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OXIME ETHER ANALOGS OF SEX PHEROMONE COMPONENTS OF TURNIP MOTH (*Agrotis segetum* SCHIFFERMÜLLER)

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Abstract—Oxime ether analogs of sex pheromone components of the turnip moth (*Agrotis segetum* Schiff.) were synthesized by the acidolytic opening of cyclic enol ethers with *O*-alkyl hydroxylamine hydrochlorides. The compounds varying in chain lengths and in the position of the C=N double bond were studied by electrophysiological single sensillum recordings (electrosensillography: ESG). The ESG data indicate in general reduced receptor interaction of all analogs investigated in comparison with natural pheromone components of the turnip moth. The data also show that the grade of decrease of receptor interaction depends on specific structural changes within the molecule. The results demonstrate high complementary pheromone–receptor relationships, predominantly depending on the position of the unsaturated group in the chain, whereas analogs with other structural changes are still recognized as a pheromone-like compound by the receptor.

Key Words—Oxime ether, NMR data, pheromone mimics, ESG studies, structure–response relationships, turnip moth, *Agrotis segetum* Schiff., Lepidoptera, Noctuidae.

INTRODUCTION

Derivatization of natural pheromone structures enables study of the properties of a receptor structure via electrophysiological valuation of response data of the receptor site to the synthesized compounds using electroantennographic (EAG)

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or electrosensillographic (ESG) techniques. Results of synthesis and biological activity of structurally modified lepidopteran pheromone components have been reported by several authors (e.g., Bestmann et al., 1986; Camps et al., 1984; Prestwich et al., 1990; Sun and Prestwich, 1990). Analogs of natural pheromone structures of the sex pheromone of *Agrotis segetum* Schiff. (Lepidoptera: Noctuidae) have been synthesized and studied for their biological significance, e.g., by Sun et al. (1992), Jönsson et al. (1991), and Bengtsson et al. (1990).

The male moth of *Agrotis segetum* is attracted by a specific female sex pheromone bouquet, consisting mainly of (Z)-5-decenyl acetate **(1a)** (Z5–10:OAc), (Z)-7-dodecenyl acetate (Z7–12:OAc), (Z)-9-tetradecenyl acetate (Z9–14:OAc), and decyl acetate at a ratio of about 1:5:2.5:0.6 (Arn et al., 1992; Hansson and Baker, 1991). Furthermore, three physiologically different pheromone-sensitive cell types were found occurring in the male antenna, which interact with single components of the sex pheromone bouquet. The authors mentioned above showed that, in wild populations of *Agrotis segetum* from Sweden, about 66% of the sensillum cells are specialized to Z5–10:OAc, and that the males, when placed in a wind tunnel, prefer a pheromone bouquet in the ratio mentioned above.

The male olfactory receptor structures in general respond to the Z-isomers of the different compounds, whereas in only one published case has E5–12:OAc been determined as a component of an *Agrotis segetum* pheromone composition (Arn, 1980; see also summarized bibliography in Arn et al., 1992).

Preliminary ESG studies (unpublished data) revealed that the male receptor structure responded in general to the E/Z isomeric mixtures as well as to the E-isomers of the main pheromone components, but with somewhat decreased sensitivity. This makes it possible to use the E/Z isomeric mixtures, resulting from the synthesis procedures used for the ESG studies. The investigations cited above dealt with partially fluorinated analogs of Z5–10:OAc obtained by selective regiochemical introduction of fluorine into the methyl and methylene position of the compound in order to probe hydrophobicity requirements of the receptor site (Sun et al., 1992), and alkyl substitution in the terminal chain of Z5–10:OAc (Jönsson et al., 1991). Azomethine analogs of natural *Agrotis segetum* pheromones have not yet been analyzed for their electrophysiological activity. In the present work, we followed a bioisosteric concept to probe the influence of the replacement of the C=C double bond with an azomethine group as well as changing of the position of the unsaturated group within the chain.

METHODS AND MATERIALS

Synthesis of Oxime Ether Analogs of Pheromones

We started with the corresponding hydroxy compound (E/Z)-5-decen-1-ol **(1b)**, where the C=C double bond should be exchanged by the C=N group. One of the simple azomethine analogs is excluded, because it exists in a cyclic

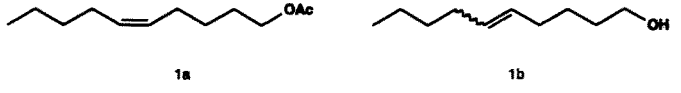
structure as 2-butylaminotetrahydropyran (Potekhin et al., 1976; Potekhin and Zhdanov, 1979; Glacet and Gaumeton, 1955). Therefore we used the corresponding oxime ethers as model substances, where the sequence $-[CH_2-CH=CH-CH_2]-$ is substituted by $-[O-N=CH-CH_2]-$ or $-[CH_2-CH=N-O]-$ (Scheme 1).

The synthesis of the oxime ethers **2** started from 5-hydroxypentanal oxime occurring exclusively in the acyclic form (Potekhin et al., 1976; Potekhin and Zhdanov, 1979), but the alkylation to **2** always yielded mixtures of the oxime ethers and nitrones. However, we found, in support of Gerecs and Windholz (1958), that 2H-3,4-dihydropyran or 2,3-dihydrofuran yields *O*-alkyl-5-hydroxypentanal oximes **(2a–d)** as well as *O*-alkyl-4-hydroxybutanaloximes **(3a–e)** by regioselective opening of the enol ether ring using *O*-alkyl hydroxylamine hydrochloride. The reaction requires a weak acid medium (pH 3–4) and produces oxime ethers **2** and **3** with a yield between 75 and 93% (details see Table 1) (Scheme 2).

The ^{13}C NMR spectra (Table 2) shows a signal doubling for most of the C atoms. This proves the occurrence of a mixture of *E* and *Z*-oxime ethers. The high-field shifted signals belong to the *Z*-configuration by means of the steric compression shift, which is also congruent with the ^{13}C shifting calculated with the increment scheme (Kleinpeter and Borsdorf, 1981). The same signal doubling has also been observed in the ^1H NMR spectra. Two doublets for **2a** (J = 11.8 Hz) were found for the methyl group at 3.78 and 3.72 ppm; for the olefinic proton the triplet of the *E*-isomer at 7.30 ppm (J = 6 Hz); for the *Z*-isomer at 6.57 ppm (J = 6 Hz).

The *E*- and *Z*-isomers of selected compounds occurring at a mixture ratio of about 3 : 1 were separated by high-pressure liquid chromatography using a Si-60-column (see experimental part) and tested subsequently for their purity by their ^1H NMR spectra. **(*E*)-2a** (retention time: 4.38 min) shows a triplet only at ~7.3 ppm, and **(*Z*)-2a** (retention time: 5.19 min) results in a triplet at ~6.6 ppm. A similar separation procedure was successful for the separation of the **(*E*)-2b** (4.34 min) and **(*Z*)-2b** (5.21 min) isomers. More details on the separation and structural elucidation will be published elsewhere.

To prove the dependence of the pheromone receptor response to the orientation of the oxime ether group within the chain, the isomeric compound **4** was synthesized by condensation of valeraldehyde with *O*-[3-hydroxypropyl]hydroxylamine.



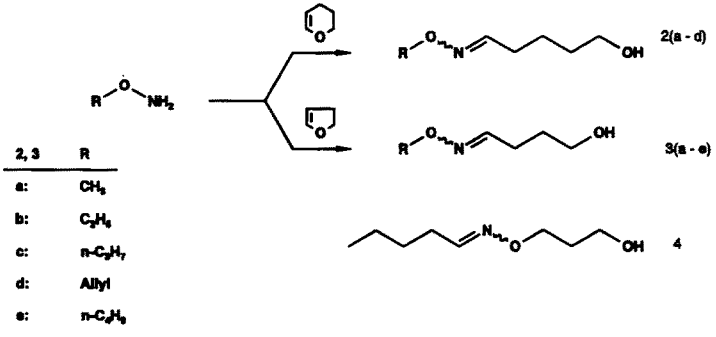
1a 1b

SCHEME 1.

TABLE 1. PREPARED *O*-ALKYL 5-HYDROXYPENTANAL OXIMES **2** AND *O*-ALKYL 4-HYDROXYBUTANAL OXIMES **3**[a,b]

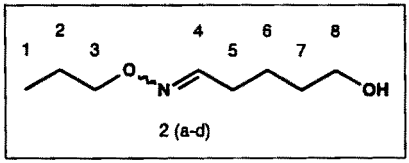
	R	Formula	Molecular peak,[c] intensity (%)	Yield (%)	bp (°C/torr)	n_D^{20}
2a	CH_3	$C_6H_{13}NO_2$ (131.2)	131 (2.1)	87	67–68/0.7	1.4523
2b	C_2H_5	$C_7H_{15}NO_2$ (145.2)	145 (0.4)	78	77–78/0.8	1.4517
2c	n-C_3H_7	$C_8H_{17}NO_2$ (159.2)	159 (0.4)	86	87–88/0.5	1.4516
2d	Allyl	$C_8H_{15}NO_2$ (157.2)	157 (0.3)	95	84–86/0.6	1.4675
3a	CH_3	$C_5H_{11}NO_2$ (117.1)	117 (0.3)	75	46–47/0.4	1.4510
3b	C_2H_5	$C_6H_{13}NO_2$ (131.2)	131 (1.1)	87	53–55/0.3	1.4465
3c	n-C_3H_7	$C_7H_{15}NO_2$ (145.2)	145 (6.6)	73	61–62/0.3	1.4472
3d	Allyl	$C_7H_{13}NO_2$ (143.2)	143 (4.9)	82	66–67/0.3	1.4474
3e	n-C_4H_9	$C_8H_{17}NO_2$ (159.2)	159 (0.4)	93	75–77/0.4	1.4513

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds.
[b] IR spectra (film): ν_{OH} 3360–3396, ν_{CH} 2920–2944, $\nu_{C=N}$ 1630–1635, ν_{C-O} 1035–1062 cm^{-1}.
[c] The main peaks are $N{=}CH{-}(CH_2)_n{-}OH]^+$ (n = **3**, **4**) and R^+ or RO^+, respectively, depending on the nature of R.

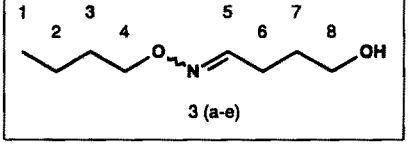


SCHEME 2.

TABLE 2. ^{13}C NMR SPECTRA OF *O*-ALKYL 5-HYDROXYPENTANAL OXIMES **2**, *O*-ALKYL 4-HYDROXYBUTANAL OXIMES **3**, AND *O*-[3-HYDROXYPROPYL] PENTANAL OXIME **4**



2 (a-d)



3 (a-e)

	C1	C2	C3	C4	C5	C6	C7	C8
2a			61.05	150.65	25.14	22.48	32.11	60.65
				151.48	28.88	22.92	32.36	
2b		14.44	68.14	150.15	25.21	22.53	32.14	60.67
		14.59	68.54	151.15	29.03	22.99	32.38	
2c	10.18	21.95	74.11	150.08	25.04	22.32	31.97	60.40
		22.08	74.43	151.66	28.81	22.79	32.22	
2d	116.41	134.80	73.72	150.86	25.26	22.45	32.07	60.64
	116.93	134.90	74.04	151.66	28.94	22.91	32.34	
a					25.40	19.70	33.60	62.70
b					29.80	23.40	33.90	
3a[c]				60.80	150.17	21.68	28.38	60.45
					150.94	25.41	28.77	60.75
3b			13.85	68.24	149.84	21.81	28.47	60.57
			13.98	68.66	150.63	25.58	28.90	60.86
3c[c]		9.72	21.80	74.41	149.65	21.69	28.52	60.61
		9.75		74.78	150.51	25.59	28.93	60.89
3d		116.79	133.56	73.65	150.44	21.86	28.37	60.52
		117.01	133.70	73.89	151.17	25.48	28.77	60.83
3e	13.30	18.53	30.51	72.59	149.52	21.80	28.52	60.57
	13.31	18.57	30.62	72.99	150.40	25.58	28.93	60.85
4	13.73	22.17	25.37	28.78	151.35	70.37	32.02	59.16
	13.94	22.44	28.25	29.15			32.30	59.70

[a] Calculated values for the *Z* isomer.
[b] Calculated values for the *E* isomer (Kleinpeter and Borsdorf 1981).
[c] The underlined values could not be clearly assigned and may be interchangeable.

Preparations and Spectra

Synthesis of O*-alkyl ω-Hydroxyalkanal Oximes (2, 3).* Freshly distilled 2,3-dihydrofuran (3.51 g, 50 mmol) or 2H-3,4-dihydropyran (4.21 g, 50 mmol) was added dropwise with stirring to *O*-alkyl hydroxylamine hydrochloride (50 mmol) in water (30 ml). Each reaction mixture was stirred for 2 hr at room temperature. Subsequently, $NaHCO_3$ (4.20 g, 50 mmol) was added, and the reaction mixture was extracted after saturation with NaCl four times with ether.

After drying with Na_2SO_4, the ether was removed, and the colorless residue was distilled (details see Table 1).

O-[3-Hydroxypropyl] Pentanal Oxime (4). To *O*-[3-hydroxypropyl]hydroxylamine (4.55 g, 50 mmol; bp 71.5–73°C/1 torr, n_D^{20} 1.4593, prepared from 3-bromopropanal and *N*-ethoxycarbonyl hydroxylamine, followed by alkaline hydrolysis (for a similar procedure see Zeeh and Metzger, 1971)), was added pentanal (freshly distilled under argon), with stirring. The temperature reached about 50°C. After 1 hr at this temperature, the mixture was cooled, small pieces of solid KOH were added and distilled: 5.67 g (71%) colorless oil, bp 70–72°C/0.6 torr, n_D^{20} 1.4462, NMR data see Table 2.

^{1}H NMR spectra were obtained with a Tesla BS 567 instrument (100 MHz, tetramethylsilane as internal standard). ^{13}C NMR spectra were recorded with an Brucker AXR 300 (75 MHz, HMDS as internal standard). All spectra were measured in $CDCl_3$. IR spectra were taken with an M 80 instrument (Fa. Zeiss) in thin layer. Mass spectra were determined with a Hewlett Packard 5988 at 70 eV. The HPLC separation was carried out with a Knauer HPL 64 instrument at a Si-60 column (solvent: *n*-hexane–EtOH 97:3 (v/v), flow rate: 6 ml/min, detection: 217 nm).

Electrophysiological Method

Single sensillum recordings were carried out on freshly prepared male antennae of juvenile *Agrotis segetum* moths according to standard procedures (see e.g., Kaissling and Thorson, 1980). The pheromone analogs were applied to filter paper strips in the order of increasing concentration levels via a defined (1 liter/min) and filtered airstream, using consistent measurement standards. The electrodes used were Ag–AgCl wires inserted into glass capillaries filled with a specific Ringer solution (Beadle-Ephrussi-Ringer). The electrode tips were additionally filled with a solution of polyvinylpyrrolidone in Ringer solution and sealed with vaseline in order to prevent drying out of the sensillum hairs.

The amplitudes of the slow (AC coupled) receptor potentials of the receptor neurons in the sensilla trichodea of the male antenna caused by this stimulation were recorded and measured subsequently for a statistical analysis (standard deviation).

RESULTS AND DISCUSSION

Table 3 summarizes the arithmetical means of the standardized ESG data, together with their standard deviations and their number of replicates. The results show that in no case did a pheromone analog reach the response values of the natural component of the *Agrotis* pheromone (Z5–10:OAc), and that most of them caused a clearly reduced ESG response or had no electrophysiological

TABLE 3. ARITHMETICAL MEANS OF STANDARDIZED ESG VALUES (ESG/ESG_{max}) OF ANTENNAL PREPARATIONS AT DIFFERENT CONCENTRATIONS

Sample[a]	Amount (μg), mean (SD)					
	0.002	0.02	0.2	2.0	20	200
***E*-2a** (5)	0.33 (0.09)	0.31 (0.18)	0.31 (0.20)	0.41 (0.18)	0.39 (0.27)	0.36 (0.24)
***Z*-2a** (5)	0.48 (0.21)	0.47 (0.24)	0.53 (0.24)	0.60 (0.13)	0.60 (0.14)	0.56 (0.09)
***E*-2b** (5)	0.29 (0.25)	0.31 (0.24)	0.32 (0.28)	0.34 (0.28)	0.42 (0.23)	0.32 (0.08)
***Z*-2b** (5)	0.34 (0.30)	0.33 (0.28)	0.36 (0.29)	0.34 (0.28)	0.42 (0.30)	0.41 (0.24)
2c (10)	0.48 (0.21)	0.53 (0.23)	0.55 (0.21)	0.58 (0.22)	0.57 (0.29)	0.61 (0.18)
2d (8)	0.51 (0.19)	0.47 (0.19)	0.51 (0.18)	0.49 (0.21)	0.58 (0.18)	0.59 (0.15)
3a (4)	0.38 (0.18)	0.23 (0.16)	0.28 (0.18)	0.38 (0.08)	0.46 (0.05)	0.45 (0.01)
3b (4)	0.22 (0.08)	0.18 (0.02)	0.30 (0.09)	0.27 (0.07)	0.30 (0.06)	0.27 (0.23)
3c (5)	0.18 (0.05)	0.17 (0.09)	0.17 (0.09)	0.21 (0.07)	0.16 (0.03)	0.27 (0.24)
3d (4)	0.15 (0.03)	0.14 (0.04)	0.17 (0.02)	0.15 (0.02)	0.18 (0.02)	0.13 (0.04)
3e (6)	0.49 (0.24)	0.36 (0.22)	0.47 (0.26)	0.46 (0.25)	0.44 (0.24)	0.41 (0.19)
4 (4)	0.49 (0.26)	0.50 (0.31)	0.43 (0.26)	0.48 (0.31)	0.43 (0.25)	0.51 (0.21)
Z5–10:OAc (10)	0.65 (0.21)	0.58 (0.23)	0.59 (0.22)	0.72 (0.24)	0.79 (0.15)	0.79 (0.15)

[a]Number of replicates is given in parentheses.

effect. Only at higher concentrations (>2.0 μg), did three of the analogs reach response values between about 50 and 60% **(Z-2a, 2c, 2d).** At concentrations of ≥20 μg, two further clusters of dose–response values are recognizable (Figure 1). With the exception of compounds **3b, 3c,** and **3d,** with ESG response values below 30% (also at higher concentrations), a second main group of compounds, comprising the rest of the studied analogs, yielded dose–response values between about 30 and 60%. Surprisingly, these results demonstrate in general that the decenyl acetate receptor also responds to pheromone analogs with a large degree of molecular change. Obviously, the loss of receptor response depends on some essential structural properties of the molecule, whereas other changes, such as the introduction of an oxime ether group and/or additional olefinic groups **(2d)** are still recognized and tolerated by the receptor structure as more or less a pheromone-like compound.

The smallest ESG values were measured for compounds **3b–d.** Analogs showing a change in the position of their C=N double bond within the chain (i.e., a shortening or elongation of the chain length between the double bond and the functional groups) obviously can not be recognized by the receptor site as a pheromone structure.

Although not researched in the present study, the comparatively higher ESG response values of **3a** could be explained by the higher volatility caused by the reduced chain length, and to a lesser degree the same may be true also for **4.** For the given experimental (ESG) technique, a comparatively higher amount of substance per time unit is transported by the airstream to the antenna

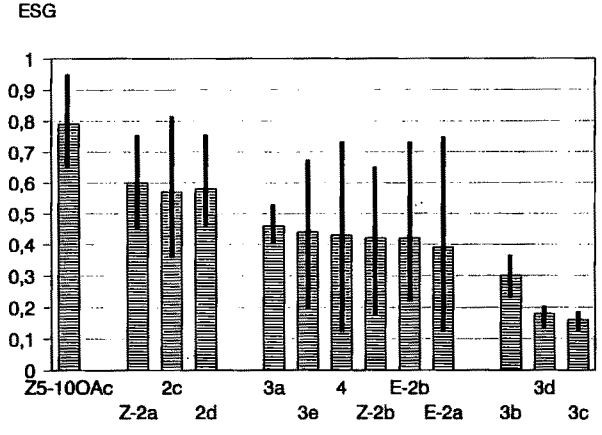


FIG. 1 Comparison of the standardized dose–response value (ESG/ESG_{max}) at 20 μg active compound on the filter paper strip.

preparation and thus causes the higher ESG signals (for details see Bengtsson et al., 1990).

Compounds *Z*-**2a**, **2c**, and **2d** (the last with a second double bond in the terminal position) show the highest ESG response among the analogs studied. However, all of these compounds have an unchanged chain length between the unsaturated and the functional groups in relation to the natural pheromone. Compounds **3a–e** [with a shifting of the double bond from position (*E*/*Z*)-5 to (*E*/*Z*)-4] and **4**, show in no case a response value over 65%.

The electrophysiological response values of the *E*- and *Z*-isomers demonstrate that the receptor prefers the *Z*-isomer of **2a**, whereas with **2b**, no distinction between the isomers was found. Further experiments are required to clarify the reason for this different reaction.

The distinct decrease of the electrophysiological activity of all pheromone analogs analyzed indicates again that the pheromone–receptor interaction is a highly complementary process. Single cell studies on *Agrotis segetum* demonstrate that, in general, chain-shortened (Bengtsson et al., 1990) or chain-elongated (Liljefors et al., 1985) analogs of pheromone structures result in a lower electrophysiological activity of the compounds in comparison with natural pheromones. Bengtsson et al. (1990) interpreted their results in terms of a receptor interaction model (see also Liljefors et al. 1987), suggesting an interaction of the terminal alkyl chain with a hydrophobic "pocket" of the receptor site extending over the two methylene groups closest to the terminal methyl group of the pheromone. Prestwich et al. (1990) reported electrophysiological studies on perfluorinated moth pheromones. The authors showed that replacement of terminal alkyl groups with perfluoroalkyl groups in pheromone components yields electrophysiologically active compounds with reduced ESG response and suggested that the binding of the fluorinated analogs to the receptor is reduced as a result of the less favorable interaction between the polar perfluoroalkyl compounds and the hydrophobic protein binding site of the receptor structure. Furthermore, Jönsson et al. (1991) showed that the replacement of the terminal methyl group of *Z*5–10:OAc with larger and branched alkyl groups reduces the biological activity of these analogs dramatically and suggested a highly steric selectivity of the receptor with regard to the terminal alkyl group.

The results described in the present paper support, in general, receptor models, which suggest a predominantly steric conditioned selectivity of the receptor site. The ESG responses of the sterically changed analogs (especially **3b–d**) are apparently more reduced than those with the same molecular constitution, such as natural structures, along with any replacement of C atoms with heteroatoms within their chain (e.g., **2c**, **2d**).

The clearly graduated distribution of the dose–response profiles of the oxime ether analogs (Figure 1) supports also pheromone–receptor models discussed by Bestmann and coworkers (e.g., Bestmann et al., 1979; Bestmann et al., 1986).

According to such models, the majority of the moth pheromone components can occur in different conformations, especially the long-chained, nonbranched and free rotating pheromone molecules. Their interaction with a putative receptor is characterized by a flexible and a step-wise adaptation to the pheromone receptor structure. Such models could also explain rather easily why the receptor also still responds to highly modified pheromone analogs with weak ESG signals, whereas responses at the optimum level strictly depend on some essential steric properties, which are required by the specific receptor structure (e.g., position of the functional groups within the molecule, chain length of the terminal alkyl group, polarity of the terminal rest, etc.). The triggering of a useful and specific behavioral pattern apparently requires the complete repertoire of constitutional and configurative properties of the natural pheromone structure being highly complementary to the receptor structure.

CONCLUSIONS

Oxime ether analogs **(2, 3)** of the natural pheromone component **(1a)** of the turnip moth interact with the receptor site to a rather reduced degree. Single sensillum recordings support that the recognition of a pheromone structure by the receptor is a flexible adaptation of the pheromone molecule to the receptor site, but, on the other hand, the optimum receptor potential level (possibly corresponding with a specific behavioral pattern) exclusively depends on the occurrence of a molecule with the complete structural properties of the corresponding natural pheromone.

Apparently, several constitutional and configurative properties of the molecule are of special significance to the recognition process. The chain length of the terminal alkyl group, i.e., the position of the unsaturated group within the chain, seems to be one of the essential molecular properties required for an optimal receptor response.

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REFERENCES

ARN, H., STÄDLER, E., RAUSCHER, S., BUSER, H.R., MUSTAPARTA, H., ESBJERG, P., PHILIPSEN, H., ZETHNER, O., STRUBLE, D.L., and BUES, R. 1980. Multicomponent sex pheromone in *Agrotis segetum*: Preliminary analysis and field evaluation. *Z. Naturforsch.* 35c:986–989.

ARN, H., TOTH, M., and PRIESNER, E. 1992. List of sex pheromones of Lepidoptera and related

attractants. Internatl. Org. Biol. Control, West Palearctic Reg. Sec. Working Group: Use of Pheromones and other Semiochemicals in Integrated Control. 180 pp.

BENGTSSON, M., LILJEFORS, T., HANSSON, B.S., LÖFSTEDT, C., and COPAJA, S.V. 1990. Structure–activity relationships for chain-shortened analogs of (*Z*)-5-decenyl acetate, a pheromone component of turnip moth, *Agrotis segetum*. *J. Chem. Ecol.* 16:667–684.

BESTMANN, H.J. 1986. Synthesis, structure activity relationships and mode of action of insect pheromones. A contribution for the transmission of chemical information in nature, pp. 45–64, *in* Natural Product Chemistry. Atta-ur-Rahman (ed.). Springer-Verlag, Berlin.

BESTMANN, H.J., RÖSEL, P., and VOSTROWSKY, O. 1979. Alkylverzweigte Analoga von Lepitopterenpheromonen. *Liebigs Ann. Chem.* 1979:1189–1204.

BESTMANN, H.J., CAI-HONG WU, DÖHLA, B., and LI-KEDONG. 1986. Functional group recognition of pheromone molecules by sensory cells of *Antherea polyphemus* and *Antherea pernyi* (Lepidoptera: Saturniidae). *Z. Naturforsch.* 42c:435–441.

CAMPS, F., COLL, J., FABRIAS, G., GUERRERO, A., and RIBA, M. 1984. Fluorinated analogs of insect sex pheromones. *Experientia* 40:933–934.

GERECS, A., and WINDHOLZ, M. 1958. Synthesen aus Tetrahydrofurylalkohol (I). *Acta Chim. Acad. Sci. Hung.* 14:333–338.

GLACET, C., and GAUMETON, A. 1955. The preparation and properties of 2-butylaminotetrahydropyran and 2-diethylaminotetrahydropyran. *Bull. Soc. Chim. Fr.* 1955:224–243.

HANSSON, B.S., and BAKER, T.C. 1991. Differential adaption rates in a male moth's sex pheromone receptor neurons. *Naturwissenschaften* 78:517–520.

JÖNSSON, S., LILJEFORS, T., and HANSSON, B.S. 1991. Alkyl substitution in terminal chain of (*Z*)-5 decenyl acetate, a pheromone component of turnip moth, *Agrotis segetum*. Synthesis, single-sensillum recordings, and structure–activity relationships. *J. Chem. Ecol.* 17:103–122.

KAISSLING, K.E., and THORSON, J. 1980. Insect olfactory sensilla: Structural, chemical and electrical aspects of the functional organization, pp. 261–282, *in* D.B. Satelle, L.M. Hall, and J.G. Hildebrand (eds.). Receptors for Neurotransmitters, Horomones and Pheromones in Insects. Elsevier/North-Holland Biomedical Press, Amsterdam.

KLEINPETER, E., and BORSDORF, R. 1981. ^{13}C-NMR-Spektroskopie in der organischen Chemie. Akademie-Verlag, Berlin.

LILJEFORS, T., THELIN, B., VAN DER PERS, J.N.C., and LÖFSTEDT, C. 1985. Chain-elongated analogs of a pheromone component of the turnip moth, *Agrotis segetum*. A structure–activity study using molecular mechanics. *J. Chem. Soc. Perkin Trans.* 2:1957–1962.

LILJEFORS, T., BENGTSSON, M., and HANSSON, B.S. 1987. Effects of double-bond configuration on interaction between a moth sex pheromon component and its receptor: A receptor–interaction model based on molecular mechanics. *J. Chem. Ecol.* 13:2023–2040.

POTEKHIN, A.A., and ZHDANOV, S.L. 1979. Ring-chain tautomerism of 2-alkylamino-substituted tetrahydropyrans and tetrahydrofurans. *Chem. Heterocycl. Comp.* 15:1059–1063.

POTEKHIN, A.A., ZHDANOV, S.L., GINDIN, V.A., and OGLUBIN, K.A. 1976. Ring-chain tautomerism of substituted hydrazones (IX). Derivatives of 5-hydroxypentanal and 4-hydroxybutanal. *Zh. Org. Khim.* 12:2090–2094 (Russ.), (*Chem. Abstr.* 86:120734s).

PRESTWICH, G.D., SUN, W.-C., MAYER, M.S., and DICKENS, J.C. 1990. Perfluorinated moth pheromones. Synthesis and electrophysiological activity. *J. Chem. Ecol.* 16:1761–1778.

SUN, W.-C., and PRESTWICH, G.D. 1990. Partially fluorinated analogs of (*Z*)-9-dodecenyl acetate: Probes for pheromone hydrophobicity requirements. *Tetrahedron Lett.* 31:801–804.

SUN, W.-C., NG, C.-S., and PRESTWICH, G.D. 1992. Synthesis of partially fluorinated analogues of (*Z*)-5-decenyl acetate: Probes for hydrophobic interaction in pheromone reception, *J. Org. Chem.* 57:132–137.

ZEEH, B. and METZGER, H. 1971. Methoden zur Herstellung und Umwandlung von Hydroxylaminen. pp. 1091–1279, *in* Methoden Org. Chem. (Houben-Weyl), 4th ed. vol. 10/1:1195.