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Dienic Analogs of (*Z*)-5-Decenyl Acetate, a Pheromone Component of the Turnip Moth, *Agrotis segetum:* Synthesis, Conformational Analysis and Structure–Activity Relationships

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Structure–activity relationships for (*Z*, *E*)-dienic analogs of (*Z*)-5-decenyl acetate, a pheromone component of the turnip moth, *Agrotis segetum*, have been studied by electrophysiological single-cell recordings and molecular mechanics calculations. The biological activities of the dienic analogs are highly sensitive to the position of the additional (*E*) double bond. The experimental observations are well rationalized by the use of a receptor-interaction model in which the biological activity is determined by conformational energies required to mimic spatial relationships in the natural pheromone component. A biologically active conformation for this compound is suggested.

INTRODUCTION

Noctuid moths generally use (*Z*)-monounsaturated acetates or alcohols as sexual pheromone components (*1*). The male moth perceives the pheromone blend produced by the female moth by highly specialized olfactory receptor cells in antennal sensilla.

Although it has been shown that the receptors are very selective for a certain component in the pheromone blend, it has in a few cases been found that analogs may substitute for the natural pheromone component. During field studies, Chisholm *et al.* (*2*) observed that three moth species which use monoolefinic acetates and alcohols as sexual pheromone components were attracted to pheromone blends in which a monoolefinic component was replaced by a diolefinic analog with an additional double bond with (*E*) configuration in the $i + 3$ position (i is the position of the (*Z*) double bond in the natural component and in the dienes). Analogs with the double bond in the $i + 4$ position showed some attractancy but if the additional double bond was placed in the $i + 2$, $i - 2$, $i - 3$, or $i - 5$ position, the attractancy of the pheromone blend was essentially lost. A similar effect was observed by Priesner *et al.* in an electroantennographic (EAG) screening of the antennal response of several species of *Noctuidae* (*3*).

Recordings from single receptor cells is the method of choice for studies on

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structure–activity relationships of pheromone components. However, very few studies on moth single cell responses to a variety of monoenic and dienic acetates have been reported. The sexual pheromone of the tortricid moth *Adoxophyes orana* is a blend of (*Z*)-9- and (*Z*)-11-tetradecenyl acetate and (*Z*)-9-tetradecenol. Upon stimulation of a male antennal receptor cell selective for (*Z*)-9-tetradecenyl acetate with diolefinic compounds containing an additional (*E*) double bond in the $i + 2$ or $i + 3$ position, the activities observed were 100 and 10 times less, respectively, than that obtained on stimulation with (*Z*)-9-tetradecenyl acetate. The $E(i - 2)$ analog was shown to have about one-thirtieth of the activity of (*Z*)-11-tetradecenyl acetate when receptor cells specific for this compound were stimulated (*4*). Thus, from field tests and EAG- and single-cell investigations on various moth species, a consistent picture emerges, which indicates that at least the diolefinic analog with $E(i + 3)$ double-bond positions and configurations has a biological activity of the same magnitude as the natural $Z(i)$ component.

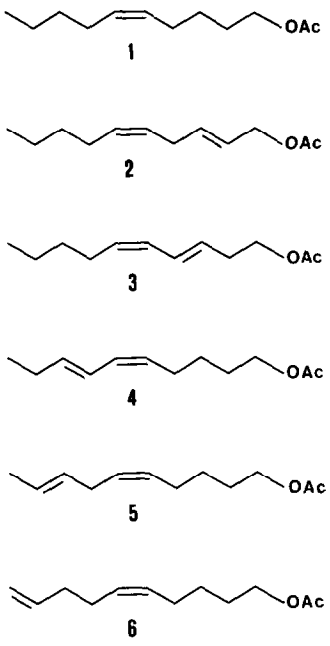
Recently we described a quantitative model for the interaction between a pheromone component and its receptor (*5, 6*). The model uses conformational energies calculated by the molecular mechanics method to rationalize observed electrophysiological single-cell activities of pheromone component analogs. A direct correlation between calculated conformational energies required to mimic spatial relationships of the natural pheromone component and measured activities was obtained. The model has successfully been applied to chain-elongated analogs and to configurational isomers (*5, 6*).

The purpose of the study presented in this paper is to apply our receptor-interaction model to dienic analogs and to investigate if the conformational energies of analogs with an additional (*E*) double bond in different positions and conformationally rearranged to mimic geometrical features of the natural pheromone component are correlated with observed biological activities. Furthermore, by replacing a CH_2–CH_2 unit by an (*E*) double bond, an *anti* conformation is simulated about that bond. Electrophysiological measurements and structure–activity analysis may reveal if this is the biologically active conformation of that part of the alkyl chains in the natural pheromone component molecule.

We report the synthesis, electrophysiological single-cell recordings, and conformational analysis of analogs of (*Z*)-5-decenylacetate **1**, a pheromone component of the turnip moth, *Agrotis segetum* (*7*). The compounds studied are shown in Scheme 1. The results of the electrophysiological measurements are compared with conformational energies calculated by the molecular mechanics method using the MM2 and MMP2 programs (*8, 9*).

MATERIALS AND METHODS

Chemicals. The products were purified by preparative GLC (column OV 351, 6 m). When necessary, further purification was carried out by argentation liquid chromatography (*10*). All final products were at least 98.5% isomerically pure, as determined by capillary GLC analysis (column Supelcowax, 30 m). Mass spectra were recorded on a Finnigan 4021 mass spectrometer, and ^1H and ^{13}C NMR

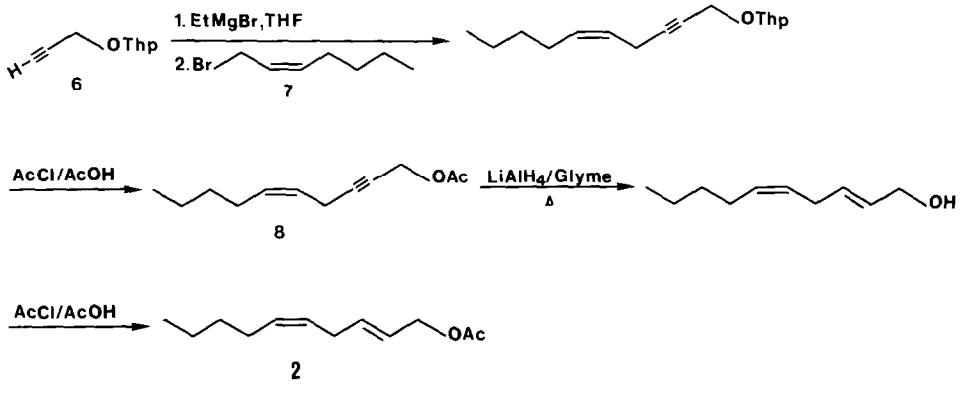


SCHEME 1.

spectra were recorded on a Varian XL-300, a Nicolet 360 WB, or a Jeol FX-60 spectrometer. NMR spectra were recorded on $CDCl_3$ solutions with Me_4Si as internal reference. The configurations of the double bonds were confirmed using ^1H NMR coupling constants and ^{13}C chemical shifts for the vinylic carbon atoms (*11, 12*). The ^{13}C signal for the carbonyl carbon in compounds **3**, **5**, and **6** was of too low intensity to be unambiguously identified.

(*Z*)-5-decenyl acetate **1** was prepared as previously described (*13*).

(*E*)-2, (*Z*)-5-Decadienyl acetate **2** was prepared as outlined in Scheme 2. The Grignard reagent prepared from 1-(2-tetrahydropyranyloxy)-2-propyne (1.8 g, 0.013 mol), ethyl bromide (1.7 g, 0.015 mol), and magnesium (0.3 g, 0.014 mol) in

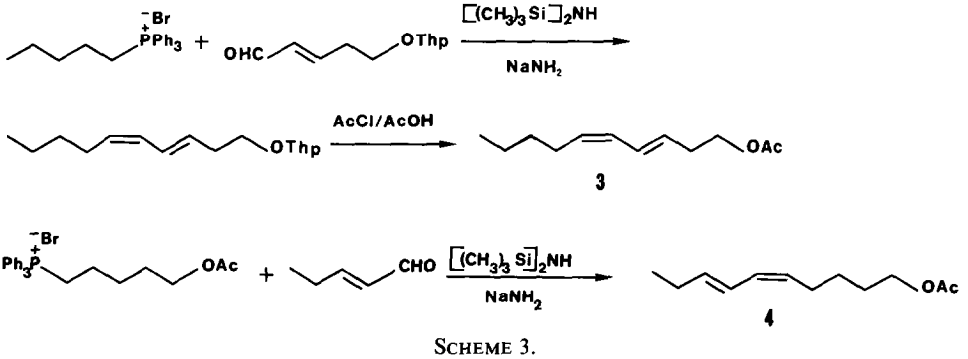


SCHEME 2.

anhydrous tetrahydrofuran (THF) was reacted with (*Z*)-2-heptenyl bromide **7** (2.3 g, 0.018 mol) in the presence of cuprous bromide (0.11 g, 0.008 mol) (*14*). Acetylation of the reaction product with acetyl chloride (excess) in acetic acid gave the enyne acetate **8**. Reduction with $LiAlH_4$ in boiling dry glyme, followed by reacetylation, gave the final product (2.0 g, 77%). The Grignard coupling step gave a 4 : 1 mixture of (*Z*)- and (*E*)-enyne. Pure **2** was obtained by argentation liquid chromatography (*10*). δ_H (300 MHz) 0.89 (3H, t, Me), 1.30–1.36 (4H, m, CH_2CH_2), 1.98–2.07 (2H, m, $CH_2C{=}$), 2.06 (3H, s, MeC=O), 2.78–2.83 (2H, m, $=CCH_2C{=}$), 4.52 (2H, dd, OCH_2), 5.31–5.52 (2H, m, J_{AB} 10.7 Hz, CH=CH), 5.53–5.65 (1H, m, J_{AB} 15.2 Hz, CH=CH), 5.71–5.82 (1H, m, J_{AB} 15.2 Hz, CH=CH), δ_C (75.4 MHz) 14.0, 21.0, 22.3, 26.9, 30.0, 31.8, 65.2, 124.0, 126.0, 131.6, 134.6, 170.9, *m/e* 136 (M^+-60, 8%), 107 (2), 93 (9), 79 (42), 70 (3), 67 (12), 55 (13), 43 (100).

(*E*)-3, (*Z*)-5-Decadienyl acetate **3** and (*Z*)-5, (*E*)-7-decadienyl acetate **4** were synthesized via a (*Z*)-stereoselective Wittig reaction as described by Bestmann *et al.* (*15*). Sodium bis(trimethylsilyl)amide (*16*) was used to prepare the lithium-salt-free ylide solution from the triphenylphosphonium salt (Scheme 3). The ylide solutions were cooled to −78°C and the appropriate aldehyde was added. The products obtained were of excellent stereochemical purity. However, the yields in the coupling step were quite low.

Compound **3** was prepared from pentyltriphenylphosphonium bromide (22.3 g, 0.054 mol), hexamethyldisilazane (7.9 g, 0.054 mol), $NaNH_2$ (4.2 g, 0.07 mol as a 50% suspension in toluene), and 5-(2-tetrahydropyranyloxy)-(*E*)-2-pentenal in anhydrous THF. The aldehyde was generated from the corresponding (*Z*)-2-pentanol (9.7 g, 0.054 mol) and pyridinium–chlorochromate (17.5 g, 0.081 mol) in dry dichloromethane (*17*) and the raw product was used in the subsequent step. The yield of protected **3** after flash chromatography was 4.5 g (36%). Acetylation with acetyl chloride (excess) in acetic acid gave **3**. δ_H (360 MHz) 1.02 (3H, t, Me), 1.40–1.50 (2H, m, CH_2Me), 1.60–1.70 (2H, m, CH_2CH_2), 2.04 (3H, s, MeC=O), 2.08–2.26 (4H, m, $CH_2C{=}$), 4.07 (2H, t, OCH_2), 5.23–5.32 (1H, m, J_{AB} 10.9 Hz, CH=CH), 5.66–5.76 (1H, m, J_{AB} 14.6 Hz, CH=CH), 5.93–6.01 (1H, m, J_{AB} 10.9 Hz, CH=CH), 6.23–6.33 (1H, m, J_{AB} 14.6 Hz, CH=CH), δ_C (15.03 MHz) 13.9, 20.9, 22.2, 27.4, 31.8, 32.1, 63.7, 128.0, 128.0, 128.6, 131.4, *m/e* 136 (M^+-60, 8%), 107 (2), 93 (14), 79 (48), 67 (17), 55 (5), 43 (100).

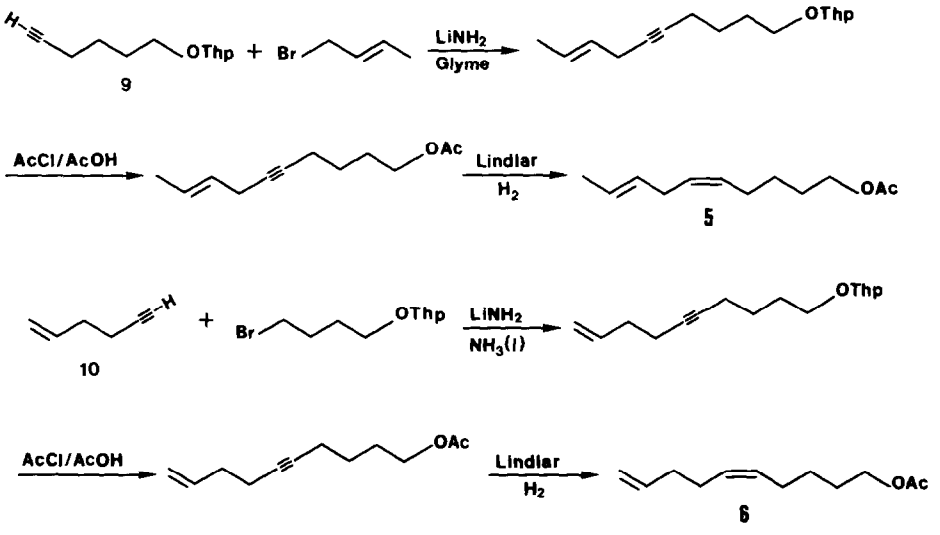


SCHEME 3.

Compound **4** was prepared from 5-acetoxy-pentyltriphenylphosphonium bromide (14.0 g, 0.03 mol), hexamethyldisilazane (4.8 g, 0.03 mol), $NaNH_2$ (2.3 g, 0.03 mol; 50% suspension in toluene), and (*E*)-2-pentenal (2.5 g, 0.03 mol) in anhydrous THF (yield, 22%). δ_H (360 MHz) 0.84 (3H, t, Me), 1.20–1.35 (4H, m, CH_2CH_2), 1.98 (3H, s, MeC=O), 2.06–2.13 (2H, m, CH_2C=), 2.32–2.40 (2H, m, CH_2C=), 4.04 (2H, t, OCH_2), 5.25–5.34 (1H, m, J_{AB} 10.9 Hz, C*H*=CH), 5.48–5.58 (1H, m, J_{AB} 15.4 Hz, C*H*=CH), 5.83–5.92 (1H, m, J_{AB} 10.9 Hz, CH=C*H*), 6.27–6.37 (1H, m, J_{AB} 15.4 Hz, CH=C*H*), δ_C (91.0 MHz) 13.6, 21.0, 25.9, 26.0, 27.2, 28.2, 64.4, 124.4, 129.0, 129.2, 136.6, 171.1, *m/e* 196 (M^+, 1%), 136 (9), 121 (4), 108 (19), 107 (19), 93 (29), 79 (100), 67 (50), 61 (1), 55 (40), 45 (1).

(*Z*)-5, (*E*)-8-Decadienyl acetate **5** and (*Z*)-5,9-decadienyl acetate **6** were synthesized via coupling of a lithium alkylacetylide with the appropriate bromo compound as shown in Scheme 4. When using a protected alkynol **9** it was necessary to use boiling glyme to overcome solubility problems (*2*), but with a simple alkyne **10** it was sufficient to use liquid ammonia (*18*). After the coupling reaction and subsequent acetylation, the triple bond was reduced with Lindlar catalyst and the products **5** and **6** were obtained in good yields and were of high stereochemical purity. Compound **5** was prepared from 5-(2-tetrahydropyranyloxy)-1-hexyne (1.8 g, 0.01 mol), $LiNH_2$ (0.3 g, 0.01 mol) and 1-bromo-2-butene (1.2 g, 0.009 mol) in dry glyme (yield, 1.7 g (88%)). δ_H (360 MHz) 1.30–1.40 (2H, m, CH_2CH_2), 1.50–1.62 (2H, m, CH_2CH_2), 1.58 (3H, d, Me), 1.98 (3H, s, MeC=O), 1.98–2.05 (2H, m, CH_2C=), 2.62–2.68 (2H, m, =CCH_2C=), 3.99 (2H, t, OCH_2), 5.27–5.38 (2H, m, J_{AB} 11 Hz, CH=CH), 5.30–5.42 (2H, m, J_{AB} 15.5 Hz, CH=CH), δ_c (15.03 MHz) 17.9, 20.9, 25.9, 26.6, 28.2, 30.4, 64.4, 125.1, 128.2, 129.5, 129.5, *m/e* 196 (M^+, 0.5%), 136 (27), 121 (16), 107 (32), 93 (46), 79 (100), 68 (81), 61 (5), 55 (56), 45 (2).

Compound **6** was prepared from 1-hexen-5-yne (0.4 g, 5 mmol), $LiNH_2$ (0.1 g, 5



SCHEME 4.

mmol) and 4-(2-tetrahydropyranyloxy)-1-bromobutane (0.7 g, 3 mmol) in liquid ammonia with dry ether as cosolvent (yield, 0.6 g (95%)). δ_H (360 MHz) 1.36–1.46 (2H, m, CH_2CH_2), 1.59–1.69 (2H, m, CH_2CH_2), 2.04 (3H, s, MeC=O), 2.03–2.14 (6H, m, CH_2C=), 4.06 (2H, t, OCH_2), 4.93–5.06 (2H, m, =CH_2), 5.32–5.42 (2H, m, J_{AB} 11 Hz, CH=CH), 5.75–5.88 (1H, m, CH=CH_2), δ_C (15.03 MHz) 20.9, 25.8, 26.6, 28.1, 33.7, 64.4, 114.4, 129.4, 129.4, 138.2, *m/e* 196 (M^+, 0.5%), 136 (2), 121 (2), 108 (3), 95 (17), 79 (14), 67 (47), 61 (2), 55 (17), 43 (100).

Molecular mechanics calculations. Energy-minimized geometries and conformational energies were calculated using the molecular mechanics programs MM2 and MMP2 developed by Allinger *et al.* (*8, 9*). Starting structures for the energy-minimization program were constructed using the MOLBUILD module of the molecular modeling system MIMIC (*19*). This system was also used for the superimposition studies.

Electrophysiology. The biological activities of compounds **1–6** were determined by measuring the electrical responses of (*Z*)-5-decenyl acetate **1** receptors on male *Agrotis segetum* antenna. Olfactory receptor cells specifically tuned to compound **1** are present in antennal sensilla type SW1 and are readily accessible for single-cell recordings (*7, 20, 21*). The recording procedure has previously been described (*6*).

THE SUBSTRATE–RECEPTOR INTERACTION MODEL

The details of our substrate–receptor interaction model have previously been reported (*5, 6*), and thus only the main features will be described here. The model assumes geometrically well-defined receptor sites complementary to the terminal methyl group, the (*Z*) double bond, and the acetate group of the natural substrate **1**. An analog may achieve biological activity by a change of its conformation in order to place the corresponding molecular parts in the required positions in space. The concomitant increase of the conformational energy may be interpreted in terms of the probability for the compound to mimic the decisive structural relationships of the natural compound. This energy should according to our model be a measure of the biological activity; a small conformational energy should correspond to a high biological (electrophysiological) activity and vice versa.

(*Z*)-5-Decenyl acetate **1**, the natural substrate for the receptor studied in this work, can exist in three low-energy conformations with all-*anti* alkyl chains (*6*). Two of these conformers have a *cisoid* arrangement of the alkyl chains and one has a *transoid* arrangement (Fig. 1). We assume that one of these conformers corresponds to the "biologically active conformation" of compound **1**. Since we cannot a priori select one of the conformers as the biologically active one, the following investigation was made for all three possibilities denoted the *cisoid 1*, *cisoid 2*, and *transoid* models, respectively, according to Fig. 1.

The five diene analogs **2–6** were rearranged into conformations that had the crucial molecular parts, as described above, in the same positions in space as those of compound **1**. This was done for each of the three conformers of **1** and was

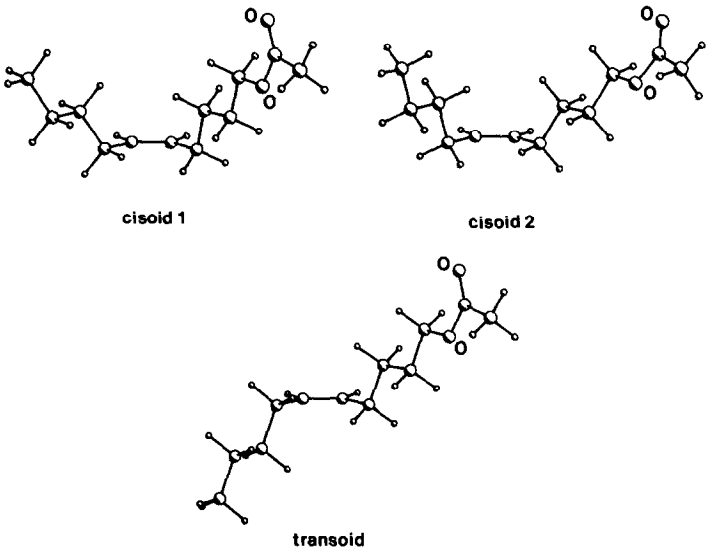


FIG. 1. Energy-minimized geometries of the *cisoid* and *transoid* conformers of (Z)-5-decenyl acetate **1** with alkyl chains in an all-*anti* arrangement.

accomplished by the use of molecular graphics modeling. In the subsequent calculations the positions of the encircled atoms in Fig. 2 were held fixed during the molecular mechanics energy minimization of the molecules. The two olefinic and the two vinylic carbons were allowed to move in the plane defined by the corresponding parts in compound **1**. The remaining alkyl chain atoms and other nonrestricted atoms were allowed to find positions that minimize the total energy of the molecule. Several conformationally rearranged structures for each compound were used as trial structures, and in each case the structure with the lowest energy after energy minimization was selected as the most probable "biologically active conformation" of the dienic analog.

In a second series of calculations, the energy of the thermodynamically most stable conformer of each of the compounds **2–6** was calculated. In order to find the conformation with the lowest energy, an extensive conformational analysis was carried out for all dienes. The biological activity of each of the dienes was then compared to the calculated conformational energy difference between the thermodynamically most stable conformation and the lowest energy, conformationally rearranged structure which fits the geometrical requirements of the

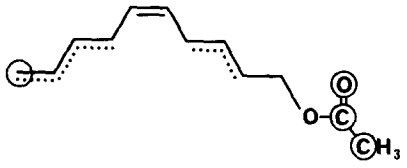


FIG. 2. Atoms (circled) held in fixed positions in the molecular mechanics calculations of structures and energies of biologically active conformations of **2–6**. Dotted lines indicate the different positions of the (*E*) double bond.

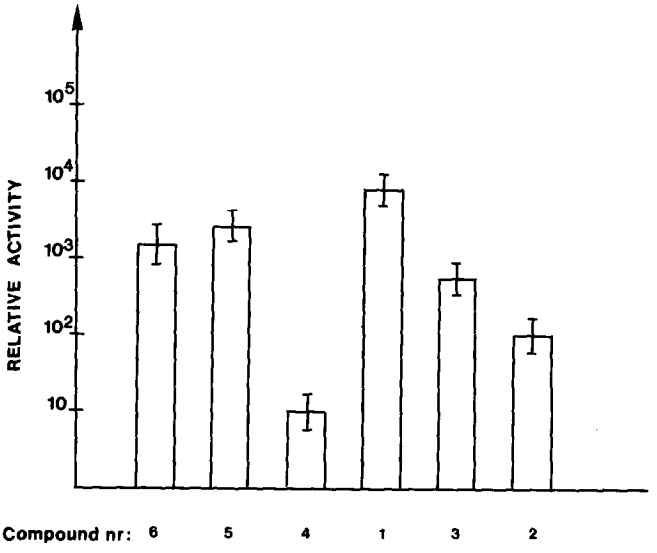


FIG. 3. Experimental electrophysiological single-cell activities for compounds **1–6**.

model. Thus, three sets of conformational energies for compounds **2–6** were calculated, corresponding to the energies required for these compounds to mimic each of the three conformers of the natural compound **1** shown in Fig. 1.

RESULTS AND DISCUSSION

Receptor cell responses. The measured electrophysiological single-cell activities of compounds **2–6** relative to the natural pheromone component **1** are shown in Fig. 3. The replacement of a CH_2–CH_2 unit by an (*E*) double bond in any of the investigated positions around the (*Z*) double bond of **1** results in a decrease in the biological activity. However, depending on the position of the introduced additional double bond, this decrease in activity differs significantly. It is of particular interest to note that the movement of the (*E*) double bond the same number of steps in the two possible directions with respect to the (*Z*) double bond causes very different changes in the observed activity. While the (*E*)-3,(*Z*)-5 diene **3** has almost 100 times *higher* activity than the (*Z*)-5, (*E*)-7 analog **4**, the (*E*)-2, (*Z*)-5 diene **2** has about 50 times *lower* activity than the (*Z*)-5, (*E*)-8 diene **5**. This is in line with field trapping results obtained by Chisholm *et al.* (*2*).

Bestmann and Vostrowsky (*22*) conclude from extensive EAG investigations of noctuid moths that structural variations of the alkyl parts of a pheromone component produce a more drastic loss of activity if the end alkyl part (the $(CH_2)_n$ part) is varied than if the equivalent changes are made in the $(CH_2)_m$ part (Scheme 5).

SCHEME 5.

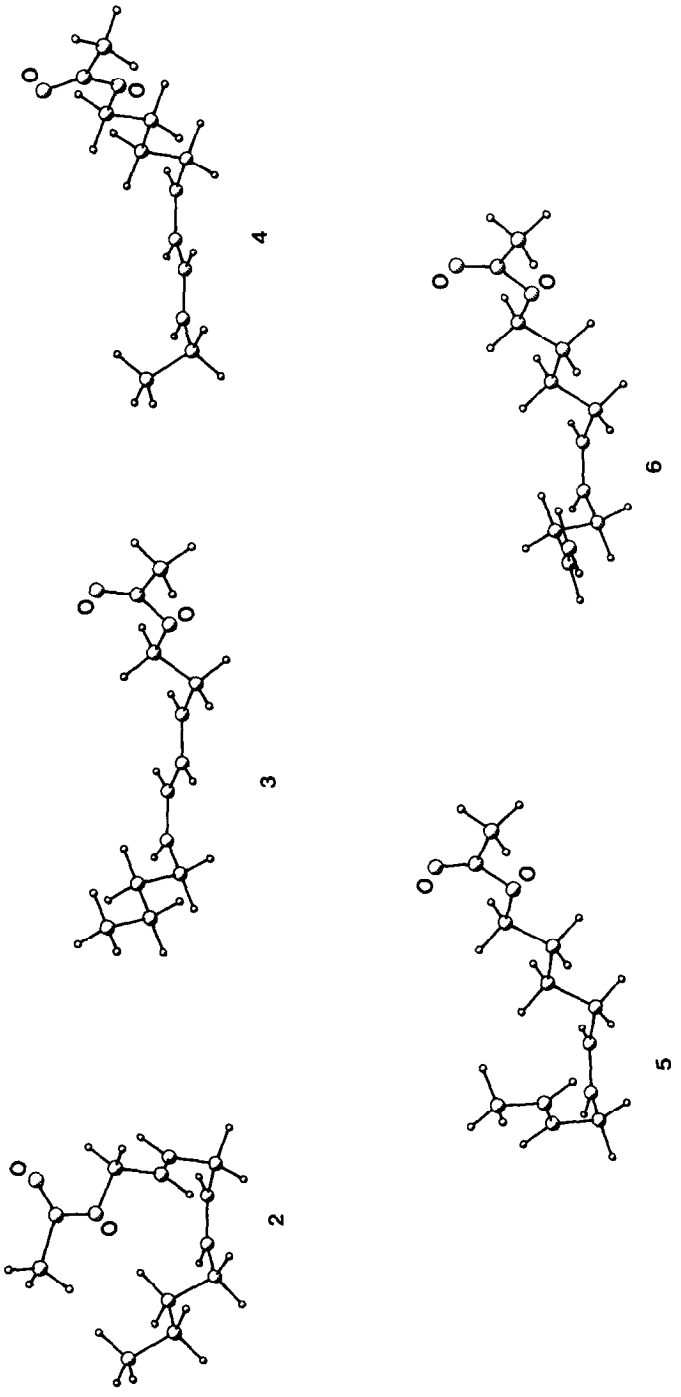


FIG. 4. Calculated lowest energy conformers for compounds **2–6**.

This "structure–activity rule" is not in agreement with the results in Fig. 3. We find that the loss of activity due to the (*E*) double bond in one case is more drastic for the $(CH_2)_n$ part (compounds **3** and **4**) but less drastic in another case (compounds **2** and **5**).

Calculated structures and conformational energies. The calculated thermodynamically most stable conformers of the dienes **2–6** are shown in Fig. 4. In all cases the alkyl chains prefer a *cisoid* arrangement, but there are several other conformers, both *cisoid* and *transoid*, within 1 kcal/mol above the energy of the most stable conformer.

The calculated difference in conformational energy between the lowest energy structure suitable for receptor interaction according to our model and the global energy minima are given in Table 1 for each of the diene analogs **2–6** and for each of the three models of the biologically active conformation of **1**, according to Fig. 1. On comparing the results in Table 1, the most striking feature is the great difference in the calculated energies for the two conjugated dienes **3** and **4** with respect to the *cisoid 1* and *cisoid 2* models. Only for the *cisoid 2* model is there a correspondence between the calculated conformational energy for the biologically active conformation and the observed electrophysiological activity.

The calculated conformational energies assuming the *cisoid 2* model are summarized in Fig. 5. A comparison of Figs. 3 and 5 clearly shows that there is a close correlation between calculated conformational energies using this model and the observed activities.

The calculated conformational energies correspond to enthalpies. However, since the translational, rotational, and conformational entropies should be very

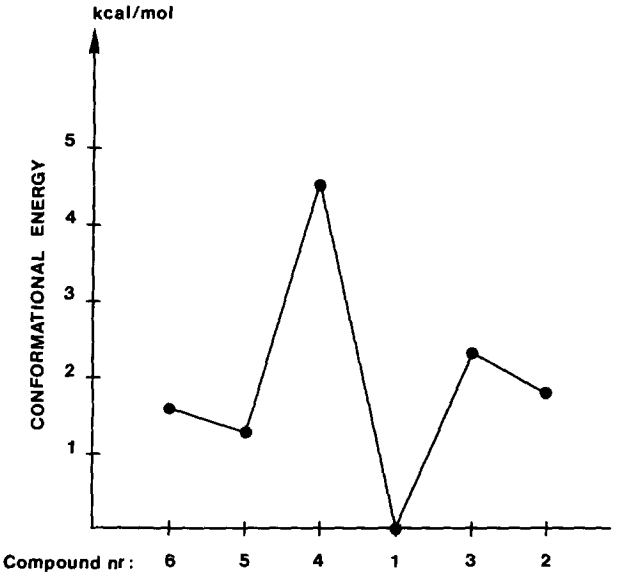
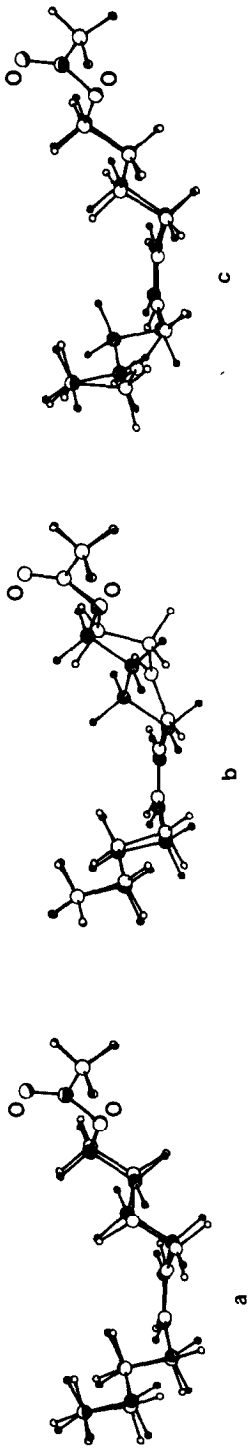


FIG. 5. Calculated conformational energies (*cisoid 2* model) for the biologically active conformations of **1–6**.



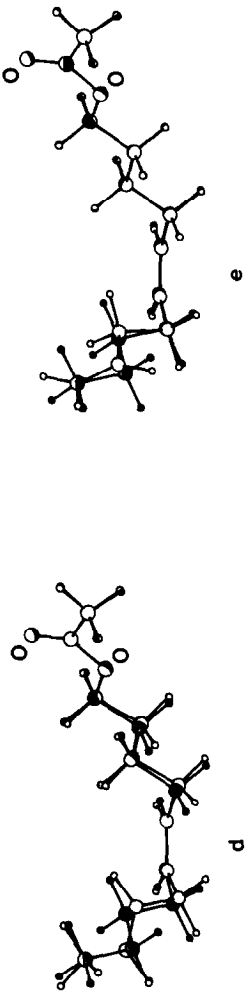


FIG. 6. Molecular superimpositions of the *cisoid 2* conformer of compound 1 (filled atoms) and the calculated biologically active conformations of (a) **2**, (b) **3**, (c) **4**, (d) **5**, and (e) **6**.

TABLE 1

Calculated Differences in Conformational Energy between the Biologically Active Conformations and the Lowest-Energy Conformers of Compounds **2–6**

Compound	Relative energy in kcal/mol		
	Cisoid 1	Cisoid 2	Transoid
2	2.9	1.8	1.9
3	4.6	2.3	4.2
4	2.2	4.5	4.9
5	1.0	1.3	1.1
6	0.8	1.6	1.6

similar for compounds **2–6**, the calculated energies may be treated as free energies and may thus be directly used in comparisons with the experimental data. Superimpositions of compound **1** in the *cisoid 2* conformation (Fig. 1) and the calculated biologically active structures of compounds **2–6** are shown in Fig. 6.

Since the replacement of a CH_2–CH_2 unit with an (*E*) double bond in a carbon chain simulates an *anti* conformation about that bond, this study strongly indicates that the all-*anti* conformation of (*Z*)-5-decenyl acetate **1** is the biologically active conformation. For bond positions 3 and 8 this may be inferred directly from the experimental data shown in Fig. 3, considering the high activities of compounds **3** and **5**. The close correlation between conformational energy and observed electrophysiological activity assuming all-*anti* alkyl chains in **1** makes it

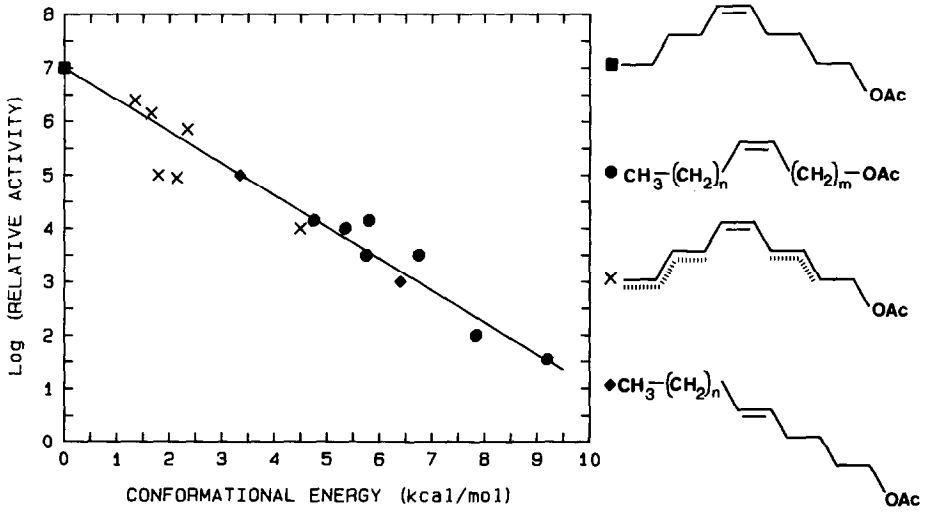


FIG. 7. Relationship between calculated conformational energies needed to structurally mimic the *cisoid 2* conformer of the natural pheromone component **1** and observed relative single-cell electrophysiological activities.

highly probable that also bonds 2 and 7 have *anti* conformations in the biologically active structure of **1**.

In our previous structure–activity studies on chain-elongated analogs and double-bond configurational isomers of **1**, we found that there is a fairly constant conformational energy increase, 1.7 kcal/mol, corresponding to a 10-fold decrease of the observed electrophysiological activity (*6*). For the dienes **3–6** the corresponding number is calculated to be 1.9 ± 0.4 kcal/mol. Thus, for 15 analogs of **1** belonging to three different structural classes there is a good linear relationship between calculated conformational energies and experimental activities. This relationship is shown in Fig. 7. The correlation coefficient for the regression line is 0.965. This correlation suggests that the *cisoid 2* conformer (Fig. 1) or a conformation close to it may be the biologically active one for the natural pheromone component **1**.

SUMMARY AND CONCLUSIONS

The electrophysiological single-cell activities of the dienic analogs **2–6** of the natural pheromone component **1** are highly sensitive to the position of the (*E*) double bond. For instance, the two possible conjugated dienes **3** and **4** differ in activity by about a factor of 100.

The receptor-interaction model used in the present work satisfactorily rationalizes the experimental observations. The observed differences in biological (electrophysiological) activity seems to be determined by the conformational energies required to mimic spatial relationships in the natural pheromone component, assumed to be critical for a productive receptor interaction. Of the three different low-energy conformers of **1** employed as possible biologically active conformations, only one is fully compatible with experimental data. This conformer (*cisoid 2*) or a conformation close to it is suggested to be the biologically active conformer for compound **1**.

Furthermore, the results obtained strongly indicate that the biologically active conformation of the alkyl chains in **1** is all *anti*.

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