ABSTRACT

Jasmonic acid, also known as jasmonates, (JA), a molecule formed by the oxygenation of fatty acids, is an organic compound and is found in many plants, especially jasmine. The conformation of this compound is found according to the location in the chiral centers. In this study, the molecular structure of JA (labeled C-4 and C-5 in this study) which has two chiral centers was investigated by DFT and TD-DFT methods. These structures have been found to have RR, RS and SS configurations relative to their chiral centers. Each configuration has cis and trans conformations depending on the orientation of the chain groups attached to the five atom ring. The minimum energies of each conformation were calculated with DFT/B3LYP/6-311++G(d,p) method and the structures of their stable form were drawn. JA_RR_trans conformer was found most stable than the other conformers. Excited state energies were calculated using TD-DFT calculations and also HOMO-LUMO energy gaps were found for all chiral conformers.

Keywords: Jasmonic acid, B3LYP, DFT/ TD-DFT, HOMO-LUMO energy

1. INTRODUCTION

Jasmonic acid (also known as jasmonates -JA), which plays an important role in the regular ripening of fruits, was obtained for the first time from mushroom culture [1]. Jasmonic and methyl jasmonic acid derived from fatty acid synthesized from linolenic acid found in chloroplast membrane [2-4] Gao et al., 2011; Jalalpour et al., 2014). JA plays an effective role such as fruit ripening and aging, sex determination, root elongation, fertility, biotic and abiotic stress tolerance. It also has systemically acquired resistance to healing plant wounds and insect attack. [5-9]. Biosynthetic studies of JA were first described by Vick and Zimmerman [10]. The importance of the centers within responses of chiral-centered JA in plants were studied by Holbrook et al [11]. In our previous study the infrared spectrum of the RS structure of allantoin was studied [12]. It has also chiral center and can exist in R- and S-enantiomeric forms like JA being studied now.

In this study, cis and trans conformations of JA molecule of RR, RS and SS forms were studied by DFT, TD-DFT and NBO methods. For each of the conformations with optimized energies, the interactions between donor and orbitals were examined and the excited state energies were calculated. HOMO-LUMO energy ranges and electrostatic potential regions were determined by calculating B3LYP++G(d,p) level.

2. COMPUTATIONAL METHODS

Calculations have been made using the fundamental laws of quantum mechanics using the computer program Gaussian 09 [13]. Equilibrium geometries at minimum energy of the studied molecule were optimized with DFT approach using the 6-311++G(d,p) fundamental set [14] and the B3LYP function created by Becke, Lee, Yang and Parr [15,16]. Orbital interactions were analyzed by the NBO method.
Using NBO 3.1 in Gaussian 09 program [17]. Time dependent density functional theory (TD-DFT) was used to obtain low energy excited transitions [18] and also HOMO-LUMO energy gaps were found. In addition, the distribution of electrostatic potential energies was obtained and mapped.

3. RESULTS AND DISCUSSIONS

The 5 carbons of the JA molecule, which has 12 carbon atoms, are in the ring structure. Others are in the chains attached from the 4 and 5 carbons numbered in our study. These chains have 2 different positions depending on the orientation of the chain groups attached to the five atom ring which named cis and trans for RR, RS and SS forms and shown in Figure 1 a, b and c.

![Figure 1. Cis and trans conformers of RR (a), SS (b), RS (c) isomers of JA calculated by B3LYP(6-311)++G(d,p) level with adopted number.](image)

As can be seen from Table 1, while the RR_trans form was calculated in the most stable structure, the SS_cis was with the highest relative energy.
Table 1. ∆E(RB3LYP), ∆(E+ZPV) and relative Gibbs (∆G) energies of JA conformers calculated as kJ mol⁻¹.

|     | ∆E  | ∆(E+ZPV) | ∆G  |
|-----|------|----------|------|
| JA–RR cis | 7.29 | 8.06 | 6.52 |
| JA–RR trans | 0    | 0     | 0    |
| JA–SS cis | 16.33 | 17.74 | 17.96 |
| JA–SS trans | 10.00 | 10.13 | 6.16 |
| JA–RS cis | 10.05 | 11.28 | 10.71 |
| JA–RS trans | 4.20 | 4.32 | 5.51 |

The energy difference between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) for JA conformers were drawn in Figure 2. The HOMO–LUMO relative energy for the RR_trans conformation was calculated as 5.71 eV, while the RS_trans with the highest relative energy was 5.60 eV. As shown in Figure 2, depending on the orbital locations, there is a little change in the difference between the HOMO and LUMO energy values of the molecule.

While LUMO orbitals were observed in 5 rings of the molecule, HOMO orbitals were found to be related to the R and S forms of the molecule.

LUMO orbitals were found to be associated with the R and S forms of the molecule, and the orbital density was concentrated on the C=C double bond in the chain group attached to the ring.
Figure 2. Calculated HOMO and LUMO orbitals for JA_RR\textit{cis} and \textit{trans}, JA_SS\textit{cis} and \textit{trans} and JA_RS\textit{cis} and \textit{trans} conformers using B3LYP/6-311++G(d,p)
Surface map of Molecular Electrostatic Potential (MEP) of JA conformers was drawn using Gauss View, and given in Figure 3. The map visualizes charge regions of the molecule. In scale bar, the red and blue colors indicate negative and positive values, respectively. The map of JA showed that the negative electrostatic potentials (red region, electrophilic attack) were intensified around the oxygen which double bonded to chlorine atom.

Figure 3. MEP surface for JA conformers calculated using B3LYP/6-311++G(d,p) level.
Table 2. Excited state, excited energy (E), wavelength of the vertical absorption (λ), oscillator strength (f) and orbital type calculated by the TD-DFT method of JA conformers

| State | E (eV) | λ (nm) | f     | type               |
|-------|--------|--------|-------|--------------------|
| RR_cis S0 | 5.8072 | 213.5  | 0.0298 | HOMO → LUMO+2     |
| RR_trans S3 | 5.7953 | 213.94 | 0.0083 | HOMO-1 → LUMO+1    |
| SS_cis S1 | 5.4612 | 227.03 | 0.0276 | HOMO-1 → LUMO+1    |
| SS_trans S1 | 5.4346 | 228.14 | 0.0234 | HOMO → LUMO+1     |
| RS_cis S4 | 5.7208 | 216.73 | 0.0221 | HOMO → LUMO+2     |
| RS_trans S6 | 5.8056 | 213.56 | 0.0182 | HOMO-1 → LUMO+1    |

The values with high excited energies were found in RR_cis (5.8072 eV), RS_trans (5.8056 eV) and RR_trans (5.7953 eV) forms. The molecule is excited with an efficient energy in the highest state from the ground state and exhibits a significant oscillator strength (Table 2). The load transfer of the RR_cis form, which is the highest oscillator strength (0.0298), was found as the transition from HOMO to LUMO+2 level. In this case, it can be considered that the possibility of Transition is higher.

Interaction energies between orbitals, \( E(2) \), donor-acceptor NBOs are determined based on the "Second Order Perturbation" theory [17]. In the formula (Eq.1), \( F_{ij} \) is the matrix element between the \( i \) and \( j \) NBO orbitals, \( q_i \) is the occupancy of the donating orbital, \( \epsilon_i \) and \( \epsilon_j \) are the energies of the acceptor and donor NBOs.

\[
E(2) = \Delta E_{ij} = q_i \frac{F_{ij}^2}{\epsilon_j - \epsilon_i}
\]  

As seen in Table 3, for most stable conformer (RR_trans), all donors participating in the interaction were lone pairs and the most significant NBO interaction was \( \text{LP}(2)\text{O}16 \rightarrow \pi^*(\text{C}14-\text{O}15) \). Donor-acceptor orbital interaction energy was calculated about 43.1 kcal mol\(^{-1}\) (Figure 4). This interaction can be considered as the main orbital interaction. Stabilization energies were calculated considering values higher than 10%.

Table 3. Donor and acceptor pairs and orbital energies for NBO pairs as calculated by the Fock matrix equation (Equation 1) in the NBO basis for JA_RR_trans (atom numbers are given in Figure 1).
Figure 4. LP(2)O16 → π*(C14–O15) donor-acceptor orbitals interactions for JA_RR_trans calculated using NBO method (atom numbers are given in Figure 1).

4. CONCLUSIONS

Optimized energies of the conformation of the RR, RS and SS forms in the chiral state of the JA molecule were found using DFT method with B3LYP/6-311++G(d,p) level. It was calculated that the RR_trans form was at the lowest energy and the most stable conformer compared to other conformations. The highest transition energy gap HOMO–LUMO range was found in RR_cis form and its value was 5.78 eV. It was seen from the electrostatic potential calculations and drawings that all the conformations have the highest attraction around oxygen bonded to hydrogen by double bond. Excited energy states were determined using TD-DFT calculations and the highest transition energy was calculated as approximately 5.81 eV at RR_cis with HOMO→LUMO+2 transition. From the results of NBO calculations, it was found that the donor acceptor interaction with the highest stabilization energy was the interaction of LP (2) O16 → π*(C14–O15) orbitals about 43 kcal mol⁻¹.

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