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(3Z,6Z,9Z)-3,6,9-NONADECATRIENE - A COMPONENT OF THE SEX PHEROMONAL SYSTEM OF THE GIANT LOOPER, BOARMIA (ASCOTIS) SELENARIA SCHIFFERMÜLLER (LEPIDOPTERA: GEOMETRIDAE)

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Summary (3Z,6Z,9Z)-3,6,9-Nonadecatriene was identified as a pheromone component from Boarmia selenaria females by means of gas chromatography, GC-coupled mass spectrometry, electroantennography and GC coupled EAG.

Boarmia (Ascotis) selenaria Schiffermüller (Lepidoptera: Geometridae) is a world-wide distributed pest of important crops: coffee in Kenya; tea in India, Japan and USSR (Georgia); peanuts in Madagascar; citrus in South Africa; avocado and pecan in Israel. In Europe it affects lemons in Sicily and alfalfa in Romania and Hungary[1)].

Avocado plantations in Israel are protected against insect pests exclusively by means of a biological control programme including Bacillus thuringiensis. Regarding B. selenaria, this programme is targeted on the young larvae only, the older ones becoming increasingly insensitive to the bacterial preparations used. Therefore, accurate monitoring is imperative. Thus-far, this is being done through the use of tethered virgin females obtained from a laboratory colony[2)], a cumbersome, expensive and sometimes erratic procedure. Because of this, research was undertaken with a view to replace females as attractants by the pheromone(s) they produce. To the best of our knowledge, the pheromone of only one geometrid, Operophtera brumata L., has been identified so far[3)].

Pheromone extraction from Boarmia selenaria, which was reared on artificial diet, was carried out as follows: The ovipositor, extruded by pressing the female's abdomen, was cut off in the middle of the 7th segment; it was then homogenized in methylene chloride.

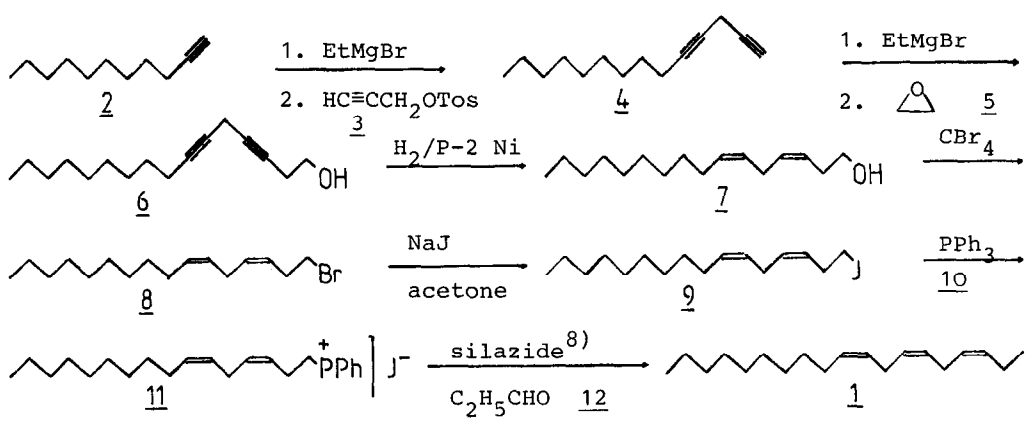
The crude extract was filtered through a short celite column using methylene chloride as solvent, and then separated by two methods: GC and LC. On GC it was divided into 20 fractions by partitioning on 2 columns: SE-30 8%, 4 m (column A) and carbowax 20 M 15%, 2 m (column B). Two active fractions

were identified by EAG activity tested according to Moore[4]; fraction I t_R 19-24 min and 5-9 min on column A and B, respectively, and fraction II 48-53 min and 19-24 on A and B, respectively. LC separation was carried out on silica gel[5]: again two EAG-active fractions were distinguished; they were identical to I and II above. According to the polarity of the eluents, it was concluded that I was a hydrocarbon. Treatment of the total extract with bromine in CCl_4 cancelled EAG activity indicating that the hydrocarbon is unsaturated.

A subsequent gaschromatographic analysis of fraction I using a 25m UCON HB glass capillary column and a male Boarmia antenna as the biological detector (EAD-detector[6]) resulted in one signal with biological activity, eluted at a retention time of a C_{19}-hydrocarbon with more than two double bonds.

A series of unsaturated hydrocarbons was tested by EAG: the most active was (3Z,6Z,9Z)-3,6,9-nonadecatriene (1) which was synthesized in the following way: the starting compound was 1-undecyne (2), the magnesium acetylenide of which was coupled with the tosylate of propargylic alcohol (3). The resulting 1,4-tetradecadiyne (4) [bp. 125°/25 Torr (bath temp.), yield 87%; ^{1}H-NMR ($CDCl_3$): δ = 0.89 (t,3H), 1.30 (mc,14H), 2.06(t,1H), 2.20(mc,2H), 3.17(dt,2H); MS(70eV): M^+ = 190] was converted into its magnesium salt and alkylated with oxirane (5) according to the formula scheme below.

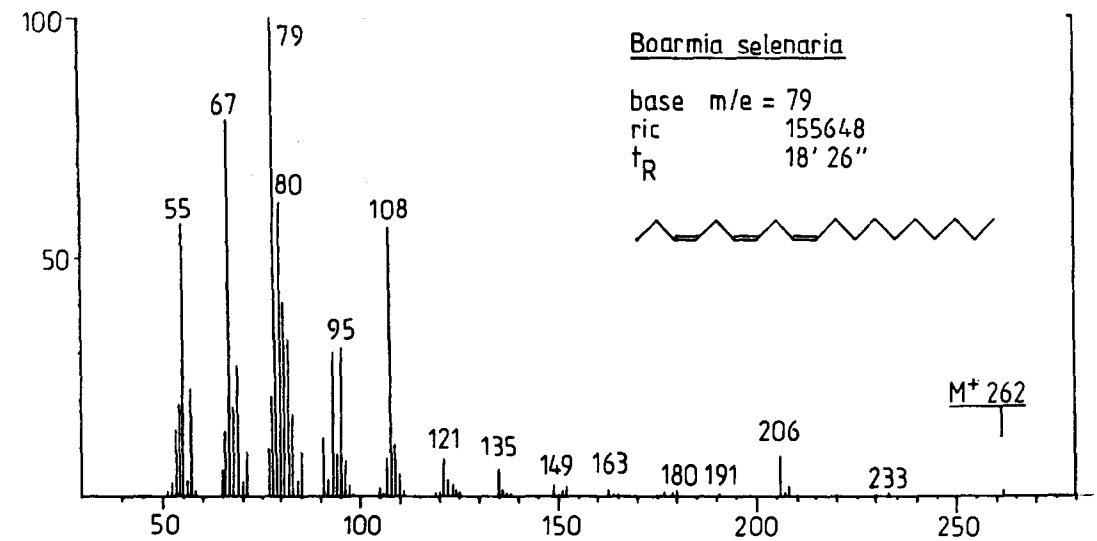
Formula scheme



This gave rise to the formation of 3,6-hexadecadiyn-1-ol (6) [bp. 134-138°/0.35 Torr, yield 47%; ^{1}H-NMR($CDCl_3$): δ = 0.90 (t,3H), 1.30 (mc,14H), 2.03 (mc, 1H), 2.17 (mc,2H), 2.46 (tt,2H), 3.16 (quin,2H), 3.73 (t,2H)] which was partially hydrogenated to the corresponding (Z,Z)-alkadienol 7 [bp. 130-132°/0.4 Torr (bath temp.), yield 84%; ^{1}H-NMR($CDCl_3$): δ = 0.89 (t,3H), 1.28 (mc,14H), 1.57 (br,1H) 1.80-2.20 (m,2H), 2.39 (br q,2H), 2.83 (mc,2H) , 3.67 (t,2H), 5.25-5.70 (mc,4H)] using P-2 nickel catalyst[7]. Reacting 7 with tetrabromo-

methane afforded (3Z,6Z)-3,6-hexadecadienyl bromide (8) [bp. 115-120°C/0.05 Torr (bath temp.), yield 88%] which was converted into the iodo compound 9 with NaJ/acetone, yield 83%. The crude product 9 was treated with triphenyl phosphane (10) and the resulting hexadecadienyl(triphenyl)phosphonium iodide (11) [oily, yield 52%] converted into its corresponding ylide according to the silazide technique[8]. The final Wittig olefination with propanal (12) gave (3Z,6Z,9Z)-3,6,9-nonadecatriene (1), as shown in the formula scheme [bp. 110-130°/0.05 Torr (bath temp.), yield 68%, ^{1}H-NMR($CDCl_3$): δ = 0.86 (t,3H), 0.98 (t,3H), 1.29 (mc,14H), 1.80-2.30 (m,4H), 2.82 (mc,4H), 5.38 (mc,6H); MS(70 eV): M^+ = 262; IR (100%): 3020, 1652, 720 cm^{-1}]. The synthetic nonadecatriene 1 had the same retention time as fraction I on the preparative GC columns A and B as well as the biologically active compound found by the EAG-gaschromatography. A subsequent GCMS analysis (Finnigan Quadrupole MS with data system) of fraction I resulted in the identification of a hydrocarbon, the retention time (glass capillary column, t_R = 18'26") as well as the mass spectrum (Fig. 1) being identical with

Figure 1



those of the synthetic nonadecatriene 1. The GCMS, the EAG-GC analysis and the electrophysiological activity unequivocally prove that (3Z,6Z,9Z)-3,6,9-nonadecatriene is one of the two components of the Boarmia selenaria pheromone system. An EAG dose/response test was carried out comparing various amounts of 1 to one female equivalent (FE) extract with the following results:

Amount[a]	Blank	0.01	1 FE	0.1	1.0	10.0	100.0
Mean EAG (mV ± SE)[b]	0.56 0.03	1.35 0.22	2.24 0.50	3.58 0.71	4.39 0.68	6.00 1.25	8.18 1.30

[a] in µg on Al-foil rolls. [b] 4 antennae in series; 3 replicates. The data were used to obtain a linear regression equation according to Steven's Power Law[9]; from this it was estimated that 1 FE corresponds to about 46 ng of 1.

Preliminary field tests are being carried out on the attractance of compound 1. The second pheromonal component is under investigation.

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