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A Theoretical study on the Sex-pheromones of the Rice Moth, *Corcyra cephalonica* Stainton

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Abstract: Molecular orbital calculations (AM1 type) were performed on the geometry optimized structures of various farnesal isomers and methyl esters of farnesoic acids. It has been found that the major component, E, E-farnesal, of the sex-pheromone for the rice moth, *Corcyra cephalonica* Stainton is chemically the most exothermic and stable of all the farnesal isomers. Then, the resemblance of molecular shapes was detrmined in order to design more stable sex-attractants.

Key Words: *Corcyra cephalonica*, Pyralidae, Galleriinae, molecular orbital calculations, pheromones.

Prinç Güvesi *Corcyra cephalonica* Stainton'un Seks Feromonları Üzerine Teorik bir Araştırma

Özet: Geometry optimize edilmiş çeşitli farnesal izomerleri ve farnesoic acid metil esterleri üzerinde moleküler yörünge hesaplamaları (AM1 tipi) yapılmıştır. Pirinç güvesi, *Corcyra cephalonica*. Stainton'un seks-feromonunun esas elemanı olan E, E-farnesal'ın, bütün farnesal izomerleri içinde kimyasal olarak en ekzotermik ve dayanaklı olduğu bulunmuştur. Müteakiben, daha dayanıklı seks-çekicileri tasarımı amacı ile, molekülsel şekil benzerlikleri tayin edilmiştir.

Anahtar Sözcükler: *Corcyra cephalonica*, Pyralidae. Galleriinae, moleküler yörünge hesapları, feromonlar.

Introduction

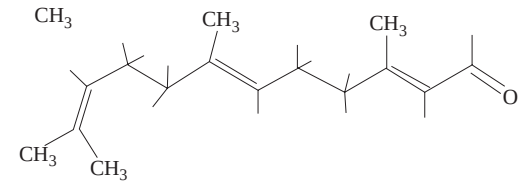
The rice moth, *Corcyra cephalonica* Stainton (Pyralidae, Galleriinae) is a major pest of stored products and quite often its population thus its harm reaches very unplesant level in subtropical countries like India that, some extensive research has been carried out about the biology of this insect as well as different aspects of the sex pheromone (1, 2).

In the Galleriinae subfamily of Pyralidae, mostly male pheromones emitted from wings glands to evoke females are common (3-7). Therefore, female-emitted pheromones in the rice moth of Galleriinea subfamily claimed by Singh and Sidhu led Zagatti et al to reconsider the communication system of this insect. They have concluded that males actually attract females and although a pheromone is also produced by females, it is not the primary attractant pheromone mediating the sexual communication of this species (2). They also menaged the isolation and chemical identification of the pheromone as (E, E)-farnesal ((2E, 6E)- 3, 7, 11-trimethyl-2 ,6

10-dodecatrienal) (I) as the main compound. The minor compound was identified as (Z. E)-farnesal (II). The other isomers of farnesal (E, Z and Z, Z) if they exist at all in the volatiles collected from male moths had to be no more than 1%. of the major component (2). Although, in experiments with pure isomers (E, E- and Z, E-) females were attracted but a gas-chromatographic quantitation of the test compounds showed a rapid increase in the relative amount of the minor compound soon reaching an equlibrium. On the other hand, a blend of synthetic farnesal isomers (70 % E, E to 30 % Z, E) evoked a strong attraction of virgin females in olfactometric tests (2). A sesquiterpene, farnesal, is an unsatureted aldehyde which is in general represents a chemically reactive system. Therefore, when the primary interest is the usage of pheromones for the pest control in the field conditions, chemical stability has the main importance.

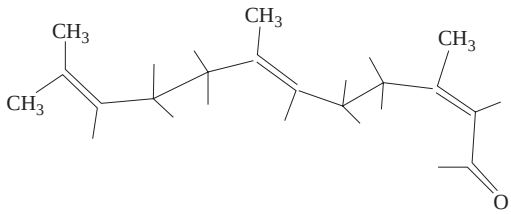
I

E, E



Z, E

II



Previously, we have overcome the chemical stability problem in the case of *Galleria mollonella* L. using esters instead of the pheromone, nononal, which is an aldehyde also (8)). In the present study, a theoretical study has been carried out on the farnesal isomers and methyl esters of farnesoic acids.

Method

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

Results and Discussion

Table 1 tabulates the heats of formation, the highest and lowest molecular orbital energies (HOMO and LUMO energies, respectively) and the total energies of farnesal and methyl esters of farnesoic acid isomers, together with the molecular volumes calculated by the method of Bodor et al (12) which is based on the atomic radii of Gavezotti (13).

Inspection of the heats of formation data reveals that formations of all these molecules are exogenic. Beside of that (E,E)-farnesal which is the major component of the pheromone of *Corcyra cephalonica* is the most exothermic and the most stable (compare the total energy values values in table 1) of all the farnesal isomers. It has the largest molecular volume among the isomeric farnesals. The stability order is expected to increase in the order of Z, Z- < E, Z- < Z, E- < E, E- for farnesals. Note that the last and one before the last are the major and minor components of the pheromone, respectively. In that respect, interestingly enough, the chemical stability seems to be followed in the component distribution of the pheromone.

Table 1. Some theoretical characteristics of farnesals and methyl farnesoates.

Molecule	$^{a}\Delta H_f$	$^{b}E_{HOMO}$	$^{b}E_{LUMO}$	^{a}Total En.	^{c}V
(E, E)-farnesal	-179.367	-1.488	-.023	-248251.277	841.4
(Z, E)-farnesal	-178.827	-1.013	-.022	-248250.737	831.3
(Z, Z)-farnesal	-164.489	-1.499	-.023	-248236.399	838.5
(E, Z)-farnesal	-164.906	-1.498	-.023	-248236.817	839.3
(E, E)-methyl farnesoate	-403.833	-1.487	.000	-294253.753	916.0
(Z, E)-methyl farnesoate	-397.932	-1.481	.006	-294247.852	911.2

Energies in ^{a} KJ/mol, $^{b}*10^{-18}$ J, ^{c} volumes in $*10^{-30}$ m^3.

On the other hand, inspection of the HOMO and LUMO energies of (E, E)- and (Z, E)-farnesals (the major and minor components, respectively) indicates that chemically the major component should be less susceptible to oxidation and reduction reactions compared to the minor one. Since, aldehydes in general vulnerable to atmospheric reactions, eg. air oxidation, nature seems to have got some measures to prevent early inactivation of the pheromone having a high percentage of the relatively stable isomer, in the pheromone admixture.

The methyl esters of (E, E)- and (Z, E)-farnesoic acids are obviously somewhat bulkier molecules compared to the corresponding farnesals, but more stable and even less susceptible to oxidation and reduction reactions (Table 1).

After the theoretical analysis of chemical stability and reactivity of these molecules, the next step requires the determination of the similarities of shapes of these structures which is very

important in the olfactory action of the pheromones. For that purpose, root-mean-square (RMS) overlay approach supplied in ChemPlus program was used. The optimized structure of (E, E)-farnesal (the major component) was taken as the base compound and the other molecules of the present interest (in the optimized geometry) were overlayed on it. The RMS data reveals that the order of molecular similarities follows the following sequence where RMS values are in paranthesis.

(E, E)-farnesal	>	(Z, E)-farnesal	>	(E, E)-ester	>	(E, Z)-farnesal>		(Z,Z)-farnesal>		(Z,E)-ester
(0)		(1.8449)		(2.0808)		(2.5263)		(2.6050)		(2.8403)

Note that the superimposition of a structure on itself results in RMS value of zero.The analysis of the similarity order information indicates that the esterification, although the smallest possible alcohol moiety, methoxide group, is attached to the corresponding farnesal backbone, the similarity with (E, E)- farnesal deviates from the ideality so that the esters in each case are less similar than the resemblance of the minor component to the major one.

Conclusion

In the light of the present study, one should consider methyl esters of farnesoic acids (especially (E, E)-ester) as quite potent alternatives of the sex-pheromone, (E, E)- farnesal. Although, somewhat less sex-attractive activity should be expected, the abovementioned esters seem chemically suitable to be tested in the laboratory and field conditions to determine their practical potency as sex-attractants for the rice-moth.

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