Polyenic Hydrocarbons as Sex Attractants for Geometrids and Amatids (Lepidoptera) Found by Field Screening in Hungary

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During field screening of polyene compounds, conducted at different localities of Hungary, in 1984, sex attractants were found for *Costaconvexa polygrammata* Bkh., as (3*Z*, 6*Z*, 9*Z*)-3,6,9-eicosatriene; *Eupithecia subnotata* Hbn., as (3*Z*, 6*Z*, 9*Z*)-3,6,9-nonadecatriene; *Synthomis phegea* L., as (3*Z*, 6*Z*, 9*Z*)-3,6,9-heneicosatriene and for *Dysauxes ancilla* L., as (3*Z*, 6*Z*, 9*Z*)-1,3,6,9-nonadecatetraene. (7*E*, 9*Z*)-7,9-dodecadienyl acetate was found to be a sex attractant for *Sterrha rubraria* Stgr.

In recent years a growing number of reports described polyenic hydrocarbons as sex pheromone components of predominantly geometrid [1–5], arctiid [6, 7] and to some extent noctuid [8, 9] Lepidoptera. The objective of this project was to study, through field screening in different biotopes, the frequency of occurrence of similar compounds as sex attractants for males of the Hungarian Lepidoptera fauna.

Among the candidate compounds tested, (6*Z*, 9*Z*)-6,9-nonadecadiene (Z,Z-6,9-19:H), (3*Z*, 6*Z*, 9*Z*)-3,6,9-nonadecatriene (Z,Z,Z-3,6,9-19:H) and (3*Z*, 6*Z*, 9*Z*)-1,3,6,9-nonadecatetraene (Z,Z,Z-1,3,6,9-19:H) have been reported as sex pheromone components in different geometrid species [1–3, 10], while (3*Z*, 6*Z*, 9*Z*)-3,6,9-heneicosatriene (Z,Z,Z-3,6,9-21:H) has been first described as the sex pheromone of an arctiid [6], and together with (3*Z*, 6*Z*, 9*Z*)-3,6,9-eicosatriene (Z,Z,Z-3,6,9-20:H) as sex pheromone components for catocalin species of Noctuidae [8, 9]. In addition to these hydrocarbons, (7*E*, 9*Z*)-7,9-dodecadienyl acetate (E,Z-7,9-12:Ac) was also included in the test, as this compound has been described as a sex attractant for the geometrid *Sterrha biselata* Hufn. [11].

Compounds

Z,Z-6,9-19:H was obtained from linoleic acid by transformation to the corresponding aldehyde, Wittig methylenation, hydroboration with 9-BBN and subsequent hydrolysis (Bestmann, unpublished). Z,Z,Z-3,6,9-19:H and Z,Z,Z-1,3,6,9-19:H were obtained by combinations of actylenic syntheses and Wittig reactions by the methods described in [1, 2]. Each of the compounds contained about 15% of other isomers, determined by gas chromatography.

Z,Z,Z-3,6,9-20:H and Z,Z,Z-3,6,9-21:H were synthesized by the methods described [8]. Each synthetic compound was purified by HPLC on a 20% $AgNO_3$ silica gel column and the purified compounds were analyzed on a 50 m OV101 capillary gas chromatographic column. The overall purity of both compounds was greater than 99%, and both of them contained about 14% of other geometrical isomers.

E,Z-7,9-12:Ac (containing 0.05% BHT as antioxidant; overall purity 98%; 96% E,Z) was a gift from H. Arn (Wädenswil, Switzerland).

Field trapping

For field tests the required amounts of the compounds were applied in hexane solutions to 1 × 1 cm pieces of rubber tubing (commercial product, purchased from Borászati Szaküzlet, Budapest, Hungary). Tetra traps with flaps [12] containing different baits were randomly set up in a row at a height of 1.5 m, in 20 m intervals. Moths captured were recorded, sticky layers were changed to new ones, and traps were moved one position forward in the row once a week. Baits were replaced at 5 to 6 week periods. Sites thought to have a rich geometrid fauna were selected. Biotopes ranged from the boundary of a pear orchard and a mixed oak forest (Gyöngyös-

Abbreviations: (6*Z*, 9*Z*)-6,9-nonadecadiene, Z,Z-6,9-19:H; (3*Z*, 6*Z*, 9*Z*)-3,6,9-nonadecatriene, Z,Z,Z-3,6,9-19:H; (3*Z*, 6*Z*, 9*Z*)-1,3,6,9-nonadecatetraene, Z,Z,Z-1,3,6,9-19:H; (3*Z*, 6*Z*, 9*Z*)-3,6,9-eicosatriene, Z,Z,Z-3,6,9-20:H; (3*Z*, 6*Z*, 9*Z*)-3,6,9-heneicosatriene, Z,Z,Z-3,6,9-21:H; (7*E*, 9*Z*)-7,9-dodecadienyl acetate, E,Z-7,9-12:Ac.

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solymos, Heves county, July 24–Oct. 10), alfalfa field bordered by bushland and oak forest (Dunaszentmiklós, Komárom county, July 26–Aug. 23), red currant plantation bordered by raspberry parcels (Bernecebaráti, Nógrád county, June 8–July 25), mixed oak forest (Aszód, Pest county, July 24–Oct. 23), and a poplar forest along the flood area of the Danube (Adony, Fejér county, July 16–Aug. 23) to a mixed oak-beech-hornbeam forest (Kétbükkfanyereg, Pest county, July 25–Nov. 1). C_{19}-hydrocarbons and their binary mixtures (ratios 10:1, 1:1 and 1:10) were tested at Gyöngyössolymos, Dunaszentmiklós, Adony and Bernecebaráti, while C_{20}- and C_{21}-hydrocarbons and their mixtures in the above ratios were tested at Gyöngyössolymos, Bernecebaráti, Kétbükkfanyereg and Aszód. At Gyöngyössolymos, Dunaszentmiklós and Adony traps baited with E,Z-7,9-12:Ac alone were also set up. Capture data were transformed to $\sqrt{\times + 0.5}$ and submitted to Duncan's New Multiple Range Test for analysis.

Results

Four species of Geometridae were captured in significant numbers.

Z,Z,Z-3,6,9-19:H alone, and in mixtures with Z,Z-6,9-19:H or Z,Z,Z-1,3,6,9-19:H, caught males of *Eupithecia subnotata* Hbn. at Gyöngyössolymos (Table I). The diene and the tetraene did not influence captures.

Male *Costaconvexa polygrammata* Bkh. were attracted to Z,Z,Z-3,6,9-20:H at Gyöngyössolymos, Bernecebaráti and Aszód. Captures at Gyöngyössolymos, which were the highest, are shown in Table II. The addition of Z,Z,Z-3,6,9-21:H did not increase captures.

Table I. Male *E. subnotata* and *D. ancilla* attracted to Z,Z-6,9-19:H, Z,Z,Z-3,6,9-19:H, Z,Z,Z-1,3,6,9-19:H and their binary mixtures in field tests at Gyöngyössolymos (3 replicates; captures followed by same letter within a column are not significantly different at P = 5% by Duncan's NMRT).

Bait [µg]			Total No. of males caught	
Z,Z-6,9-	Z,Z,Z-3,6,9-19:H	Z,Z,Z-1,3,6,9-	*E. subnotata*	*D. ancilla*
500	–	–	0 b	0 c
–	500	–	9 a	0 c
–	–	500	1 b	38 ab
500	50	–	0 b	0 c
500	500	–	8 a	0 c
50	500	–	10 a	0 c
500	–	50	0 b	1 c
500	–	500	0 b	3 bc
50	–	500	0 b	20 bc
–	500	50	10 a	8 bc
–	500	500	10 a	71 a
–	50	500	4 ab	63 a

Table II. Male *C. polygrammata* and *S. phegea* attracted to Z,Z,Z-3,6,9-20:H, Z,Z,Z-3,6,9-21:H and their mixtures in field tests (3 replicates; captures followed by same letter within a column are not significantly different at P = 5% by Duncan's NMRT).

Bait [µg]		Total No. of males caught	
Z,Z,Z,-3,6,9-20:H	Z,Z,Z-3,6,9-21:H	*C. polygrammata*[a]	*S. phegea*[b]
250	–	51 a	0 b
–	250	1 c	21 a
250	25	11 bc	1 ab
250	250	31 ab	6 ab
25	250	4 bc	18 a

[a] Gyöngyössolymos.
[b] Kétbükkfanyereg.

Sterrha rubraria Stgr. was caught by E,Z-7,9-12:Ac (500 μg, a total of 27 males in three traps) in the Gyöngyössolymos test. This compound attracted also large numbers (a total of 38 and 74 males in the Dunaszentmiklós and Adony tests, resp.) of *S. biselata* Hufn. confirming an earlier report [11].

Apart from geometrids, males of *Synthomis phegea* L. (Amatidae) were caught by Z,Z,Z-3,6,9-21:H at Kétbükkfanyereg, Gyöngyössolymos and Aszód. Highest numbers caught (Kétbükkfanyereg) are shown in Table II. Males of another amatid, *Dysauxes ancilla* L. were attracted to Z,Z,Z-1,3,6,9-19:H at Gyöngyössolymos and Dunaszentmiklós. The addition of Z,Z,Z-3,6,9-19:H to the tetraene did not influence captures. Highest captures were recorded at Gyöngyössolymos (Table I).

Concluding remarks

Z,Z,Z-3,6-9-19:H, which proved to be attractive for *E. subnotata* in this study, has been reported as a sex pheromone component for *Boarmia selenaria* Den. et Schiff. [1], *B. rhomboidaria* Den. et Schiff [13], *Alsophila pometaria* Harris [4], and *Paleacrita vernata* [5]. It was attractive in field tests in combination with other compounds for a number of other geometrids [5, 14]. On the other hand, Z,Z,Z-3,6,9-20:H is first reported to be a sex attractant in Geometridae in this paper.

In all geometrids described in the literature so far, polyenic hydrocarbons composed at least part of the pheromone or attractive blend. Despite the fact that the candidate compounds and their mixtures were tested in a variety of biotopes, and during a considerable lenght of time in this study, only two species were attracted. This may show the importance of further components in the pheromonal communication of Geometridae. Such compounds can be oxygenated derivates of unsaturated hydrocarbons, *i.e.* epoxides [5], or ketones [13].

Sterrha rubraria, described in this study, and *S. biselata* [11] differ from other geometrids in that they respond to a dodecadienyl acetate as sex attractant. A third species of this genus, *S. imbecilla* Inoue has been described to be attracted to (7*Z*)-7-dodecenyl acetate [15], a compound differing very slightly from E,Z-7,9-12:Ac. Mono and diunsaturated dodecenyl acetates have been widely reported on as pheromone components of Noctuidae, Tortricidae, and a number of other families.

No pheromone structures have been identified so far in Amatidae. In a study aimed at observing the migration behavior of *Lymantria dispar* L., Čapek *et al.* reported [16], as a chance finding, that large numbers of *S. phegea* were caught at disparlure baited traps. In a 1985 test, however, we never caught any *S. phegea* males in traps baited with 1, 10 or 100 μg of racemic disparlure (obtained from SIGMA Chem. Co., Taufkirchen, FRG), while Z,Z,Z-3,6,9-21:H (100 μg) proved to be attractive again. Disparlure added in different ratios to Z,Z,Z-3,6,9-21:H also did not influence captures of *S. phegea* (Szőcs and Tóth, unpubl.). Furthermore, in EAG tests, no response was evoked from antennae of male *S. phegea* by disparlure (10 μg). Good responses were at the same time evoked by the same amount of Z,Z,Z-3,6,9-21:H (Szőcs and Tóth, unpubl.). In conclusion, this study is the first report on sex attractants of two amatid species.

Amatidae and Arctiidae are considered to be closely related taxonomically. This relatedness may also be expressed in similarities in the structure of sex attractants described in this study and compounds reported in arctiids earlier [6, 7].

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