

Sex Pheromones of the Cereal Pest *Eurygaster integriceps* Puton (Heteroptera: Scutelleridae)- A Theoretical study

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Abstract: AM1-type molecular orbital calculations were performed on the geometry-optimized structures of various 4-(1', 5' - dimethyl -4' - heptenylidene) -1- methylcyclohexene isomers. It was found that the major component (4Z, 4'E isomer) of the sex pheromone of *Eurygaster integriceps* is very dissimilar in chemical composition to the other isomers, although the stabilities and heats of the formation characteristics are comparable. However, some small molecules resembling only a part of the pheromone might exhibit some partial activity.

Key Words: *Eurygaster integriceps*, Heteroptera, cereal pest Scutelleridae, pheromone, molecular orbital calculations.

Hububat güvesi. *Eurygaster integriceps* Puton'un (Heteroptera Scutelleridae) seks feromonları-Teorik bir çalışma

Özet: Geometri optimize edilmiş çeşitli 4-(1' , 5'-dimethyl-4'-hepteniliden)-1-metilsikloheksen izomerleri üzerinde AM1 tipi moleküler yörünge hesapları yapılmıştır. Dayanıklılık ve oluşum ısıları yönünden mukayese edilebilir olmalarına rağmen *Eurygaster integriceps* seks feromonunun ana elemanının (4Z, 4'E izomeri) diğer izomerlerden çok farklı olduğu bulunmuştur. Mamafih, feromonunun sadece bir kısmına benzeyen bazı ufak moleküller kısmi bir aktivite gösterebilirler.

Anahtar Sözcükler: *Eurygaster integriceps*, Heteroptera, hububat güvesi. Scutelleridae. feromon. moleküler yörünge hesapları.

Introduction

In several countries, especially in the Middle and Near East, where substantial amounts of wheat and cereals are harvested, the Sunn bug *Eurygaster integriceps* is a major pest which causes a great deal of problems (1, 2). The experiments reported by Likvenkov have indicated that mature males of *Eurygaster integriceps* signal to females by producing a volatile sexual attractant (3). Ubik et al. have presented evidence that the strong adorus substance resembling vanillin which is emitted by calling males is indeed vanillin (4). It is produced and released by males only during the period of sexual activity. Vrkoc et al. subsequently isolated and identified

ethyl acrylate as another component of the male pheromone and reported that the stimulatory effect of a mixture of vanillin and ethyl acrylate on receptive females was greater than that of either compound tested alone (5). Much later on, Staddon et al. (6) isolated and identified a homosesquiterpenoid. (4Z, 4'E) -4- (1', 5' - dimethyl - 4' - heptenylidene) -1-methylcyclohexene, as a major component of the scent emitted by the calling males of *Eurygaster integriceps*. Thus, an additional sesquiterpenoid substance was identified as a compound of male-attractant sex pheromones in pentatomoid Heteroptera (6-9). Some other sesquiterpenoids have also been detected as minor components in the scent of *Eurygaster integriceps* males (6).

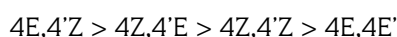
In this study, some isomers of the major component (4Z, 4'E) -4- (1', 5' - dimethyl - 4'-heptenylidene) -1-methylcyclohexene were tested in terms of similarity relationship in order to investigate the theoretical bases of whether the other isomers may exhibit any pheromonic activity with respect to receptive females of *Eurygaster integriceps*.

The geometry optimizations and molecular orbital calculations of this study were carried out using the AM1 (Austin Model-1 (10)) method at the restricted Hartree-Fock (RHF) level and a conjugate gradient minimization (Polak-Ribiere) approach was used to obtain the optimized geometries. The conformational analysis of the molecules was performed using the method of molecular mechanics on the already geometry-optimized structures, followed by reoptimization (AM1 method), resulting in global minima. All these calculations were carried out using the Hyperchem (release 4) and ChemPlus 1.5 programs (11).

Results and Discussion

The homosesquiterpenoid sex pheromone of *Eurygaster integriceps* and its three configurational isomers are shown in Figure 1. Of these four geometry-optimized γ -bisabulens derivatives, the 4Z, 4'E form is the sex pheromone. Table 1 shows the total energies and heats of formation values of these isomers calculated via AM1-type molecular orbital calculations.

As can be seen from the table, the stabilities of the isomers are in the order:



However the 4E,4'Z form is the most exothermic as is implied by the heats of formation data. Hence, the pheromone (4Z,4'E isomer), although none of the four are very different from each other, is not the most stable according to AM1-type semi-empirical molecular orbital calculations.

Isomer	Total En.	Heats of formation
4Z,4'E	-55519.5285	-19.5500
4E, 4'Z	-55519.6795	-19.7010
4E, 4'E	-55519.2877	-19.3093
4Z, 4'Z	-55519.4984	-19.5199

Table 1. The total energies and heats of formation of various isomers of 4-(1',5'-dimethyl-4'-heptenylidene)-1-methylcyclohexene. Energies in kcal/mol.

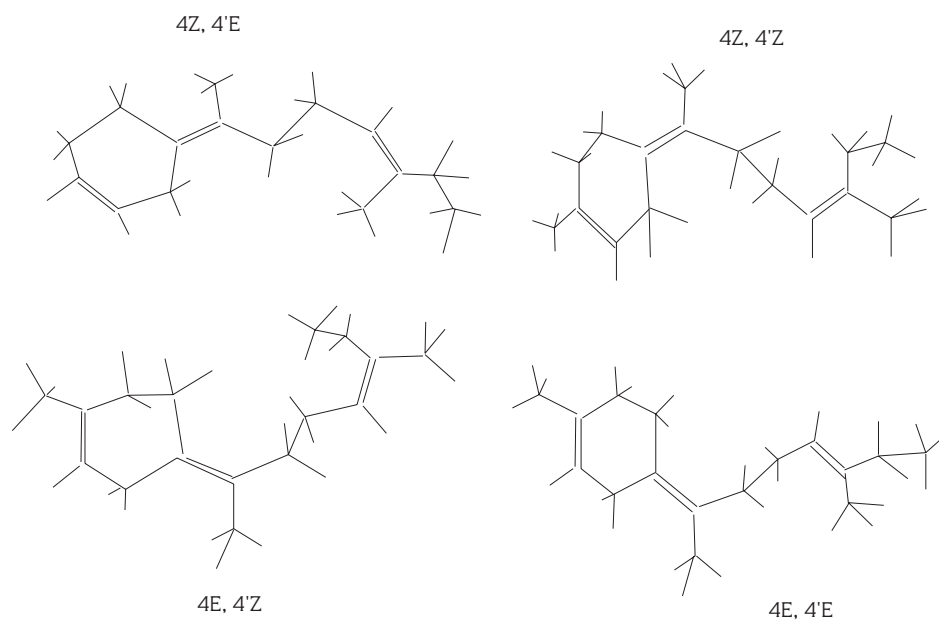
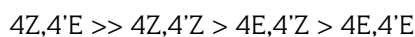


Figure 1. Various configurational isomers of 4-(1', 5'-dimethyl-4'-heptenyldene)-1-methylcyclohexene.

Table 2 shows the root-mean-square (RMS) overlay values of the isomers based on the 4Z,4'E form as the reference structure. RMS values inversely reflect the degree of similarity between two structures. As can be seen, the similarity order of the isomers, is as follows:



Thus, theoretically, the 4Z,4'E form, which exhibits pheromonic activity, should be highly dissimilar to the other isomers. In other words, the other isomers are not expected to exhibit any pheromone-like characteristics.

Inspection of the similarity data (Table 2) of the 4Z,4'E and 4E,4'E, and 4Z,4'E and 4Z,4'Z pairs reveals that configurational changes in the vicinity of the exocyclic double bond are more effective than the 4' double bond.

Isomer	RMS
4Z, 4'E	0
4E, 4'Z	4.4035
4E, 4'E	4.5779
4Z, 4'Z	4.3678

Table 2. The RMS overlay values of various isomers of 4-(1', 5'-dimethyl-4'-heptenyldene)-1-methylcyclohexene. Values in Å²

On the other hand the pheromonic activities of vanillin and ethyl acrylate are interesting. These substances either trigger the attraction response via completely different biochemical mechanisms or, more probably, they mimic structurally certain regions of the true pheromone, the 4Z,4'E isomer. Figures 2 and 3 show different RMS overlay fit positions on the pheromone for vanillin and ethyl acrylate, respectively. As can be seen, the RMS values imply effective regional fits for the above-mentioned small molecules. Therefore, it is very probable that in the biological system, on the receptor site for the 4Z,4'E isomer two or three regions exist, which more or less fit vanillin or ethyl acrylate, causing short-distance attraction in sexually receptive females, as observed by Vrkoc et al. (5). These authors further showed that the stimulatory activity of a mixture of (1:1) vanillin and ethyl acrylate was greater than the activities of these compounds tested separately. An explanation for this observation now becomes clear in the light

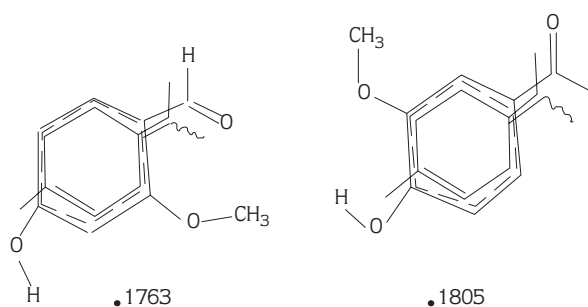


Figure 2. RMS data resulting from different overlay patterns of the pheromone and vanillin.

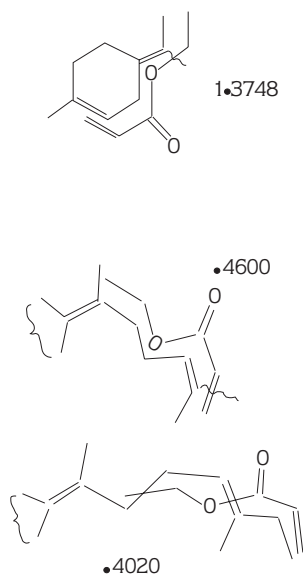


Figure 3. RMS data obtained from various overlay possibilities of ethyl acrylate on the pheromone.

of the theoretical similarity analysis presented in this paper. In the case of a 1:1 mixture, the receptor site for the pheromone is blocked simultaneously by vanillin and ethyl acrylate in such a way that the net effect is similar to that of a single molecule similar to the pheromone involved. Figure 4 illustrates a plausible overlay of vanillin and ethyl acrylate on the 4Z,4'E isomer obtained through RMS overlay analysis.

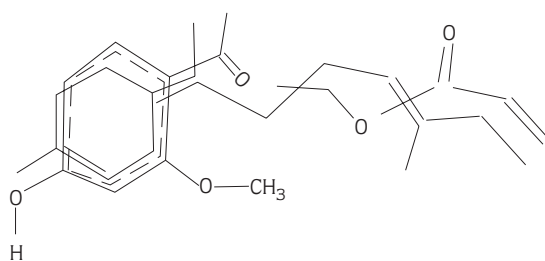


Figure 4. A possible overlay of vanillin and ethyl acrylate on the pheromone.

Conclusion

This theoretical study implies that pheromonic activity initiated by other chemicals requires either resemblance to the ring or the side-chain moieties of the true pheromone, the 4Z,4'E isomer. Each part individually exhibits some activity but the combined effects are more pronounced. In contrast, the configurational isomers of the pheromone are expected to be inactive.

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