

## INVESTIGATION OF ANTIOXIDANT EFFECTS OF VARIOUS ORGANIC OIL COMPONENTS BY THEORETICAL METHODS

Vildan Enisoğlu ATALAY,<sup>a,\*</sup> Merve Gözdenur DEMIRBEK,<sup>b</sup> Yarkın Aybars ÇETİN<sup>c</sup>  
and İbrahim Barış ÖLÜ<sup>d</sup>

<sup>a</sup>Department of Molecular Biology and Genetic, Uskudar University, Uskudar, Istanbul, Turkey +902164002222

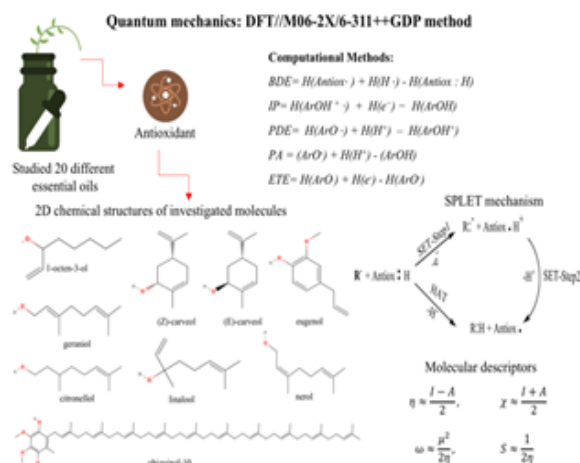
<sup>b</sup>Department of Chemical Engineering, Rovira i Virgili University, 26 Països Catalans Av., 43007, Tarragona, Catalonia, Spain

<sup>c</sup>Department of Computer Engineering and Mathematics, Rovira i Virgili University, 26 Països Catalans Av., 43007, Tarragona, Catalonia, Spain

<sup>d</sup>Institute of Sciences / Bioengineering, Uskudar University, Uskudar, Istanbul, Turkey

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Many biological systems include antioxidants for controlling free radicals, lipid oxidation catalysts, oxidation intermediates and secondary degradation products. Various plant species are known to be good antioxidant sources. In the quantum mechanical side of this study, three main antioxidant reaction mechanisms, HAT, SET and SPLET, were modelled to elucidate the antioxidant mechanism. These mechanisms were modelled through the DFT/M06-2X//6-311++G(d,p) method based on IP, PDE, BDE, ETE, PA values.  $\chi$ ,  $\eta$ ,  $\mu$ ,  $S$  and  $\omega$  parameters that are important molecular determinants of antioxidant activity. The energetic stability of the molecules considered through energy levels calculations required the transfer of the  $E_{\text{HOMO}}-E_{\text{LUMO}}$  values to the upper orbital level of the electrons of the corresponding molecules.



### INTRODUCTION

Essential oils are aromatic and volatile liquids derived from plants, including flowers such as petals, roots, barks, leaves, seeds, and fruits.<sup>1</sup> For many years, essential oils have been studied with great interest, but their use has been diminished.<sup>2</sup> Essential oils have different uses for different purposes and obtained from plants or fruits by distillation or pressing methods.<sup>3</sup> Much of the trace amounts of sulfur and nitrogen compounds are found in their content as terpenoids (such as

monoterpenes, sesquiterpenes, and diterpenes), while lesser amounts of organic acids, alcohols, ketones, aldehydes, esters are present.<sup>4-6</sup>

Essential oils are commonly used as antiseptics: thyme, lavender, and ginger<sup>7,8</sup> though some essential oils are the most important raw materials used in the industry for perfumes and aromas and as therapeutic, antimicrobial and antioxidant properties.<sup>9-14</sup> Several epidemiological studies have shown that the consumption of fruits and vegetables and selected natural antioxidants such as plant polyphenols, vitamin C,

\* Corresponding authors: vildan.enisoglu@uskudar.edu.tr

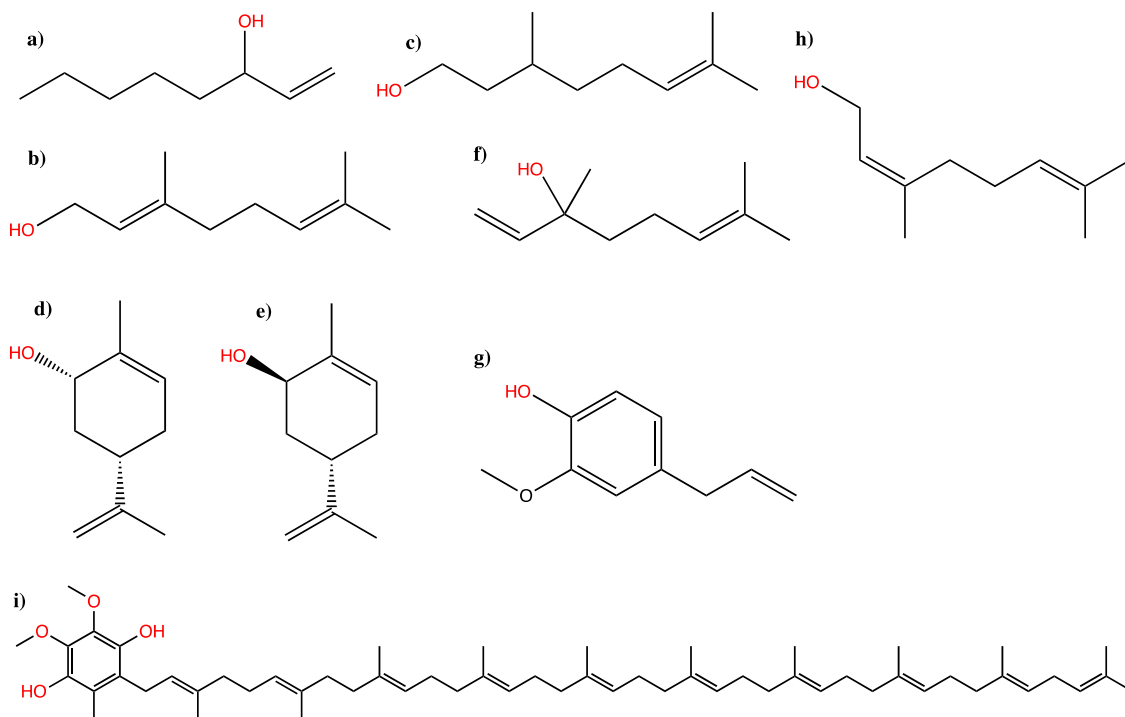


Fig. 1 – 2D chemical structures of **a)** 1–octen–3–ol, **b)** geraniol, **c)** citronellol, **d)** (Z)-carveol, **e)** (E)- carveol, **f)** eugenol, **g)** linalool, **h)** nerol and **i)** ubiquinol–10.

and flavonoids correlate with cardiovascular and chronic diseases and a decrease in some cancer cases.<sup>12–16</sup> Much effort has been made to discover vital safer natural antioxidants.<sup>17,18</sup> There is renewed interest in using plant-based antimicrobial and antioxidant compounds to control foodborne diseases and diseases caused by microorganisms.<sup>19,20</sup> The antioxidant and antimicrobial activities of herbs and plants are attributed to the presence of essential oils, bioactive components and phenolic components.<sup>17,18,21</sup> Essential oils have significant contributions in the treatment of skin diseases, the regulation of digestive and respiratory systems, as well as in providing various active ingredients for painkillers, and in wound healing, calming, germ and fungicidal treatment, refreshment, stress-reducing effects as well as the elimination of contractions and spasms.<sup>22,23</sup> In general, alcohols, esters, terpenes, aldehydes, and coumarins within the contents of essential oils give them their therapeutic value.<sup>24</sup>

This study used quantum chemical approaches to find the active molecular structure in all investigated essential oils. The reason for the selection of phenolic compounds in this work is that they are effective compounds. Theoretical methods investigated antioxidation mechanisms and molecular descriptors of the nine compounds (Fig. 1) by theoretical methods

(DFT/M062X and HF). The results are given in order of molecular activity.

## METHODS

### 1. Antioxidant analysis

#### 1.1. Quantum mechanics

All molecules studied were identified by phenolic structures, logP values, dipole moment and volume of each molecule obtained from 20 different plants. The 3-dimensional structures of all molecules were taken from the NIST Chemistry WebBook (National Institute of Standards and Technology US Department of Commerce) database,<sup>25</sup> and the research set was created. The conformational analysis was performed with Spartan'14,<sup>26</sup> and semi-empirical PM6.<sup>27</sup> HF/6-311++G(d,p) level of theory<sup>28</sup> was used for geometry optimizations, DFT//M062X/6-311++G(d,p) level of theory<sup>29</sup> was used for antioxidant mechanism modelling and time-dependent energies. All of the visualizations and calculations were carried out by the methods implemented in GaussView 5.0,<sup>30</sup> and Gaussian 09 package<sup>31</sup> in gas and ethanol phases. The value of  $H(H^+)$ ,  $H(e^-)$ , and  $H(H)$  in the gas phase calculated with the same

methods are -0.15995 au, -0.51943 au, -0.49819 au; in ethanol -0.15998 au, -0.64272 au, -0.49822 au respectively.

Antioxidants are known to scavenge free radicals through mechanisms such as hydrogen atom transfer (HAT), single electron transfer (SET) and sequential proton loss electron transfer (SPLET) mechanisms, each mechanism involving different kinetics. The HAT mechanism to the free radical takes a hydrogen atom from

$$\text{BDE} = \text{H}(\text{Antiox}) + \text{H}(\text{R:H}) - \text{H}(\text{Antiox:H}) - \text{H}(\text{R}) \quad (\text{Eq. 1})$$

The SET reaction mechanism is mimicked by the natural flavonoid substrate single electron transfer, and a radical intermediate is produced in any sequence, as shown in Fig. 2. In the SET mechanism, the antioxidant provides an electron to the free radical and becomes a radical cation in the following step (AntioxH<sup>+</sup>). The electron-donating ability of antioxidants is related to an extended electronic delocalization over the entire molecule. The SET-PT mechanism involves the formation and breakdown of the flavonoid cation radical with a positive charge. The SET-Step 1 mechanism is the most important energetic factor in assessing the antioxidant effect of ionization potential (IP) (Eq. 2). The lower the ionization potential, the more facilitated the electron abstraction becomes.

$$\text{IP} = \text{H}(\text{ArOH}^+) + \text{H}(\text{e}^-) - \text{H}(\text{ArOH}) \quad (\text{Eq.2})$$

$$\text{PDE} = \text{H}(\text{ArO}^\cdot) + \text{H}(\text{H}^+) - \text{H}(\text{ArOH}^+) \quad (\text{Eq.3})$$

SPLET mechanism takes place in three steps:

Step 1: Antiox:H → Antiox<sup>·</sup> + H<sup>+</sup> (Associated with proton interest)

Step 2: Antiox<sup>·</sup> + R<sup>·</sup> → Antiox<sup>·</sup> + R<sup>·</sup> (Associated with e<sup>-</sup> transfer enthalpy)

Step 3: R<sup>·</sup> + H<sup>+</sup> → RH

In the SPLET mechanism, the formation of Antiox<sup>·</sup> is associated with acidity (PA, Eq.4) of the OH group of the compound in charge, Step 2 is responsible for e<sup>-</sup> transfer enthalpy (ETE, Eq.5) and neutralization of free radical form is obtained. If the antioxidant molecules had low

antioxidants, and the antioxidant itself becomes a radical, as depicted in Fig. 2. In this mechanism, bond dissociation enthalpies (BDE) (Eq.1) have a numerical value, the most important parameter when evaluating antioxidant activity. Due to weaker O–H binding, it will be easier to react with free radical inactivation since lower BDE values are associated with potential antioxidant activity.

PA and ETE values, they would have higher antioxidative activity.

$$\text{PA} = \text{H}(\text{ArO}^\cdot) + \text{H}(\text{H}^+) - \text{H}(\text{ArOH}) \quad (\text{Eq.4})$$

$$\text{ETE} = \text{H}(\text{ArO}^\cdot) + \text{H}(\text{e}^-) - \text{H}(\text{ArO}^\cdot) \quad (\text{Eq.5})$$

Specific parameters such as molecular descriptors characterizing the antioxidant property of a compound, electronegativity ( $\chi$ ), electron affinity (A), hardness ( $\eta$ ), softness (S), electrophilicity index ( $\omega$ ) shall be computationally defined through computational chemistry methods. The properties are significant for the characterization of flavonoids' antioxidant activity.<sup>33</sup> Pauling defined the concept of  $\chi$  as the ability to attract an electron from a molecule of electrons to itself.<sup>34</sup>  $\eta$  and  $\chi$ , values specified by Parr and Pearson.<sup>35,36</sup>

I presents ionization potential, and A is electron affinity. In this study, Koopman's theorem is used to determine I and A values. These values are obtained by the orbital energies of the optimized neutral molecules. According to this theory, the negative highest occupied molecular orbital energy (-E<sub>HOMO</sub>) and the negative lowest unoccupied molecular orbital energy (-E<sub>LUMO</sub>) correspond to the ionization potential and electron affinity (*i.e.*, I=-E<sub>HOMO</sub> and A=-E<sub>LUMO</sub>). At the same time, according to Koopman's theorem, Eq. 7, chemical hardness and electronegativity are defined in terms of orbital energies.

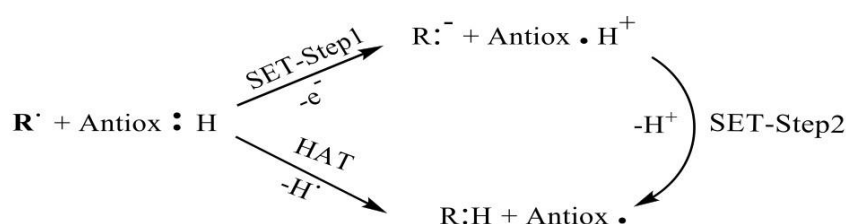


Fig. 2 – Two mechanisms of antioxidant, SET and HAT.<sup>32</sup>

Table 1

BDE, PDE, PA, ETE and IP values (kJ.mol<sup>-1</sup>) of investigated molecules calculated by DFT/M062X//6-311++G(d,p) method

Molecule	BDE		PDE		PA		ETE		IP	
	gas	ethanol	gas	ethanol	gas	ethanol	gas	ethanol	gas	ethanol
1-octen-3-ol	196.506	187.967	392.695	538.385	810.206	722.032	-1401.853	-1656.674	905.944	375.004
(Z)-carveol	230.856	231.950	490.164	616.481	857.968	768.231	-1415.265	-1658.890	858.348	358.381
citronellol	188.704	206.638	<b>363.403</b>	<b>469.591</b>	836.769	796.966	<b>-1436.217</b>	<b>-1712.935</b>	903.127	418.224
eugenol	283.540	293.754	494.320	657.631	853.335	773.809	-1363.949	-1597.663	776.639	313.533
geraniol	494.640	528.203	762.392	917.443	844.790	813.093	-1138.304	-1083.808	921.119	414.870
linalool	241.484	253.421	451.910	569.499	871.229	799.023	-1417.899	-1668.211	872.515	381.832
nerol	233.654	246.000	515.504	641.715	827.494	797.717	-1381.993	-1674.327	901.715	400.967
(E)-carveol	219.075	223.854	492.623	601.577	842.699	766.946	-1411.776	-1665.701	865.330	358.521
ubiquinol-10(57O)	61.150	87.093	605.709	696.785	613.512	<b>531.341</b>	-1340.515	-1566.857	-	-
ubiquinol-10(58O)	<b>45.380</b>	<b>86.051</b>	539.939	695.743	<b>600.417</b>	531.770	-1343.190	-1568.328	-	-
ubiquinol-10	-	-	-	-	-	-	-	-	<b>-1332.712</b>	<b>-1732.301</b>

The electrophilicity index factor ( $\omega$ ) has determined that the maximum electron flow between a donor and an acceptor is governed and determined by the dissociation of the binding energy between the atoms.<sup>37</sup> The  $\omega$  and S values are calculated by the following:

## RESULTS AND DISCUSSION

The BDE values of the phenolic compounds calculated from the HAT mechanism obtained by the DFT/M062X//6-311++G(d,p) method in gas and ethanol are listed in Table 1. It is observed that BDE values increased in all compounds in ethanol phase, with the exception, 1-octen-3-ol. Ubiquinol-10(58O) molecules are determined in the lowest BDE values in the gas and ethanol phase, respectively. In the gas phase, antioxidant activities according to the BDE values of the determined molecules are ubiquinol-10(58O) > ubiquinol-10(57O) > citronellol > 1-octen-3-ol > (E)-carveol > (Z)-carveol > nerol > linalool > eugenol > geraniol, ubiquinol-10(58O) > ubiquinol-10(57O) > 1-octen-3-ol > citronellol > (E)-carveol > (Z)-carveol > nerol > linalool > eugenol > geraniol in ethanol phase, respectively.

Charged molecules are highly sensitive to the polarity of the solvent.<sup>29,31</sup> PDE values obtained from the second step of the SET-PT mechanism (Table 1) have been determined in gas and

ethanol phases, indicating that the PDE values have changed compared to environment polarity. The polar solvent significantly increases PDE values when compared to the gas phase. The change in the PDE values have increased to approximately 100 KJ mol<sup>-1</sup> – 150 KJ mol<sup>-1</sup>. The lowest PDE value has been obtained for citronellol molecule in gas and ethanol phases (363.403 KJ mol<sup>-1</sup> and 469.591 KJ mol<sup>-1</sup>, respectively). The PDE value comparison follows the sequence as citronellol < 1-octen-3-ol < linalool < (Z)-carveol < (E)-carveol < eugenol < nerol < ubiquinol-10(58O) < ubiquinol-10(57O) < geraniol in the gas; citronellol < 1-octen-3-ol < linalool < (E)-carveol < (Z)-carveol < nerol < eugenol < ubiquinol-10(58O) < ubiquinol-10(57O) < geraniol in the ethanol phases.

When the PA values obtained from the SPLET mechanism calculated in the gas and ethanol phases (in Table 1) are determined, it is found that the PA values in the ethanol phase are approximately 30-100 KJ mol<sup>-1</sup> lower than the gas phase values. Ubiquinol-10(58O) is the molecule with the highest antioxidant effect when the PA values (600.417 KJ mol<sup>-1</sup>) are considered in the SPLET mechanism in the gas phase. Ubiquinol-10(58O) molecule is the second in the ethanol phase with a little difference of (0.43 KJ mol<sup>-1</sup>), ubiquinol-10(57O) structure is the most effective antioxidant molecule in the ethanol phase. The antioxidant sequence of other molecules in the

gas phase is ubiquinol-10(58O) > ubiquinol-10(57O) > 1-octen-3-ol > nerol > citronellol > (E)-carveol > geraniol > eugenol > (Z)-carveol > linalool.

When the calculated ETE values in gas and ethanol phases (in Table 1) the sequence is as: citronellol < linalool < (Z)-carveol < (E)-carveol < 1-octen-3-ol < nerol < eugenol < ubiquinol-10(58O) < ubiquinol-10(57O) < geraniol; in the ethanol phase citronellol < nerol < linalool < (E)-carveol < (Z)-carveol < 1-octen-3-ol < eugenol < ubiquinol-10(58O) < ubiquinol-10(57O) < geraniol, respectively. The lowest ETE values have been obtained for citronellol in the gas and ethanol phases which means it has the highest antioxidant property effective in gas and ethanol.

The IP values of the compounds calculated by the SET-PT mechanism in Table 1 were determined, and approximately 400 KJ mol<sup>-1</sup> - 500 KJ mol<sup>-1</sup> were obtained between gas and ethanol. As seen in Table 1, there is a significant difference (2000 KJ mol<sup>-1</sup>) between ubiquinol-10 and the other molecules. An electron is easily broken from ubiquinol-10, and this molecule is the most antioxidant molecule. In gas-phase it is followed by eugenol > (Z)-carveol > (E)-carveol > linalool > nerol > citronellol > 1-octen-3-ol > geraniol, and in the ethanol phase eugenol > (Z)-carveol > (E)-carveol > 1-octen-3-ol > linalool > nerol > geraniol > citronellol.

Antioxidant activity is related to the E<sub>HOMO</sub>-E<sub>LUMO</sub> values of frontier orbitals and their distributions. The obtained frontier energy values and their distribution for the investigated molecules in the gas and ethanol solvents are depicted in Table 2 and Fig. 3. Lower E<sub>HOMO</sub> shows the weaker ability to the proton, and higher E<sub>HOMO</sub> shows the stronger e<sup>-</sup> donating ability.<sup>28,38</sup> Table 2 shows that ubiquinol-10 (-6.7459 eV and -7.0047 respectively) has the highest E<sub>HOMO</sub>, the lowest E<sub>LUMO</sub> levels, and the smallest bandgap in the studied phases ubiquinol-10 has more effective antioxidant capacity. On the other hand, eugenol is determined as the second effective molecule. We must emphasize that ubiquinol-10 and eugenol have similar molecular structures (Fig. 1). The reason why ubiquinol-10 is more effective than eugenol is that it has two methanol and hydroxyl groups, but eugenol has one group in both of them.

When analyzed, the molecular structures of other molecules show no benzene ring, five of them have aliphatic saturated and unsaturated structures, one hydroxyl group, two of them have nonaromatic cyclic structure and one hydroxyl group. An important outcome for this study is that the molecules, including phenolic groups, are more essential for antioxidant activity. The E<sub>HOMO</sub>, E<sub>LUMO</sub> energies sequence is geraniol > nerol > (Z)-carveol > citronellol > linalool > (E)-carveol > 1-octen-3-ol in gas phase, geraniol > nerol > citronellol > linalool > (E)-carveol > 1-octen-3-ol in the ethanol phase, respectively. Bandgap indicates the chemical stability of the molecule, a small bandgap energy indicates the reactivity of the reactants and the ease of reaction, and therefore more antioxidant properties. Therefore, the most stable and most antioxidant molecule sequence is ubiquinol-10 (6.4248 eV) > eugenol (6.9811 eV) > geraniol (7.4298 eV) > linalool (7.500 eV) > nerol (7.5601 eV) > (Z)-carveol (7.5704 eV) > citronellol (7.6578 eV) > (E)-carveol (7.9288 eV) > 1-octen-3-ol (8.3280 eV) in the gas phase. The calculated  $\chi$ ,  $\eta$ ,  $\mu$ , S and  $\omega$  molecular characteristics demonstrate that the studied molecules prefer to act as e<sup>-</sup> donors instead of recipients in the studied phases. It is an indication of antioxidative activity.

The frontier orbital distributions appear to be concentrated on the unsaturated bonds for the studied five aliphatic molecules such as 1-octen-3-ol, nerol, geraniol, linalool and citronellol (Fig. 3). The 1-octen-3-ol and citronellol molecules have only one unsaturated bond. However, the frontier orbitals are localized on it, for the other studied three aliphatic molecules with two unsaturated bonds where frontier orbitals were located. The frontier orbitals are localized on the ring for the investigated cyclic (Z)-carveol and (E)-carveol molecules. For the ubiquinol-10 molecule, the HOMO distributions on the unsaturated benzene ring are diffused, but the LUMO distributions on the unsaturated benzene ring and unsaturated aliphatic straight chain. All the molecules provided the highest E<sub>HOMO</sub> followed by ubiquinol-10 (-6.7459 eV) < eugenol (-7.1125 eV) < geraniol (-7.6197 eV) < nerol (-7.7726 eV) < (Z)-carveol (-7.7957 eV) < citronellol (-7.8338 eV) < linalool (-7.8975 eV) < (E)-carveol (-8.0945 eV) < 1-octen-3-ol (-8.5669 eV) in the gas phase (Table 2).

Table 2

Molecular descriptors calculated by DFT/M062X//6-311++G(d,p) level of theory (eV)

	1-octen-3-ol		citronellol		geraniol		linalool		eugenol	
	gas	ethanol	gas	ethanol	gas	ethanol	gas	ethanol	gas	ethanol
E <sub>HOMO</sub>	-8.5669	-8.6513	-7.8338	-7.7495	-7.6197	-7.6768	-7.8975	-7.8621	-7.1125	-7.3209
E <sub>LUMO</sub>	-0.2389	-0.077	-0.176	-0.0702	-0.1899	-0.1066	-0.1474	-0.0742	-0.1314	-0.0677
Bandgap	8.328	8.5743	7.6578	7.6793	7.4298	7.5702	7.7500	7.7879	6.9811	7.2532
χ	4.4	4.3641	4.0049	3.9098	3.9048	3.8917	4.0225	3.9682	3.6219	3.6943
η	4.16	4.2871	3.8289	3.8396	3.7149	3.7851	3.875	3.8939	3.4905	3.6266
S	0.12	0.1166	0.1305	0.1302	0.1345	0.132	0.129	0.1284	<b>0.1113</b>	<b>0.1378</b>
ω	2.3277	2.2212	2.0944	1.9906	2.0522	2.0006	2.0878	2.0219	<b>1.8791</b>	<b>1.881</b>
μ	-4.4029	-4.3641	-4.0049	-3.9098	-3.9048	-3.8917	-4.0225	-3.9682	-3.6219	-3.6943
	nerol		(Z)-carveol		(E)-carveol		ubiquinol - 10			
	gas	ethanol	gas	ethanol	gas	ethanol	gas	ethanol	gas	ethanol
E <sub>HOMO</sub>	-7.7726	-7.7397	-7.7957	-8.0412	-8.0945	-8.1566	-6.7459	-7.0047		
E <sub>LUMO</sub>	-0.2125	-0.0952	-0.2253	-0.1205	-0.1657	-0.0878	-0.321	-0.2587		
Bandgap	7.5601	7.6445	7.5704	7.9207	7.9288	8.0687	<b>6.4248</b>	<b>6.7459</b>		
χ	3.9925	3.9174	4.0105	4.0808	4.1301	4.1222	<b>3.5335</b>	<b>3.6317</b>		
η	3.78	3.8222	3.7852	3.9603	3.9644	4.0343	<b>3.2124</b>	<b>3.3729</b>		
S	0.1322	0.1308	0.132	0.1262	0.1261	0.1239	0.1556	0.1482		
ω	2.1084	2.0074	2.1246	2.1024	2.1513	2.106	1.9433	1.9551		
μ	-3.9925	-3.9174	-4.0105	-4.0808	-4.1301	-4.1222	<b>-3.5335</b>	<b>-3.6317</b>		

On the other hand, the calculated IP and BDE values are higher than the PA values when the thermodynamically preferred mechanism is determined. From the thermodynamic point of view, the SPLET mechanism has been found to represent the most suitable process in the gas phase. The antioxidative capacity increases in the gas phase from the lowest PA value in the form of ubiquinol-10(58O) > ubiquinol-10(57O) > 1-octen-3-ol > nerol > citronellol > (E)-carveol > geraniol > eugenol > (Z)-carveol > linalool. The large reduction in PAs from the gas phase to the ethanol phase makes SPLET a more suitable mechanism than HAT and SET-PT. This study for flavonoids confirms that the SPLET mechanism plays an important role in polar solvents.

## CONCLUSIONS

In this study, three major antioxidative mechanisms are investigated: HAT, SET-PT

and SPLET for 1-octen-3-ol, citronellol, (Z)-carveol, (E)-carveol, nerol, linalool, eugenol, geraniol, and ubiquinol-10 molecules and BDE, ETE, PA, ETE and PDE values are calculated with DFT//M062X level of theory in the gas and ethanol phases. The gas phase antioxidant sequence according to BDE for the HAT mechanism are ubiquinol-10(58O) > ubiquinol-10(57O) > citronellol > 1-octen-3-ol > (E)-carveol > (Z)-carveol > nerol > linalool > eugenol > geraniol, ubiquinol-10(58O) > ubiquinol-10(57O) > 1-octen-3-ol > citronellol > (E)-carveol > (Z)-carveol > nerol > linalool > eugenol > geraniol in ethanol, respectively. For the SET-PT mechanism, the lowest antioxidant capacity in the gas phase is the antioxidant ability of citronellol < 1-octen-3-ol < linalool < (Z)-carveol < (E)-carveol < eugenol < nerol < ubiquinol-10(58O) < ubiquinol-10(57O) < geraniol in gas, citronellol < 1-octen-3-ol < linalool < (E)-carveol < (Z)-carveol < nerol < eugenol < ubiquinol-10(58O) < ubiquinol-10(57O) <

geraniol in the ethanol phase. When the PA values obtained from the SPLET mechanism are examined, the highest antioxidant action order is ubiquinol-10(58O) > ubiquinol-10(57O) > 1-octen-3-ol > nerol > citronellol > (E)-carveol > geraniol > eugenol > (Z)-carveol > linalool. From the thermodynamic point of view, the SPLET mechanism was found to represent the most suitable process in the gas phase, since the calculated IP and

BDE values are higher than the PA values. In this study, the SPLET mechanism in the gas and the SET-PT mechanism in the ethanol phases are preferred. The difference between the  $E_{\text{HOMO}}-E_{\text{LUMO}}$  values defines the reactivity of the reactants and the ease of reaction with a small bandgap energy, which is more antioxidant for the ubiquinol-10 (-6.7459 eV) molecule, the lowest of this energy.

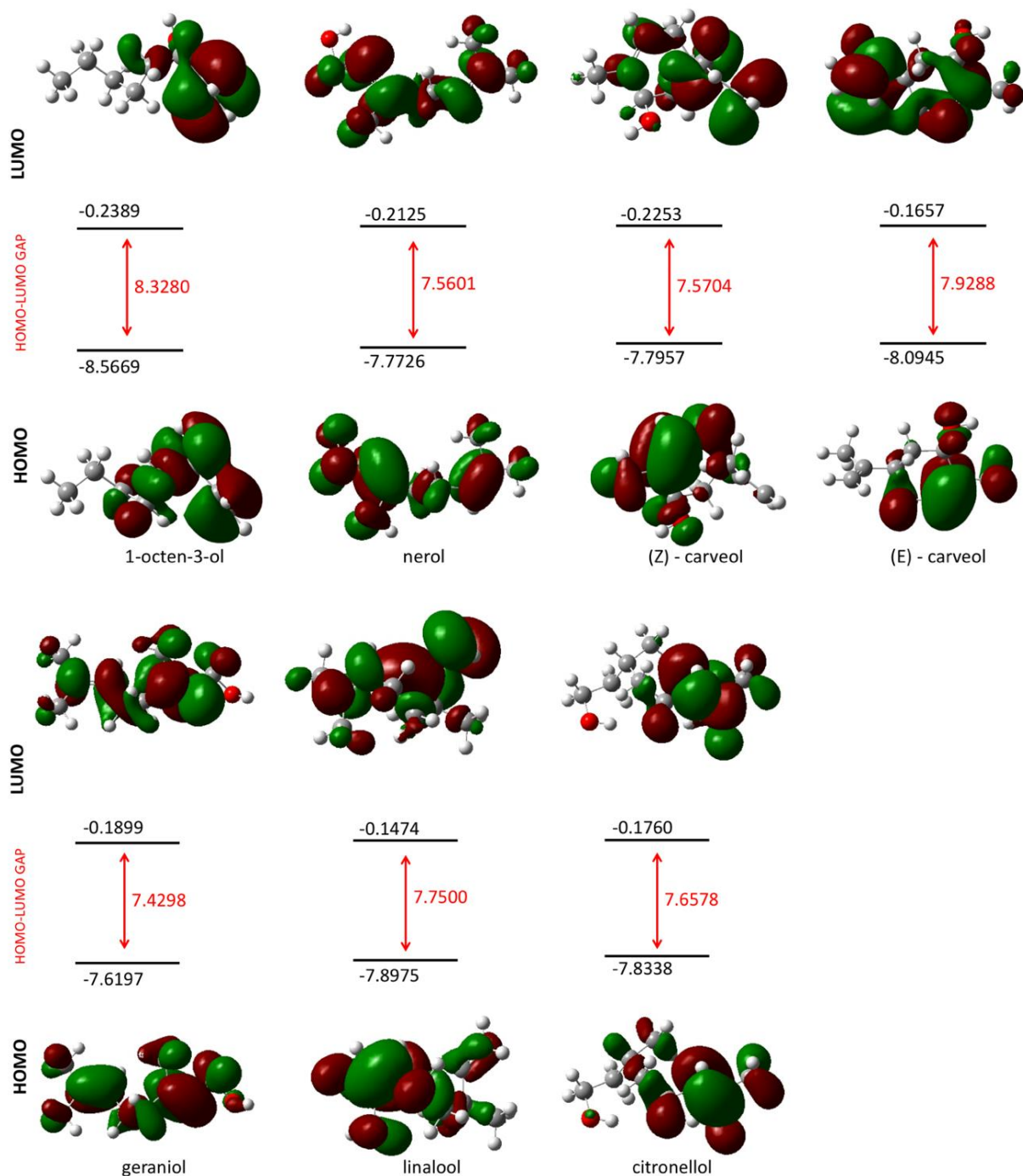


Fig. 3 – The energy and distribution of HOMO and LUMO for the investigated molecules in the gas phase.

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