

**QUANTITATIVE RELATIONSHIP BETWEEN ANTIOXIDANT ACTIVITY
OF 4-HYDROXYCINNAMIC ACID DERIVATIVES AND PARTICULARITIES
OF THEIR ELECTRONIC STRUCTURE: DFT STUDY**

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The derivatives of trans-4-hydroxycinnamic acid are well known as food antioxidants which can effectively ‘quench’ free radicals. As a measure of the antioxidant activity of these derivatives, the rate constants of their reaction with the stable radical DPPH* can be used [1].

To reveal the electronic factors determining the rate of reaction between the title compounds and the radical DPPH*, we have studied a number of these compounds using the DFT B3LYP(6-31G) method. The calculated molecular systems along with the corresponding experimental data [1] are given in the Table 1. The two last columns of the Table 1 contain the calculated energy values E of the HOMOs of the neutral molecules and their phenoxide anions. The calculations were performed taking into account the ethanol reaction medium.

Table 1. The experimental and theoretical data

Ns	Compound	$k^{(a)}$ [M ⁻¹ s ⁻¹]	lgk	E _{HOMO} (eV)	
				neutral form	phenoxide anion
1	p-Coumaric acid	1	0	-6.125	-4.413
2	Ferulic acid	240	2.380	-5.894	-4.256
3	Sinapic acid	4000	3.602	-5.792	-4.139
4	Methyl ferulate	278	2.444	-5.860	-4.210
5	Methyl sinapate	20000	4.301	-5.760	-4.093

^(a) The values of k were determined in the ethanol medium at T = 298.15 K.

The two regression equations describing the linear dependences between the quantities lgk and E for both the neutral forms (1) and their phenoxide anions (2) were found:

$$\lg k = 11.257E + 68.809 \quad (1) \quad \text{and} \quad \lg k = 13.120E + 57.957, \quad (2)$$

(R = 0.985; S = 0.320) (R = 0.993; S = 0.226)

whose plots are presented in the Figure 1.

Eq. (2) means that the rate of electron transfer from the phenoxide anion to DPPH* (which is the rate-determining step) depends on its potential energy E_{HOMO}. At the same time, Eq. (1) shows that the other pathway of the studied reaction is also possible. It consists in the electron transfer from the neutral systems 1–5 to the protonated form of DPPH*. So, in our previous work [2] we have shown the similar pathway involving the protonated form of DPPH* takes place also for the reactions of dihydroxyfumaric acid and its dimethyl ethers with DPPH* and includes formation of the charge-transfer complex between reagents.

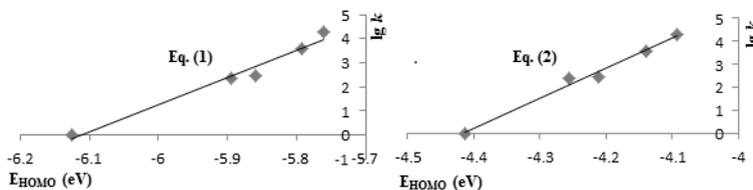


Fig. 1. The graphical view of Eqs. (1) and (2)

1. M.C.Foti, C. Daquino, C. Geraci, J.Org.Chem., 2004, vol. 69, 2309–2314.
2. M. Gorbachev, N. Gorinchov, I. Arsene, Chem. J. Mold. 2015, 10(1), 89–94.