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PHOTOOXIDATION OF THE SEX PHEROMONE (Z,E)-9,12-TETRADECADIENYL-1-ACETATE

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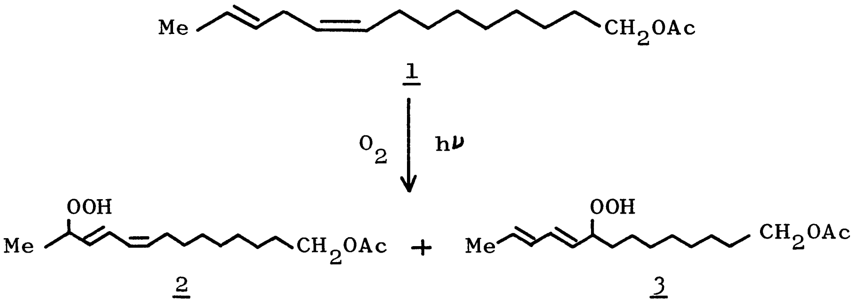
The sex pheromone (Z,E)-9,12-tetradecadienyl-1-acetate (1) was readily converted into inactive 13-hydroperoxy-(Z,E)-9,11-tetradecadienyl-1-acetate (2) and 9-hydroperoxy-(E,E)-10,12-tetradecadienyl-1-acetate (3) by exposure to air and sunlight without intentional addition of sensitizer.

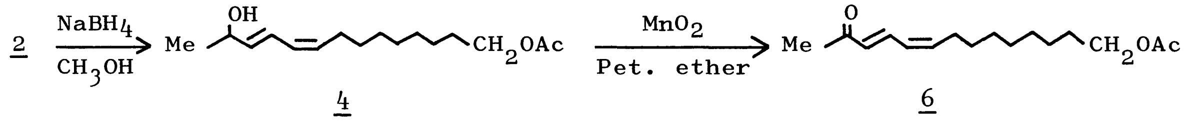
The sex pheromone (Z,E)-9,12-tetradecadienyl-1-acetate (1) was first isolated from Prodenia eridania[1] by Jacobson and has an interesting cis,trans 1,4-diene moiety in the molecule. 1 has also been shown to be the sex pheromone of Cadra cautella,[2,3] Cadra figulilella,[4] Plodia interpunctella,[2,3,5] Anagasta kuehniella,[6] Ephestia elutella,[7] Spodoptera exigua[8] and Spodoptera litura.[9] In the course of synthetic studies on the sex pheromone of S. litura, we found that 1 was readily converted into an inactive substance by exposure to air and sunlight in open glass vessel. This communication describes the structures of the photoproducts.

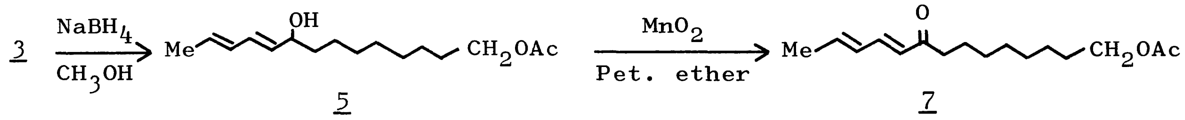
Irradiation (sunlight, in film form) of 1 for three days at room temperature without intentional addition of sensitizer resulted in the formation of a polar product (24% yield) which was purified by preparative thin layer chromatography (silica gel; benzene-AcOEt 5:1). The IR,[10] UV[11] and NMR[12] spectra suggest that the product is a mixture[13] of 13-hydroperoxy-(Z,E)-9,11-tetradecadienyl-1-acetate (2) and 9-hydroperoxy-(E,E)-10,12-tetradecadienyl-1-acetate (3). The high resolution mass spectrum of the mixture shows a molecular peak[14] at m/e 284 and fragment peaks at 268.2084 (M-16, Calcd. for $C_{16}H_{28}O_3$: 268.2038), 266.1920 (M-18, Calcd. for $C_{16}H_{26}O_3$: 266.1882), 251.2029 (M-33, Calcd. for $C_{16}H_{27}O_2$: 251.2011) and 191.1801 (M-93, Calcd. for $C_{14}H_{23}$: 191.1799). These data also supported the hydroperoxide structures. Location of terminal methyl protons at δ 1.22 and 1.76

(total 3H) indicated that the ratio of 2 and 3 was 4:1.

The structures and configurations of newly formed double bonds of 2 and 3 were further confirmed by the following experiments. $NaBH_4$ reduction[15] of the mixture in methanol and the following preparative thin layer chromatography (silica gel; benzene-AcOEt 5:1) yielded two alcohols: 4, UV λ_{max} (EtOH) 232 nm (ε 19000); IR ν_{max} (film) 3450 (OH), 1735 (OAc), 990, 950 cm^{-1} (cis, trans-conjugated diene); NMR δ_{ppm} (CCl_4), 1.19 (3H, dd, J=6Hz, 1.5Hz, Me-CH-OH), 1.93 (3H, s, OAc), 3.95 (2H, t, J=6Hz, CH_2-OAc), 4.20 (1H, qd, J=6Hz, 6Hz, C_{13}-H), 5.2-6.4 (4H, m, vinyl H); Mass m/e 268.2027 (M^+, Calcd. for $C_{16}H_{28}O_3$: 268.2038) and 5, UV λ_{max} (EtOH) 228.5 nm (ε 24000); IR ν_{max} (film) 3450 (OH), 1735 (OAc), 1650, 985 cm^{-1} (trans, trans-conjugated diene); NMR δ_{ppm} (CCl_4) 1.71 (3H, d, J=6Hz, Me-CH=), 1.94 (3H, s, OAc), 3.95 (2H, t, J=6Hz, CH_2-OAc), 4.21 (1H, td, J=6Hz, 6Hz, C_9-H), 5.2-6.4 (4H, m, vinyl H); Mass m/e 268.2039 (M^+, Calcd. for $C_{16}H_{28}O_3$: 268.2038), in a ratio of 4:1.







Oxidation of 4 and 5 with active manganese dioxide[16] in petroleum ether afforded 6, UV λ_{max} (EtOH) 276 nm (ε 21000); IR ν_{max} (film) 1695, 1685, 1635, 1595 (conjugated dienone), 1000, 965 cm^{-1} (cis, trans-conjugated diene); NMR δ_{ppm} 2.14 (3H, d, J=1.5Hz, Me-C=O), 5.7-6.2 (3H, m, vinyl H), 7.35 (1H, dd, J=16Hz, 10Hz, C_{11}-H); Mass m/e 266.1897 (M^+, Calcd. for $C_{16}H_{26}O_3$: 266.1882) and 7, m.p. 34°, UV λ_{max} (EtOH) 274 nm (ε 26000); IR ν_{max} (KBr) 1695, 1685, 1640, 1595 (conjugated dienone), 1000 cm^{-1} (trans, trans-conjugated diene); NMR δ_{ppm} (CCl_4) 1.87 (3H, d, J=5Hz, Me-CH=), 2.43 (2H, t, J=7Hz, $-CH_2-C=O$), 5.9-6.2 (3H, m, vinyl H), 7.04 (1H, dd, J=16Hz, 10Hz, C_{11}-H); Mass 266.1880 (M^+, Calcd. for $C_{16}H_{26}O_3$: 266.1882), respectively. The coupling constant (16Hz)[17] of C_{11}-H in 6 and 7 showed that newly formed double bonds of 2 and 3 have E-configuration. These chemical and spectral data are in good agreement with the structures.

The results are quite interesting in view of the fact that the insect mates at night in the field. For the practical use and the field test of the pheromone, this photooxidation may be a troublesome problem. But addition of antioxidants such as 4-methyl-2,6-di-*t*-butylphenol into 1 was effective to protect against the oxidation without any mating inhibitory effects.[18]

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References and Footnotes

1. M. Jacobson, R. E. Redfern, W. A. Jones, and M. H. Aldridge, Science, 170, 542 (1970).
2. Y. Kuwahara, C. Kitamura, S. Takahashi, H. Hara, S. Ishii, and H. Fukami, Science, 171, 801 (1971).
3. U. E. Brady, J. H. Tumlinson III, R. G. Brownlee, and R. M. Silverstein, Science, 171, 802 (1971).
4. U. E. Brady and R. C. Daley, Ann. Entomol. Soc. Amer., 65, 1356 (1972).
5. K. H. Dahm, I. Richter, D. Meyer, and H. Röller, Life Science, 10, Part II, 531 (1971).
6. Y. Kuwahara, H. Hara, S. Ishii, and H. Fukami, Agr. Biol. Chem., 35, 447 (1971).
7. U. E. Brady and D. A. Nordlund, Life Science, 10, Part II, 797 (1971).
8. U. E. Brady and M. C. Ganyard Jr., Ann. Entomol. Soc. Amer., 65, 898 (1972).
9. Y. Tamaki, H. Noguchi, and T. Yushima, Appl. Entomol. Zool., 8, 200 (1973).
10. ν_{max} (film) 3400 (OOH), 1735, 1720 (OAc), 1660 (C=C), 990, 950 cm^{-1} (conjugated diene).

11. λ_{max} (EtOH) 229 (sh), 231 nm.

12. δ_{ppm} (CCl_4) 1.22 (dd, J=6Hz, 1.5Hz, Me-CH-OOH), 1.76 (d, J=6Hz, Me-CH=), 1.95 (3H, s, OAc), 4.02 (2H, t, J=6Hz, CH_2-OAc), 4.3-4.7 (1H, m, CH-OOH), 5.3-6.7 (4H, m, vinyl H), 8.6 (1H, br, OOH, exchangeable with D_2O).

13. All attempts to separate the mixture were unsuccessful.

14. Owing to the low intensity of the molecular ion peak, it was difficult to calculate the high mass unit.

15. H. Morimoto, I. Imada, and G. Goto, Ann. Chem., 735, 65 (1970).

16. J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, J. Chem. Soc., 1094 (1952).

17. J. A. Pople, W. G. Shneider, and H. J. Bernstein, High Resolution Nuclear Magnetic Resonance, p. 238, McGraw-Hill Book Co., Inc., New York 1959.

18. H. Fujiwara, unpublished results.

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