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Density Functional Theory for Exploring the Structural Characteristics and Their Effects on the Antioxidant Properties

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Abstract: Gallic acid is a ubiquitous phenolic compound, widely distributed in the plant kingdom and frequently found in the human diet. In this study, we explored its antioxidant potential through the determination of HOMO and LUMO energies, O–H bond dissociation enthalpy, ionization potential, electron affinity, and spin density distribution using the density functional theory. We have interpreted the radical scavenging capacity of gallic acid with the help of its structure and noted that the higher antioxidant potential of gallic acid was primarily due to the formation of radicals after abstraction of H atoms from –OH groups. In addition, we have found that the H atom transfer mechanism is preferable over single-electron transfer mechanism and the sequential proton loss-electron transfer mechanism for free radical scavenging capacity. On the basis of calculated results, it was also concluded that the antioxidant activity of gallic acid was due to the 3-OH and 4-OH groups, because of their low BDE values. Moreover, gallic acid is predicted to be among the best antioxidants identified so far. These theoretical researches will be helpful to the development for the antioxidant compounds.

Keywords: Antioxidant, Bond dissociation enthalpy, Density functional theory, Gallic acid, Hydrogen bonding

1 Introduction

Gallic acid (3,4,5-trihydroxybenzoic acid) and its derivatives are naturally occurring phenolic compounds found in wide range of vegetal kingdom and beverages, such as grapes, gallnuts, sumac, cherries, honey, wine, and tea as one of the main phenolic components[1]. It has been widely accepted that gallic acid has several beneficial biological properties, including anti-fungal, anti-viral, anti-cancer, anti-mutagenic, anti-hyperglycemic and cardio-protective activities[2-4]. It is also extensively used as source material in tanning, ink dyes, as antioxidants in food, cosmetics and pharmaceutical industry, as well as in the manufacturing of paper[5].

The chemical and biochemical properties of gallic acid are well described in the literature. In addition, it has been widely demonstrated as a strong natural antioxidant[6-8]. It is able to scavenge hypochlorous acid at a rate sufficient to protect α–1–antiproteinase against inactivation by this molecule. It also decreases the peroxidation of ox brain phospholipids[9]. Free radicals have been implicated in the etiology and pathogenesis of numerous disease states including cardiovascular disease, cancer and diabetes[10].

It has been noticed that the antioxidant activity of polyphenolic compounds, including gallic acid depends upon their structural characteristics,[11] as well as on their ability to donate protons and electrons to resist the effect of energetic oxidants such as free radicals. The biological activity of phenolic compounds is governed by electronic interactions of the biomolecules within the cell. Therefore, study of the electronic and molecular properties is of great importance to understand the mechanism of antioxidant activity of the compounds[12]. There are three possible reaction pathways through which phenolic compounds (ROH) scavenge free radicals ($RO_2^{\cdot}$)[13, 14].

(i) First mechanism involved hydrogen atom transfer (HAT) from antioxidant to free radical $RO_2^{\cdot}$.

$$RO_2^{\cdot} + ArOH \rightarrow ArO^{\cdot} + ROOH \qquad (1)$$

This mechanism is governed by the O–H bond dissociation enthalpy (BDE). The lower the BDE the easier the O–H

bond breaking, and stronger will be the antioxidant potential[15].

(ii) Second mechanism involves electron transfer from the molecule to the radical leading to indirect H-abstraction

$$RO_2^{\cdot} + ArOH \rightarrow ArOH^{\cdot+} + RO_2^{-} \quad (2)$$

$$ArOH^{\cdot+} + RO_2^{-} \rightarrow ArO^{\cdot} + ROOH \quad (3)$$

Antioxidant gives an electron to the free radical and becomes a radical cation. This reaction is governed by the IP and the reactivity of $ArOH^{\cdot+}$.These are most significant factors for scavenging activity evaluation.

(iii) In third mechanism sequential proton loss-electron transfer occurs (SPLET) as under;

$$ArOH \rightarrow ArO^{-} + H^{+} \quad (4)$$

$$ArO^{-} + RO_2^{\cdot} \rightarrow ArO^{\cdot} + RO_2^{-} \quad (5)$$

In third mechanism O–H heterolytic bond dissociation takes place while ionization potential of ArO^{-} is another controlling parameter. From the antioxidant action viewpoint, the net result of the three mechanisms is same, i.e. the formation of phenoxy radical. However, it is possible that under certain conditions one of the possible mechanisms may prevail.

Lu et al., [8] theoretically investigated antioxidant ability of gallic acid but they had not studied the different free radicals formed after the abstraction of H atoms from different hydroxyl groups. They had also ignored the electronic properties of gallic acid and its free radicals. Therefore, due to the prime importance of gallic acid, detailed investigation was required. Electron paramagnetic resonance spectroscopy can be used to study the free radicals produced by the dissociation of hydroxyl groups of gallic acid. And other electronic properties can also be determined experimentally. But the experimental studies required long time, they are tough and costly. On other hand theoretical investigation provides same information in very less time with ease, economy, and reasonable accuracy[16].

The objective of this work was to evaluate the antioxidant properties of the gallic acid and its free radicals by means of density functional theory (DFT) with the purpose to gather more accurate information for better understanding of its scavenging mechanism. In this work, the equilibrium geometry of gallic acid and its free radicals has been computed to explain the efficiency of their antioxidant activity. Many other significant parameters, such as O–H BDE, electronic properties including HOMO and LUMO energies of neutral and radical species, electronic structures (neutral and radical species), dipole moments, ionization potential, electron affinity (EA) and spin densities have also been studied.

2 Computational Details

Density functional theory (DFT) method was implemented in the Gaussian 09W suite of programs[17]. The molecular properties of the compounds have been computed by using standard 6-31G (d, p) basis set. In the DFT calculations the Lee, Yang and Parr correlation functional is used together with Becke's three parameters exchange functional B3LYP[18]. Lowest energy structures of the species were determined by conformational analysis. Geometry optimization was performed at the B3LYP density functional theory with the same basis set. Harmonic vibrational frequencies were computed at the same level of theory for both neutral molecule and radicals to estimate Zero point energies (ZPE) and vibrational contributions to enthalpy. Rotational and translational frequencies were also computed to estimate rotational and translational contributions to enthalpy. Natural bond orbital (NBO) analysis was used to evaluate bond order in all the systems. The total enthalpies of the species X, H(X) at temperature T can be estimated from the formula:

$$H(X) = E_0 + ZPE + \Delta H_{trans} + \Delta H_{rot} + \Delta H_{vib} + RT$$

where, E_0 is the calculated total electronic energy, ZPE stands for zero-point energy, ΔH_{trans}, ΔH_{rot}, and ΔH_{vib} are the translational, rotational and vibrational contributions to the enthalpy, respectively. Finally, RT represents PV-work term and is added to convert the energy into enthalpy. The O–H bond dissociation enthalpy is calculated at 298.15 K as follows:

$$BDE = H_r + H_h - H_n$$

where,H_r is the enthalpy of the radical generated through H-abstraction, H_h is the enthalpy of hydrogen atom [-0.4962 Hartree] and H_n is the enthalpy of neutral molecule. In this work, we also calculated the electronic properties such as dipole moment ionization potential (IP) and electron affinities (EA) of gallic acid and free radicals. Ionization potential and electron affinity can be calculated as follows[19].

$$\text{Ionization potential (IP)} = - \varepsilon_{HOMO}(eV)$$

$$\text{Electron affinity (EA)} = - \varepsilon_{LUMO}(eV)$$

To elucidate the relative stability of radicals, spin densities were also computed.

3 Results and Discussions

3.1 The equilibrium geometries and energetic stability

In polyphenolic compounds, the behavior of the different OH groups is largely influenced by the neighboring groups as well as by the geometry. Hence, the conformation can be regarded as the first parameter of interest to analyze the antioxidant ability of phenolic compounds.

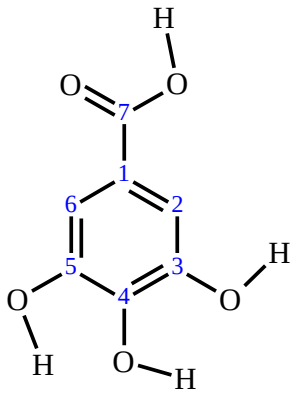

Figure 1 Optimized structure of gallic acid

All the possible structures were optimized to identify the one with the least energy (most stable). The optimized structure of gallic acid is shown in Figure 1. It should be planar, because the three hydroxyl groups on the ring are oriented in the same direction. Figure 2 shows the detailed geometries of gallic acid and its free radicals formed after the abstraction of H atoms from different OH groups. In neutral gallic acid, two intramolecular O—H--- O hydrogen bonds are present. The length of intramolecular hydrogen between H atom of 5-OH and O atom of 4-OH is 2.175 Å, while the length of intramolecular hydrogen between H atom of 4-OH and O atom of 3-OH is 2.170 Å.

The results of our theoretical investigation are in close agreement with the experimental results[20]. There is no intramolecular hydrogen bond present between oxygen atom of carboxylic group (C=O) and hydrogen atom of 7-OH group, while the oxygen atom of carboxylic group (C=O) and oxygen atom of 7-OH group forms intermolecular hydrogen bond[20]. The intramolecular hydrogen bonds can stabilize the ground state molecule resulting in the slow abstraction of H atoms. On the other hand, intramolecular hydrogen bond present in the free radicals formed after the abstraction of H atom, makes reaction very fast.

As shown in Figure 2, two intramolecular hydrogen bonds are present in the free radicals of 7-OH and 3-OH groups, while one in the case of 4-OH and 5-OH groups. It has already been reported that semiquinone structures are present in 3-OH and 4-OH radicals, and they plays an important role in their stability[21]. The optimized semiquinone structures of 3-OH and 4-OH radicals are shown in Figure 3. These results prove that the resonance stabilization is mainly responsible for the enhancement of the energetic stability of 3-OH and 5-OH radicals.

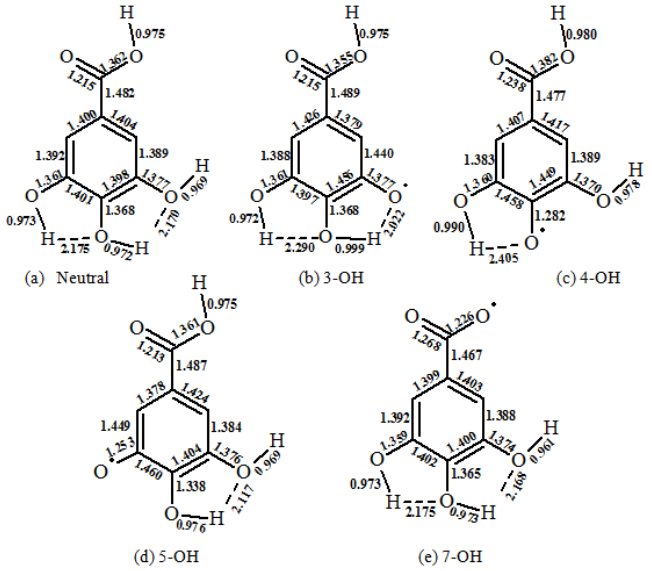

Figure 2 Detailed geometries of ground state gallic acid and its radicals

3.2 HOMO and LUMO energies

The frontier molecular orbital energies, ε_{HOMO} and ε_{LUMO} are also very crucial factors of molecular electronic structure. The lower the ε_{HOMO}, the weaker is the electron donating ability, while higher the ε_{HOMO} implies that the molecule is a good electron donor. The ε_{LUMO} represents the ability of a molecule to accept electron. The ε_{HOMO} energies are in the order of 7-OH < 4-OH < 3-OH < 5-OH < Neutral. The ε_{HOMO} and ε_{LUMO} energies of gallic acid and its free radicals are given in Table 1. The order of ε_{LUMO} energies can be shown as 4-OH < 3-OH < 5-OH < 7-OH < Neutral. The LUMO disposition of a phenolic compound represents the electron accepting ability of compounds.

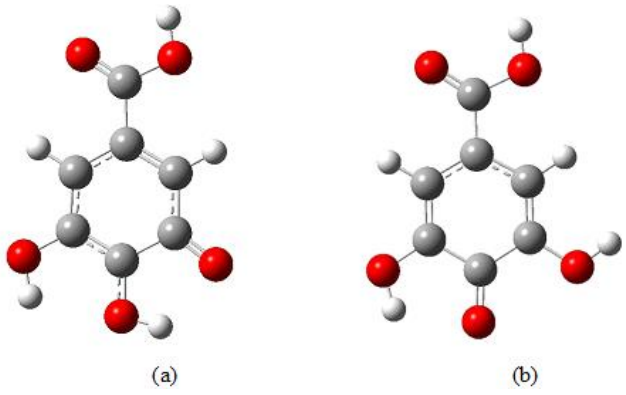

Figure 3 Equilibrium semi-quinone geometries of radicals of gallic acid (a) 3-OH and (b) 4-OH.

The HOMO and LUMO dispositions of gallic acid and its free radicals are shown in Figure 4. In order to understand the relationship between the electron delocalization and the reactivity of the radicals, one can examine the electron distribution in the HOMO and LUMO.

3.3 Bond dissociation energy (BDE)

BDE is also very important parameter to study antioxidant ability especially for hydrogen atom transfer mechanism (HAT). BDE values for different free radicals are given in Table 1.

Table 1 Frontier orbital energies of gallic acid and its radicals, the bond dissociation energies of OH groups

Compounds	$\varepsilon_{HOMO/au}$	$\varepsilon_{LUMO/au}$	E_{total}/ Hartree	BDE/ kcalmol^{-1}
Neutral	-0.221	-0.039	-646.381	
3-OH	-0.23	-0.062	-645.769	72.79
4-OH	-0.232	-0.068	-645.768	73.54
5-OH	-0.223	-0.059	-645.755	82.01
7-OH	-0.234	-0.056	-645.727	99.46

The trend in BDE values clearly demonstrates that the H-transfer is more energetically favorable. From the literature survey, it can be observed that the numbers of hydroxyl substituents for each structure are crucial but not necessarily essential, since the antioxidant ability depends largely on the BDE value of each substituent. This means that an effective antioxidant compound should have lower BDE values. The BDE values for different free radicals can be given in following order: 3-OH < 4-OH < 5-OH < 7-OH.

Table 2 Electronic properties of gallic acid and its radicals

Compounds	Dipole Moment	IP (kcal mol^{-1})	EA (kcal mol^{-1})
Neutral	4.62	138.59	24.44
3-OH	4.59	144.36	38.97
4-OH	4.07	145.51	42.66
5-OH	6.70	139.98	36.89
7-OH	5.66	146.89	35.05

The BDE values are in the range of 72.79 Kcalmol^{-1} to 99.46 Kcalmol^{-1}. This long range of BDE values proves the diversity present in the structure of gallic acid. The BDE values of 3-OH and 4-OH groups are very low as compared to the 5-OH and 7-OH groups. The reason for low BDE values of 3-OH and 4-OH groups is their extra stability.

3.4 Electronic properties

The electronic properties of gallic acid and its free radicals are presented in Table 2. The molecular dipole moment represents a generalized measure of bond properties and charge densities in a molecule. It essentially constitutes an index of reactivity, which is very important to define the biological properties particularly related to the interaction with enzyme active sites. Dipole moment of gallic acid and its free radicals are in the range of 4.07 D-6.70 D. The ionization potential of gallic acid and its free radicals are in following order; Neutral < 5-OH < 3-OH < 4-OH < 7-OH.

As very low ionization potential of neutral gallic acid indicates its (low) antioxidant ability in the neutral form, as it can scavenge the free radicals through SET-PT mechanism. The ionization potential of 5-OH free radical is also very low as compared to other free radicals. This is probably due to the absence of intramolecular hydrogen bond between 5-O$^{\cdot}$ and H atom of 4-OH group. On the other hand, 3-O$^{\cdot}$ and 4-O$^{\cdot}$ are engaged in intramolecular hydrogen bonding in 3-OH and 4-OH free radicals, respectively. Therefore, electrons on 3-O$^{\cdot}$ and 4-O$^{\cdot}$ cannot donate easily, so they have relatively higher ionization potential. The 7-OH has very high ionization potential that can be explained on the basis of resonance of 7-O$^{\cdot}$with neighboring oxygen. The order of electron affinity of gallic acid and its free radicals can be given as follow; Neutral < 7-OH < 5-OH < 3-OH < 4-OH. The electron affinity of gallic acid is very low (24.44) as compared to its free radicals. The electron affinity of 3-OH and 4-OH radicals is very high, which indicates that these radicals have low electron accepting tendency but high electron donating ability.

3.5 Spin densities

The spin density is the important parameter to characterize the stability of the free radicals because the energy of a radical can be efficiently decreased if the unpaired electron is highly delocalized through a conjugating system[22]. It is important to analyze the spin density of gallic acid and its radicals in order to rationalize the differences in reactivity of the different OH sites and consequently to find the difference in BDE values. Because the more delocalized spin density in the radical, results in the easier radical formation and thus the lowers the BDE value[23]. Spin density of O-atom of free radicals formed after the abstraction of H atom in each radical is shown in Figure 5.

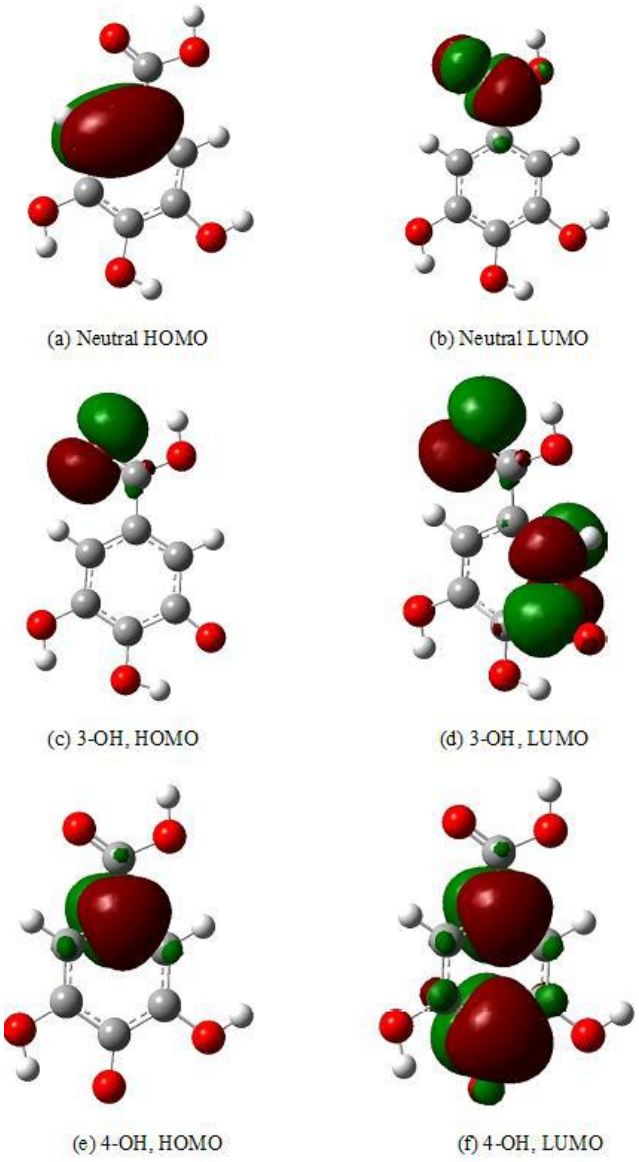

Figure 4 HOMO and LUMO compositions of neutral gallic acid and radical species

Spin densities of different (GA) free radicals shows the following trend: $O_3 < O_4 < O_5 < O_7$. This trend indicates a good relationship between H atom abstraction and unpaired electron delocalization. For example, the 3-OH radical has a better unpaired electron delocalization so the BDE value of its parent molecule is the lowest. It has spin density and BDE values of 0.393 and 72.79 respectively. This 3-OH free radical has two intramolecular hydrogen bonds; length of one bond is very less (2.022), which results in the stability of free radical and decreases the BDE value. Low spin density can also be explained on the basis of semiquinone structure present in 3-OH free radical. The semiquinone structure is responsible for better delocalization of electronic cloud.

3.6 Mechanism of free radical scavenging

The hydrogen donating capacity and the ability to form radicals can be interpreted by bond dissociation enthalpy and ionization potential. The molecules with low BDE values are expected to have antioxidant properties.

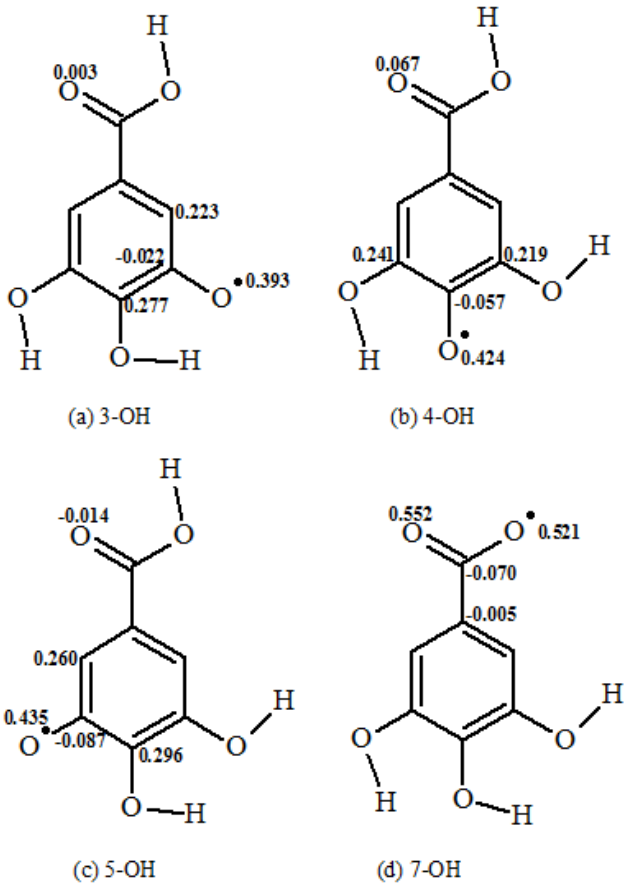

Figure 5 Spin densities of gallic acid free radicals

In particular, low value of BDE indicates that the antioxidant is able to donate hydrogen atom during free radical scavenging mechanism. However, low values of IP do not guarantee about the high antioxidant potential of antioxidants. This parameter is favorable to increase the electron-transfer reactivity and allows assessing the thermodynamic preference of the first step of the SET-PT free radicals scavenging reaction pathway. By comparison, we observe that IP values are significantly higher than BDE ones. Hence, we found that the H-atom transfer mechanism is more preferable than the single-electron transfer mechanism. The antioxidant potential of gallic acid is mainly due to the 3-OH and 4-OH groups, because of their extremely low BDE values.

Also, the low spin densities of 3-O· and 4-O· atoms indicate the stability of 3-OH and 4-OH free radicals, because of the better delocalization of electrons.

The third mechanism involved sequential proton loss-electron transfer (SPLET), in this mechanism O–H heterolytic bond dissociation takes place that results in the formation of ions. This mechanism is favorable in polar solvents which stabilize the ions[24]. We have not focused on SPLET mechanism because all the calculations have been performed in the gas phase while SPLET is not common in gas phase. The BDE values and ionization potential of some phenolic acids are given in Table 3 for comparison. We have found that the BDE values of 3-OH and 4-OH radicals are lower than all other acids. The ionization potential of neutral gallic acid and its free radical is also very low as compared to all the phenolic acids except rosmarinic acid. This comparison clearly demonstrates the high antioxidant potential of gallic acid.

Table 3 BDEs and Ionization potential of some phenolic acid antioxidants

Compound	BDE (kcal/mol)	IP (kcal/mol)
Ferulic acid		167.38[25]
Ferulic acid radical	76.58[25]	
Vanillic acid		174.14[25]
Vanillic acid radical	79.41[25]	
Sinapic acid		160.99[25]
Sinapic acid radical	76.87[25]	
Syringic acid		167.96[25]
Syringic acid radical	79.42[25]	
p-Coumaric acid		175.62[25]
p-Coumaric acid radical	81.20[25]	
p-Hydroxybenzoic acid		190.67[25]
p-Hydroxybenzoic acid radical	85.12[25]	
Rosmarinic acid		128.64[26]
Rosmarinic acid radical	75.64[26]	
Ellagic acid		181.24[27]
Ellagic acid radical	77.00[27]	

4 Conclusions

In this work, we have given a detailed study of gas-phase properties for gallic acid and its free radicals. The two primary indicators of antioxidant activity, BDE and IP were calculated for gallic acid and its free radicals. The results indicate that the BDE values of 3-OH and 4-OH are very low than the other free radicals due to their extraordinary stability, intramolecular hydrogen bonding, and the semiquinone resonance structure. The results also support the fact that intramolecular hydrogen bonding is responsible for the dissimilarity of antioxidant activity among different hydroxyl groups in the gallic acid and its radicals. The hydrogen atom transfer (HAT) is the most favorable mechanism for free radical scavenging. Because the single electron transfer- proton transfer (SET-PT) has less chance to occur due to high ionization potential and sequential proton loss-electron transfer (SPLET) is not favorable due to less stabilization of the ions produced in gas phase.

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