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(E,Z)-2,13-OCTADECADIEN-1-OL ACETATE. A NEW PHEROMONE STRUCTURE FOR SESIID MOTHS

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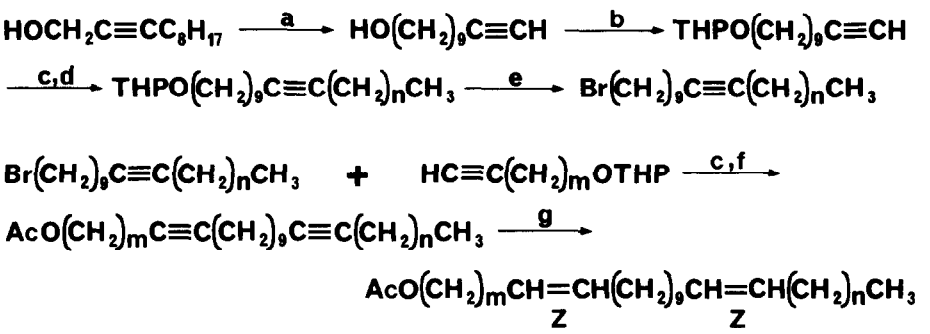
Summary: (E,Z)-2,13-Octadecadien-1-ol acetate was identified from ovipositor extracts of the grape root borer and was shown to attract males of the species.

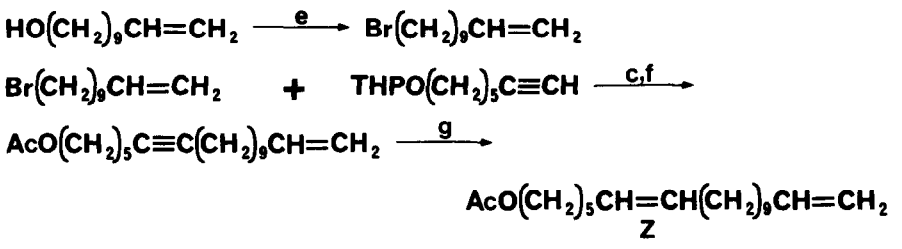
The grape root borer, Vitacea polistiformis (Harris) (Lepidoptera: Sesiidae) is considered a destructive pest in viticulture.[1] It thus became of interest to identify the female grape root borer (GRB) sex pheromone. We depended on field-collected female pupae for our work because no laboratory cultures of this insect were available. Adults were allowed to emerge in the laboratory and the ovipositors were excised and extracted with heptane by the technique described by Klun, et al.[2]. Seven GRB females were available to us for identification of the pheromone. Gas-chromatographic analysis of the ovipositor extracts on polar- and non-polar capillary columns revealed the presence of one major peak with a retention time in the range of a primary C_{18} acetate. GC-MS analysis of this peak, on a fused silica DB-1[3] capillary column, showed the parent ion at m/e 308, corresponding to a molecular formula of $C_{20}H_{36}O_2$ and a fragment at m/e 248 (M-60) diagnostic of the loss of acetic acid. These data indicated that the pheromone was most likely an octadecadien-1-ol acetate (ODDA). Microozonolysis of a portion of the extract yielded undecanedial, the identity of which was verified by comparison with an authentic sample on capillary GC. This result thus established a nine carbon interval between the double bonds. No acetoxyaldehyde or other low molecular weight aldehyde as the other fragments could be identified in the ozonolysis reaction mixture. Paucity of the natural product prevented us from carrying out further direct experimentation to define the exact double bond positions. Thus, we had to resort to the matching of GC retention times of the natural product on polar and non-polar capillary columns with those of synthetic materials. In non-conjugated dienylacetates ZZ isomers generally elute last from capillary GC columns; elution sequence: EE, ZE, EZ, ZZ on polar- and non-polar columns. We therefore synthesized the Z,Z isomers of 2,13-ODDA, 3,14-ODDA, 4,15-ODDA, 5,16-ODDA, and (Z)-6,17-ODDA as candidate compounds. The first four compounds were prepared as shown in Scheme 1. 6,17-ODDA was prepared from 10-undecen-1-ol as is shown in Scheme 2. Among the compounds prepared (Z,Z)-3,14-, (Z,Z)-4,15- and (Z)-6,17-ODDA had retention times on a non-polar DB-1[3] column that were shorter than that of the natural product. Therefore, they as well as their geometrical isomers having shorter retention times, were excluded as candidate structures. (Z,Z)-5,16-ODDA, which had a retention time considerably longer than the natural product, was equilibrated at 100° in the presence of benzenethiol[8] to obtain a mixture of its geometrical isomers. All four isomers had retention times different from the natural product. (Z,Z)-2,13-ODDA had a retention time that was shorter than that of the natural product; however it was known to us from prior work[9], that in the case of allylic acetates, an inversion of retention times occurs, i.e. the E-isomer will elute after the Z-isomer. Thus, (E,Z)-2,13-ODDA became a logical candidate, and was synthesized as shown:

SCHEME 1



ODDA	2,13	3,14	4,15	5,16
n	3	2	1	0
m	1	2	3	4

SCHEME 2



Reagents: a. $H_2N-(CH_2)_3NH_2/NaH$[4]. b. dihydropyran/H^+. c. MeLi, THF-HMPA[5]. d. $CH_3(CH_2)_nBr(I)$. e. $\emptyset_3P.Br_2, CH_2Cl_2$[6]. f. AcOH/$Ac_2O$. g. P_2-Ni[7].

$$AcOCH_2C{\equiv}C(CH_2)_9C{\equiv}CC_4H_9 \xrightarrow{a,b,c} \underset{E}{AcOCH_2CH{=}CH(CH_2)_9CH{=}CHC_4H_9}\ \underset{Z}{}$$

a. $LiAlH_4$-MeONa(1:2)[10], b. Ac_2O/pyridine, c. P_2-Ni[7]

This acetate had retention times coincident with the natural product on three liquid phases (SP2340, SP1000 and DB-1[3]) and no difference was detected between the mass spectrum of the synthetic compound and that of the natural product. For verification purposes (Z,Z)-2,13-ODDA was isomerized in the presence of benzenethiol[8]. Only one of the four isomers had a retention time that was coincident with previously prepared authentic (E,Z)-2,13-ODDA, confirming the identity of this compound with the natural product.

Biological activity of (E,Z)-2,13-ODDA was evidenced by the capture of GRB males albeit in low numbers, in traps baited with this compound; in addition visual observations of male flight activity in the vicinity of these traps or other objects having been in contact with the compound. It was impossible to compare the attractiveness of the synthetic pheromone with virgin females because of the unavailability of females and/or ovipositor extracts. We did observe in the ovipositor extracts however, the presence of a minor component which eluted on non-polar columns after (E,Z)-2,13-ODDA and whose GCMS corresponded to an octadecenyl acetate. Therefore it is likely that (E,Z)-2,13-ODDA does not represent the full complement of the GRB-sex pheromone.

Interestingly, traps baited with (E,Z)-2,13-ODDA captured large numbers of male Synanthedon acerrubri (Engelhardt), a pest of maples in the northeastern United States. Also analysis of the ovipositor extract of a field-collected female squash vine borer, Melittia satyriniformis (Hübner), revealed the presence of the same compound as its major constituent. Thus (E,Z)-2,13-ODDA represents a new chemical structure in the sex pheromones of the family sesiidae, where hitherto only the isomers of 3,13-ODDA were found to be the common attractants[11].

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References and notes

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3. All capillary columns were 60 m x 0.25 mm (ID) coated with SP1000, SP2340 (Supelco, Inc., Bellefonte, PA 16823), or DB-1 (J & W Scientific Inc., Rancho Cordova, CA 95670). Mention of a commercial product does not constitute endorsement of that product by the USDA.

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