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SEC-BUTYL (Z)-7-TETRADECENOATE. A NOVEL SEX PHEROMONE COMPONENT FROM THE WESTERN GRAPELEAF SKELETONIZER, HARRISINA BRILLIANS.

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Summary The first reported instance of an unsaturated sec-butyl ester as a lepidopteran sex pheromone is described including its identification and synthesis.

Defoliation of grapevines by the western grapeleaf skeletonizer (WGLS), Harrisina brillians, Barnes, McDunnough (Lepidoptera: Zygaenidae), poses a threat to California grape production. The stinging hairs on the larvae can also produce skin welts on vineyard workers. In order to aid in the trapping of these insects, we set out to identify the WGLS sex pheromone.

The volatiles emitted by the female moths were investigated by chemical, spectroscopic, and chromatographic techniques, resulting in the discovery of a new structural class of insect volatiles. We have identified sec-butyl decanoate, sec-butyl dodecanoate, sec-butyl (Z)-7-tetradecenoate, and isopropyl (Z)-7-tetradecenoate. The major component, sec-butyl (Z)-7-tetradecenoate has shown sex pheromone activity in laboratory tests.

Secondary butyl or isopropyl unsaturated esters have never been reported from the volatile complex of a lepidopteran species. Unsaturated long chain alcohols and acetates are typical of such pheromones, with a few exceptions. Identification of sec-butyl (Z)-7-tetradecenoate as a component of the WGLS sex pheromone is novel and unique.

The volatiles from a total of 117 female moths were collected during a period of six days. A vacuum source was applied to the end of a 6"x 1/4" stainless steel Tenax-filled tube connected to a 1.5 ℓ glass collection chamber. Air entering the chamber (~100 cc/min) passed through an activated charcoal filter. The Tenax trap was eluted with 5 ml of ether, which was

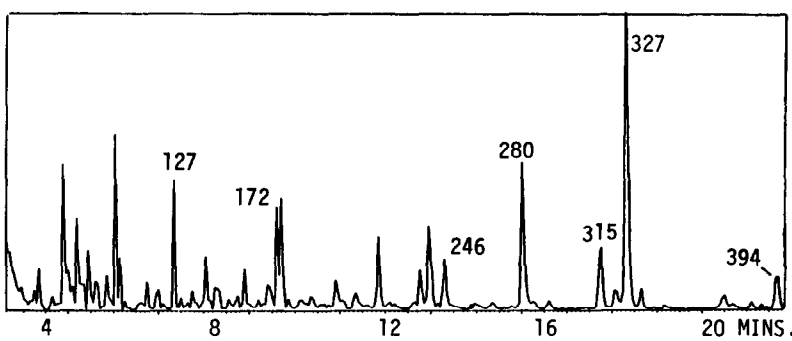

Figure 1. Reconstructed ion chromatogram of Tenax trapped volatiles. Scan 172, sec-butyl decanoate; scan 246, sec-butyl dodecanoate; scan 280, isopropyl (Z)-7-tetradecenoate, scan 327, sec-butyl (Z)-7-tetradecenoate; scans 127, 174, 239, 315, and 394, silicone artifacts.

evaporated, and the residue dissolved in hexane. GC/MS analysis (42 m x 0.25 mm I.D., pyrex OV-101 column) gave the reconstructed ion chromatogram shown in fig. 1.

An additional amount of insect extract was obtained by dipping the abdomens of 40 adult females in 0.5 ml of hexane. The resulting mixture was filtered to remove insect scales and concentrated.

The Kovat's retention index[1] of the major peak (RI=1886, scan 387) is in agreement with previous work[2] that indicated a bioactive component eluting in that area.

The EI mass spectrum of this compound is shown in fig. 2. The exact mass (282.2578), indicates a molecular formula of $C_{18}H_{32}O_2$ (calc. 282.2558). The fragment ions at 209 (M-73; loss of $-OC_4H_9$), 208 (M-74;loss of $C_4H_{10}O$), and 226 (M-56; loss of C_4H_8) indicate a butyl tetradecenoate. Mass spectra of several synthetic butyl (E)- and (Z)-tetradecenoates give results similar to fig. 2, and indicate the presence of a secondary butyl group.

Our work showed the surprising result that the single hydrogen rearangement (leading to m/z 226, M-56 in the butyl tetradecenoates) is much more prominent in the sec-butyl esters than in either n-butyl or iso-butyl esters, compared to the expected double bond hydrogen rearrangement (leading to M-55)[3]. Furthermore, as shown in fig. 3, the abundance of both the 226 and 208 rearrangement ions ($M-C_4H_8$ and $M-C_4H_{10}O$, resp.) show an unexpected correlation with double bond

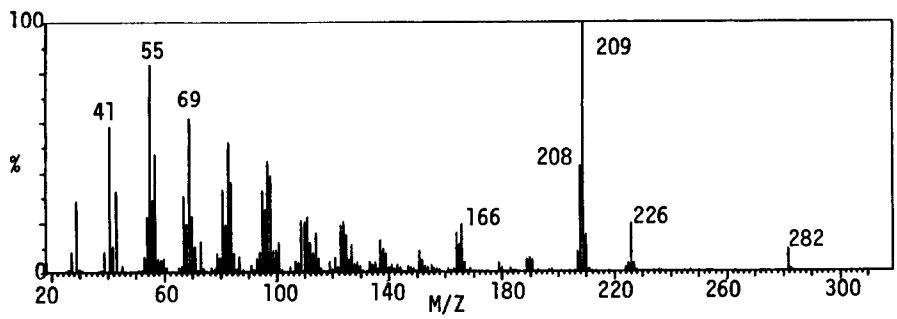

Figure 2. Mass spectrum of scan 327, sec-butyl (Z)-7-tetradecenoate.

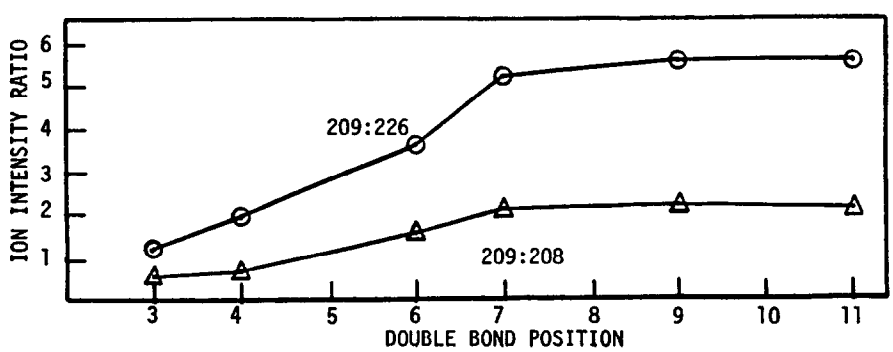

Figure 3. Ratio of ion intensities compared to double bond position in sec-butyl tetradecenoate.

position relative to the peak for homolytic cleavage leading to m/z 209 ($M-OC_4H_9$) used as an internal reference. The dependence on double bond position is approximately the same for both of these rearangement reactions, suggesting to us that formation of the m/z 226 ion may require prior transfer of hydrogen to the ester oxygen; the failure of either reaction to occur in the 2-isomer suggests the alpha hydrogen may be transferred specifically.

In order to ascertain the exact double bond position, a portion of the abdomen extract was gas chromatographed (SE-30) and the material corresponding to a retention index of 1886 was collected. The olefin was oxidized with osmium tetroxide in ether-pyridine[4] and the resulting osmate ester was reduced with hydrogen sulfide[5]. After filtration the solution was evaporated to dryness under argon, and the diol was derivitized with bis-trimethylsilylacetamide in pyridine (5 min/100°C) to form the bis-trimethylsilyl ether. GC/MS of this material showed a multiplicity of compounds, but only one of them had a mass spectrum that corresponded to any of the possible double bond isomers. As shown in fig. 4, the fragment ions at 273 and 187 indicate that the double bond is in the 7-position[4].

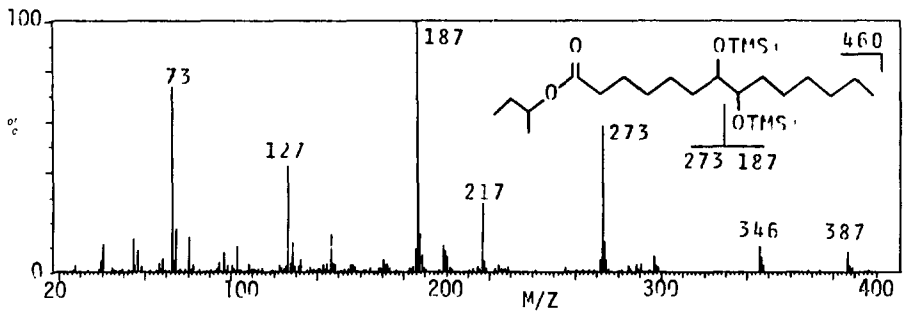

Figure 4. Mass spectrum of the trimethylsilyl derivative of the oxidised pheromone component.

An authentic sample of sec-butyl (Z)-7-tetradecenoate was prepared via a modified Jones oxidation[6] (inverse addition, 0°C, 3 days; 87% yield) of 7-tetradecyne-1-ol[7] esterification of the resulting acid (sec-butanol and BF_3etherate, 98°C, 18h; 83% yield) and catalytic hydrogenation (poisoned P-2 Nickel[8] or Pd-$BaSO_4$[9], 88% yield). The mass spectrum of this compound is identical to that shown in fig. 2, and the GC retention time (OV-101, 50 m x 0.32 mm fused silica) is the same as that observed from the insect derived material. The E-isomer, prepared by equilibration with benzenethiol[10] was shown to have a slightly longer retention time.

The minor component, isopropyl (Z)-7-tetradecenoate (Rl=1786, scan 321) was identified by the same chemical, chromatographic, and spectroscopic methods. The mass spectrum of the bis-trimethylsilyl ether derivative of the oxidized olefin shows the diagnostic fragments at

masses 259 and 187. Preparation of both the isopropyl and n-propyl esters and comparison of their mass spectra and GC retention times confirmed the identification.

The two saturated esters, sec-butyl decanoate (RI=1511, scan 172) and sec-butyl dodecanoate (RI=1710, scan 246) were also identified by comparison with synthetic samples. The partial structures of two other esters were tentatively identified as a propyl dodecenoate (RI=1588, scan 198) and a butyl dodecenoate (RI=1685, scan 235). Five of the peaks in fig. 1 were identified as silicone artifacts from the gas chromatograph (scans 127,174, 239,315 and 394). Their mass spectra showed large characteristic fragment ions at 73 and 147.

The laboratory bioassay was performed by placing ~50 ng of chromatographically purified sec-butyl (Z)-7-tetradecenoate in the proximity of the male moths. Wing fluttering, hair pencil extension, and copulatory attempts with other males was observed. The tests were done in the morning, since field observations indicate the moths are much more active at that hour. Field tests are being planned to establish the compound's long range attractancy and to determine if the pheromone consists of more than one component. Although the tests were successful with the racemic material, it is probable that the natural pheromone is optically active. This possibility is being tested by separately synthesizing and testing both enantiomers.

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