)	16.0
(Z)-5-(or 3-) tetradecene (H-4)	0.2	(Z)-5-(or 3-) dodecene (T-4)	0.3
(Z)-5-pentadecene (H-5)	15.4	(Z)-5-tridecene (T-5)	13.2
trans-5,6-epoxypentadecane (H-6)	0.1	*trans*-5,6-epoxytridecane (T-6)	0.1
cis-5,6-epoxypentadecane (H-7)	2.3	*cis*-5,6-epoxytridecane (T-7)	3.5
(Z)-10-pentadecenal (H-8)	12.6	(Z)-9-tridecenal (T-8)	11.1
trans-10,11-epoxypentadecanal (H-9)	0.2	*trans*-8,9-tridecanal (T-9)	0.2
cis-10,11-epoxypentadecanal (H-10)	4.5	*cis*-8,9-tridecanal (T-10)	6.1
trans-11,12-epoxyhexadecanal (H-11)	0.9	*trans*-9,10-epoxytetradecanal (T-11)	0.6
cis-11,12-epoxyhexadecanal (H-12)	16.3	*cis*-9,10-epoxytetradecanal (T-12)	14.1

[a] Calculated as area percentage of the total degradation products; ca. 71% and 64% of the (Z)-11-hexadecenal and (Z)-9-tetradecenal, respectively, remained after 28 days.

base peak, m/e 56; m/e 168 ($M^+ - C_2H_4$); a homologous series with decreasing intensity (m/e 69, 83, 97, 111, 125, 139, 153). However, both H-4 and T-4 were not available in sufficient quantities to permit definitive determination of the position of the double bond.

A GLC–mass spectral analysis of H-5 gave a molecular ion at m/e 210 and other significant ions as follows: base peak, m/e 69; m/e 182 ($M^+ - C_2H_4$); a homologous series with decreasing intensities (m/e 69, 83, 97, 111, 125, 139, 153, 167). T-5 gave a molecular ion at m/e 182 and other significant ions as follows: base peak, m/e 70; m/e 154 ($M^+ - C_2H_4$); a homologous series with decreasing intensities (m/e 83, 97, 111, 125, 139, 153). These spectra fit the general structure $C_{15}H_{30}$ and $C_{13}H_{26}$, respectively, which allows for one double bond. The double bond in both compounds was determined to be in the 5 position by epoxidation of the hydrocarbon with MCPBA, followed by isolation of the products by preparative GLC and subsequent GLC–mass spectral analysis. The epoxides gave a molecular ion at m/e 226 (from H-5) and m/e 198 (from T-5). The characteristic ion due to α cleavage of the epoxide function (Aplin and Coles, 1967) was at m/e 169 for the H-5 derivative and at m/e 141 for the T-5 derivative. These two products were thus identified as (Z)-5-pentadecene and (Z)-5-tridecene, respectively.

Compounds H-6 and H-7 from (Z)-11-HDAL gave the same GLC retention times and mass spectral data (Table II) as the two epoxides formed by MCPBA epoxidation of compound H-5 and were thus identified as *trans*- and *cis*-5,6-epoxypentadecene. Similar studies with T-6 and T-7 from (Z)-9-TDAL established their structures as *trans*- and *cis*-epoxytridecane, respectively.

Identification of Compounds 8, 9, 10, 11, and 12. The GLC–mass spectral analysis of H-8 and T-8 showed molecular ions at m/e 224 and m/e 196, respectively. Other significant ions obtained from H-8 were as follows: m/e 206 ($M^+ - H_2O$); m/e 180 ($M^+ - CH_2CHOH$). Significant ions obtained from T-8 were as follows: m/e 178 ($M^+ - H_2O$); m/e 152 ($M^+ - CH_2CHOH$). Mass fragmentation patterns of both compounds were very similar to those of their parent aldehydes in the lower end of the mass spectrum, and the shifting down of 14 mass units in the upper end indicated compounds with similar structure to the parent aldehyde but containing one less CH_2 group. Both H-8 and T-8 showed strong absorption in the IR spectrum at 1725 cm^{-1} and thus likely contained a carbonyl functional group. Both compounds also gave a positive reaction on TLC plates with 2,4-dinitrophenylhydrazine reagent. The position of the double bond was determined by epoxidizing the isolated compounds with MCPBA and determining the mass of the characteristic fragment due to α cleavage of the epoxide. The α-cleavage ion in the spectrum of the epoxide from H-8 was at m/e 183 ($C_{11}H_{19}O_2$), which shows that the double bond of H-8 was between carbons 10 and 11. The epoxide of T-8 yielded an α-cleavage ion at m/e 155 ($C_9H_{15}O_2$), which established

the double bond of T-8 to be between carbons 8 and 9. Therefore, H-8 and T-8 were identified as (Z)-10-pentadecenal and (Z)-8-tridecenal, respectively. The mechanisms through which H-8 and T-8 were generated from the parent aldehydes are not known, but possibly one or more short-lived or GLC-refractory intermediates were involved.

Compounds H-9 and H-10 had the same GLC retention times and mass spectral properties (Table II) as did the epoxides obtained from MCPBA treatment of (Z)-10-pentadecenal. Thus, H-9 and H-10 were identified as *trans*- and *cis*-10,11-epoxypentadecanal, respectively. Compounds T-9 and T-10 were likewise identified as *trans*- and *cis*-8,9-epoxytridecanal, respectively.

Compounds H-11 and H-12 from (Z)-11-HDAL had the same GLC retention times and mass spectral properties (Table II) as the epoxides formed on reaction of MCPBA with (Z)-11-HDAL and were thus identified as *trans*- and *cis*-11,12-epoxyhexadecanal. Components T-11 and T-12 were identified in the same manner as *trans*- and *cis*-9,10-epoxytetradecanal.

(Z)-11-HDAL and (Z)-9-TDAL degradation mixtures yielded the individual components in approximately equal ratios (Table III). For each of the epoxides, the quantity of trans isomer was about 5% that of the cis isomer. No trans isomer of the unsaturated aldehydes was detected.

DISCUSSION

Results of these studies show that the virelure components (Z)-11-HDAL and (Z)-9-TDAL undergo degradation to several derivatives when held in the laboratory in hexane solution. Each of the degradation products from both virelure components that were resolved on GLC were ultimately characterized; the structures of these compounds are shown in Figure 3. Most of these products result from rather straightforward and predictable oxidative mechanisms. The pathways in Figure 3 are shown as logical degradation sequences, although alternate or additional degradation mechanisms may have been involved in some reactions. On the basis of the structures of certain of the identified products, some were likely generated through intermediates that were not identified—presumably because they were short lived or perhaps were not resolved by the GLC parameters used. Clearly (Figure 3; Table III), these two virelure components are degraded as the result of two primary mechanisms—oxidation to carboxylic acids and epoxidation of the double bond. Carbon–carbon bond cleavage to derivatives having one or two fewer carbon atoms also occurs to an appreciable extent (Figure 3; Table III). Both (Z)-11-HDAL and (Z)-9-TDAL are degraded in hexane solution by similar pathways (Figure 3), and the quantitative distribution of homologous derivatives is essentially identical (Table III).

Under environmental conditions of use in insect control or trapping program, it may be expected that some virelure degradation will occur in the dispensers and in the vapor phase after the compounds are released into the environment. Although the current studies in hexane solution are almost surely not totally predictive of virelure degradation in the environment, they do indicate that these two major virelure components will likely be environmentally nonpersistent, that they will likely be degraded to a number of products, and that the mechanisms of degradation and quantitative distribution of homologous products generated will likely be essentially identical for both the 14- and 16-carbon components. In subsequent studies on these compounds, we have found that they degrade to generally the same products in water or soil that we observed here in hexane solution (Shaver, 1981).

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