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ISOLATION, IDENTIFICATION AND SYNTHESIS OF SEX PHEROMONE COMPONENTS OF THE CAROB MOTH, *ECTOMYELOIS CERATONIAE*

T.C. Baker[1*], W. Francke[2], C. Löfstedt[3], B.S. Hansson[3], J.-W. Du[4],
P.L. Phelan[5], R.S. Vetter[1], R. Youngman[1]

1 Department of Entomology, University of California, Riverside, CA, USA
2 Institut für Organische Chemie, Universität Hamburg, FRG
3 Department of Animal Ecology, University of Lund, Sweden
4 Shanghai Institute of Entomology, Academia Sinica, Shanghai, China
5 Department of Entomology, OARDC/OSU, Wooster, Ohio, USA

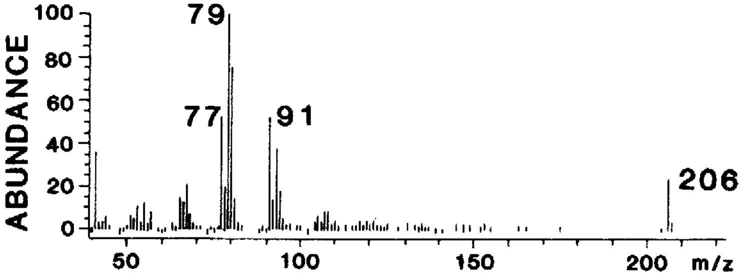
Summary: The sex pheromone of females of the carob moth, *Ectomyelois ceratoniae*, was identified to be a mixture of (*Z,E*)-9,11,13-tetradecatrienal, (*Z,E*)-9,11-tetradecadienal and (*Z*)-9-tetradecenal in the ratio of 10:1:1. A synthetic blend proved to be attractive.

The carob moth, *Ectomyelois ceratoniae* (Zeller)(Lepidoptera: Pyralidae), is a widespread pyralid moth pest of nuts and fruits, including carobs, almonds, and dates. A sensitive means of monitoring and detecting new populations, such as is offered by synthetic sex pheromone traps, is urgently needed.

Sex pheromone glands of 2- to 5-day-old virgin female moths were excised during the period of pheromone emission and extracted for 30 min in CS_2. Analysis of the concentrated extract by combined GC/EAG$^{1)}$, using DB-1 or DB-wax$^{2)}$ as the stationary phases, revealed three peaks with strong EAG activity eluting on both columns in the ratio of 1:1:10.

Upon comparison with an authentic sample, GC/MS analysis$^{3)}$ proved the first eluting minor EAG-active compounds (M^+ = 210) to be (*Z*)-9-tetradecenal. The mass spectrum of the other minor EAG-active peak (M^+ = 208) showed a base peak at *m/z* 67 and an abundant molecular ion$^{4)}$, which suggested a tetradecadienal with conjugated double bonds$^{5)}$. The major EAG-active compound (M^+ = 206) had a mass spectrum, which corresponded to a tetradecatrienal with at least one pair of conjugated double bonds. Since microozonolysis produced 8-formyloctanal, the first double bond was in the nine position, and, excluding allenes and enynes, additional double bonds would have to be in the 11 and 13 positions.

EAG tests with a series of monounsaturated straight-chain acetates and alcohols showing 12 to 16 carbon atoms revealed particularly high activity of the (*Z*)-9- and (*E*)-11-isomers in the 14-carbon series. On the basis of the identification of (*Z*)-tetradecenal it was suggestive that the other two compounds were (*Z,E*)-9,11-tetradecadienal and (*Z,E*)-9,11,13-tetradecatrienal respectively.



Mass spectrum of the major active compound of *E.ceratoniae*, Hewlett Packard 5970

(*Z,E*)-9,11-Tetradecadienal was prepared from commercially available (*Z,E*)-9,11-tetradecadienol (SIGMA) by oxidation with PDC/molecular sieve[6]. Mass spectrum and GC retention times of the synthetic sample were identical to those of the natural product.

The synthesis of (*Z,E*)-9,11,13-tetradecatrienal was carried out as a C_9-C_5-sequence: 9-Decen-1-ol (ALDRICH) was silylated with tert. butyldimethylsilylchloride[7] (TBDMSCl, ALDRICH)[8], which after ozonolysis yielded the TBDMS derivative of 9-hydroxynonanal (1)[8]. Ethyl-(*E*)-2,4-pentadienoate (ALDRICH) was converted to 1-bromo-(*E*)-2,4-pentadiene (2) through reduction with $LiAlH_4$ and subsequent treatment of the resulting alcohol with triphenylphosphonium dibromide[9]. Refluxing 2 and triphenylphosphane in benzene furnished the respective Wittig salt (3)[10]. Wittig reaction of 1 with 3 followed by cleavage of the silyl ether group with tetrabutyl ammonium fluoride[11], previously neutralized with acetic acid, gave a mixture of geometrical isomers of 9,(*E*)-11,13-tetradecatrienol which could be separated by reversed-phase HPLC[12]. The first eluting compound (M^+ = 208) showed the NMR data given below ($J_{H9,10}$ = 11,2 Hz: cis- and $J_{H11,12}$ = 14.8 Hz: trans-) and thus proved to be the (*Z,E*)-isomer; the data are in good accord with respective values for (*Z,E,E*)- and (*Z,E,Z*)-10,12,14-hexadecatrienyl acetate[13]. The alcohol could be oxidized[6] to the very sensitive (*Z,E*)-9,11,13-tetradecatrienal, which was identical to the natural product.

(*Z,E*)-9,11,13-Tetradecatrienol: ^{1}H-NMR (C_6D_6); chem. shifts/coupling const.
Data of the double bond system of the aldehyde are the same.

$C-H_x$	1	2-7	8		9	10	11	12	13		14,14'
δ	3.36	1.15 -1.45	2.15		5.46	6.09	6.58	6.18	6.37		5.00 5.13
H_x/H_y			8/9	8'/9	9/10	10/11	11/12	12/13	13/14	13/14'	14/14'
J[Hz]			8,0	8,0	11,2	11,2	14,8	10,2	10,4	16,8	1,0

Synthetic (*Z*)-9-tetradecenal, (*Z,E*)-9,11-tetradecadienal and (*Z,E*)-9,11,13-tetradecatrienal were EAG-active. Behaviour tests showed high attractivity of the trienal; the other aldehydes, per se behaviourally inactive, show a slightly synergistic effect: in a wind tunnel[14], 0.6 ng of a synthetic blend of the three compounds in naturally occuring proportions reached 80 % of the attractivity of 5 female equivalents.

1) H. Arn, E. Städler, S. Rauscher, Z. Naturforsch. **30c** 722 (1975).
2) GC conditions: 30 m x 0.25 mm i.d. fused silica; inj. temp. 250°C; program: 2 min/80°C then 10°/min to 230°C; FID temp 250°C; H_2 carrier gas flow 1,5 ml/min.
3) Hewlett-Packard 5970 coupled with a Hewlett-Packard 5890 gas chromatograph.
4) Mass spectrum: m/z (%) = 67 (100), 41 (55), 95 (42), 82 (40), 81 (36), 55 (36), 68 (30), 79 (28), 93 (14), 53 (14), 96 (13), 77 (13), 208 (13).
5) C. Löfstedt, G. Odham, Biomed. Mass Spec., **11** 106 (1984).
6) J. Herscovici, M. J. Egron, K. Antonakis, J. Chem. Soc., Perkin I 1967 (1982).
7) E.J. Corey, A. Venkatiswarlu, J. Am. Chem. Soc. **94** 6190 (1972).
8) All NMR-spectra were obtained with a Bruker WM 400 at 400 MHz. ^{1}H-NMR ($CDCl_3$): δ = 0.05 (s, 6 H); 0.86 (s, 9 H); 1.26-1.4 (m, 8 H); 1.5 (m, 2 H); 1.6 (m, 2 H); 2.4 (m, 2 H); 3.57 (t, 2 H); 9.72 (1 H). B.p. 120°C/0.5 mm.
9) G.A. Wiley, R. Hershkowitz, B.M. Rein, B.G. Chung, J. Am. Chem. Soc. **86** 964 (1964).
10) ^{1}H-NMR ($CDCl_3$) δ = 4.90 (m, 2 H); 5.13 (m, 2 H); 5.5 (m, 1 H); 6.18 (m, 1 H); 6.45 (m, 1 H); 7.68 (m, 6 H); 7.75-7.95 (m, 9H). M.p. 207-208°C.
11) E.J. Corey, B.B. Snider, J. Am. Chem. Soc. **94** 2549 (1972).
12) B.p. 108-110°C/0.1 mm. HPLC conditions: RP-18; low pressure gradient; methanol/water.
13) T. Ando, Y. Ogura, M. Koyama, M. Jurane, M. Uchima, K.Y. Seol, Agric. Biol. Chem. **52** 2459 (1988).
14) N = 100; Upwind flight at 23°C; 0.3 lux; wind velocity 50 cm/sec.

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