



---

## The Structures and Reactivity of Phenylpropane Units of Lignin

Oleg Kh. Karimov<sup>1\*</sup>, Galina Yu. Kolchina<sup>2</sup>, Eldar M. Movsumzade<sup>3</sup>

<sup>1</sup>Department of General Chemistry Technology, Ufa State Petroleum Technology University, Russia

<sup>2</sup>Department of Chemistry and Chemical Technology, Bashkir State University, Russia

<sup>3</sup>Department of General, Analytical and Applied Chemistry, Ufa State Petroleum Technology University, Russia

**Abstract** In the framework of method of the B3LYP hybrid density functional and the restricted Hartree-Fock method, quantum-chemical calculations of phenylpropane units of lignin. The structures and reactivity of derivatives *p*-oxycinnamic alcohol, i.e. (Z)-4-(3-hydroxyprop-1-en-1-yl)phenol (*p*-coumarol alcohol), (Z)-4-(3-hydroxyprop-1-en-1-yl)-2-methoxyphenol (coniferol alcohol) and (Z)-4-(3-hydroxyprop-1-en-1-yl)-2,6-dimethoxyphenol (synapol alcohol) were studied. Quantitative characteristics of the reactivity of these alcohols are given. It is found that the electronic structure of lignin is determined primarily by the charge distribution in its structural phenylpropane unit. The calculations performed are compared with the results of semi-empirical calculations of other works and with the analysis of the reactivity of compounds using the Fukui function. In the molecules of all model compounds of lignin, the center for nucleophilic attack is the carbon of aromatic ring (E-ring) with a hydroxyl group, and in the molecule of synapol alcohol, this center is also the carbon of the aromatic ring (E-ring) with a methoxy group. In all three compounds, a center with an increased electron density appears on the C $\beta$  carbon atom.

**Keywords** lignin, coumaric alcohol, coniferyl alcohol, synapol alcohol, reactivity

---

### Introduction

Lignin is a naturally occurring biopolymer which is part of wood structure and gives it strength properties. The biosphere contains more than 300 billion tons of lignin at a growth rate of about 20 billion per year [1]. Moreover, a large amount of lignin is produced annually in the pulp and paper industry. Lignin is a complex three-dimensional amorphous polymer consisting of methoxylated phenylpropane units of various types. Today, only 5% of lignin is of commercial value and is used as a low-quality fuel in the field of heat power, or as concrete additive (lignosulfonate) [2]. But the effective utilization of this biopolymer could play an important role in biorefinery conception, because, for example, the chemical structure of lignin allows us to consider it as a valuable raw material for the production of aromatic chemicals from it.

Quantum chemistry methods for modeling the electronic structure of lignin molecules began to be carried out as far back as the 60-70s of the XX century [3,4]. Due to the complex structure of the biopolymer, the study of the structural features of lignin and its effect on the reactivity of the polymer still remains an urgent issue in wood chemistry.

Of particular interest are model lignin compounds, i.e. derivatives of *n*-oxycinnamic alcohol which are the precursors of lignin structural units (monolignols): (Z)-4-(3-hydroxyprop-1-en-1-yl)phenol (*p*-coumarol alcohol) (**I**), (Z)-4-(3-hydroxyprop-1-en-1-yl)-2-methoxyphenol (coniferol alcohol) (**II**) and (Z)-4-(3-hydroxyprop-1-en-1-yl)-2,6-dimethoxyphenol (synapol alcohol) (**III**) (Figure 1). The study of the structure and reactivity of these



compounds opens up new prospects for the development of synthetic lignins or polymers that reproduce their properties since it leads to a greater understanding of the mechanism of lignification.

Previously, attempts were made to describe the electronic structure and propose mechanisms for their further transformation by quantum chemistry methods. For example, in [5], the geometry of coniferol alcohol, its radical and anion was optimized using the semi-empirical MNDO method and the total energy of the molecular structure was calculated. In [6], an attempt was made to characterize the chemical reactivity of these monolignols using the Fukui function. Given the importance of radical chemistry in the study of lignin polymerization, the authors focus on the results associated with the attack of free radicals. According to the results of the study, the highest reactivity is observed in phenolic oxygen and  $\beta$ -carbon.

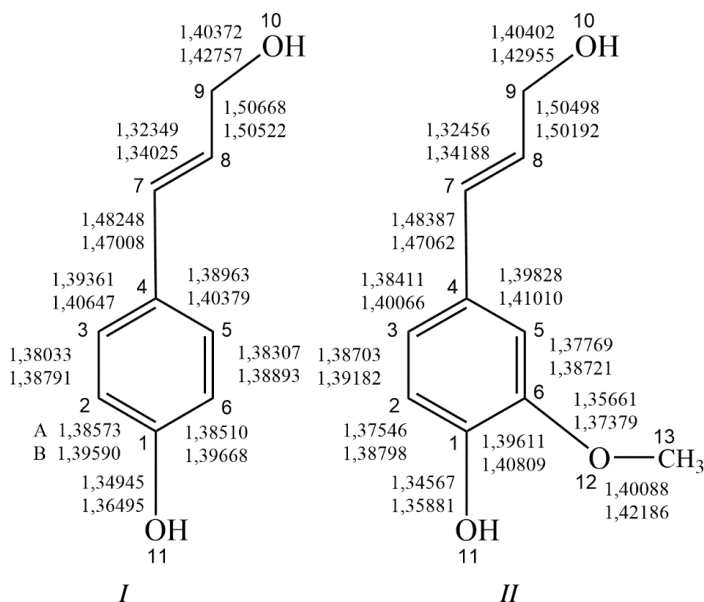
### Materials and Methods

In this work, we present the results of calculating the electronic structure and analysis of reactivity where *n*-oxycinnamic alcohol derivatives - (*Z*)-4-(3-hydroxyprop-1-en-1-yl)phenol (*p*-coumarol alcohol) (**I**), (*Z*)-4-(3-hydroxyprop-1-en-1-yl)-2-methoxyphenol (coniferol alcohol) (**II**) and (*Z*)-4-(3-hydroxyprop-1-en-1-yl)-2,6-dimethoxyphenol (synapol alcohol) (**III**) [optimized using the elegant theory of Hartree-Fock<sup>A</sup>RHF and the <sup>B</sup>B3LYP hybrid density functional method] are selected, the attractiveness of which is due to the high calculation speed [7]. Also, the small size of the molecules makes it possible to calculate quickly, providing consideration of a wide range of methods in a relatively short period of time [8]. The calculations were performed using the FireFly program (PC GAMESS) [9] which is a version of the GAMESS (USA) [10] program with new computing algorithms [11-13].

### Results & Discussion

Figure 1 shows the calculated geometric characteristics of model compounds in the basis of 6-311 (d, p).

The benzene molecule present in the model compound is characterized by two energy-degenerate external filled  $\pi$ -orbitals of  $e_{1g}$  symmetry which have different shapes. Addition of methoxy- and hydroxy groups to the benzene ring leads to shift in the electron density towards the benzene ring and to decrease in the symmetry of the molecule as well as to splitting of these molecular orbitals.



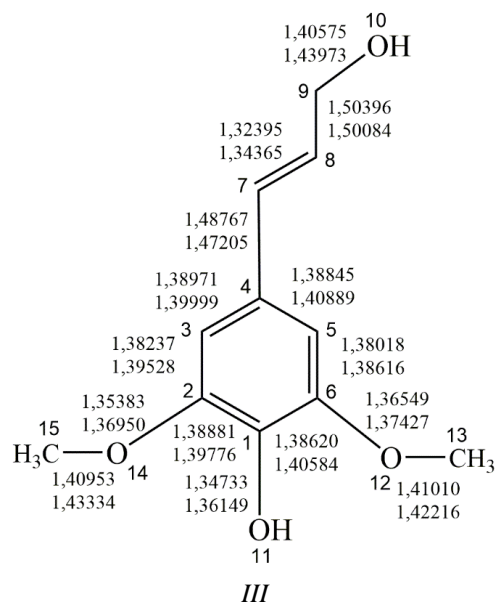


Figure 1: The geometric characteristics of the structural units of lignin calculated by the <sup>A</sup>RHF/6-311 (d, p) and <sup>B</sup>B3LYP/6-311 (d, p) methods: **I** - coumaric alcohol, **II** - coniferyl alcohol, **III** - synapyl alcohol.

Data of geometric characteristics of the calculated compounds show that the structural units of lignin contain hydroxyl groups which can be in the plane of benzene ring but can be turned up to 90° with respect to this plane. In the case of methoxy groups which are also present in coniferyl and synapyl alcohols (compounds **II** and **III**), the methyl group is turned to 90° with respect to the plane of ring, as the most favorable conformation. Moreover, these compounds contain  $\pi,\pi$ -conjugations of the aromatic ring with an aliphatic fragment of molecule that affects the geometric characteristics of the molecule. For compounds **I** and **II**, the  $C_{ap}-C_{\alpha}$  bond length is 1.47 Å, while the value of single bond should be 1.54 Å. A slight deformation  $\angle C_5C_4C_7$  equal to 118.94° and 117.72° respectively for compounds **I** and **III** instead of 120° at  $sp^2$  hybridization indicates the availability of conjugation (Table 1).

**Table 1:** The values of the valence and dihedral angles of structural units of lignin calculated by the <sup>A</sup>RHF/6-311(d,p) and <sup>B</sup>B3LYP/6-311(d,p) methods

Angles	<b>I</b>		<b>II</b>		<b>III</b>	
	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP
$\angle O_{11}C_1C_2$	117.755	117.632	119.998	120.462	119.990	120.789
$\angle C_5C_4C_7$	119.414	118.941	122.081	122.972	119.236	117.724
$\angle C_7C_8C_9$	128.412	128.774	128.527	128.967	128.050	126.704
$\angle C_8C_9O_{10}$	111.590	111.959	111.059	111.196	112.045	112.749
$\angle O_{10}C_9C_8C_7$	141.182	144.033	-137.803	-139.285	120.637	93.414

The use of a charge as a descriptor of attack selectivity of nucleophilic and electrophilic particles allows us to draw the following conclusions. Table 2 shows that the maximum positive charge is concentrated on the atom  $C_1$  (0.156) of the aromatic ring of compound **I** which determines the center of nucleophilic attack. The highest concentration of electron density and hence, the maximum negative charge in the aromatic ring is at the atom  $C_6$  (-0.125) which corresponds to the center of electrophilic attack. According to the orientation rule, the hydroxyl group in the aromatic ring being an electron-donating substituent directs the electrophilic agents to free *o*-positions.



For the aliphatic chain of compound **I**, due to the presence of hydroxyl group at the end atom  $C_\gamma$ , the following distribution of charges is characteristic: the maximum negative charge is located on the  $C_\beta$  atom (-0.152), and the  $C_\beta$  -  $C_\gamma$  linkage is the weakest in this aliphatic fragment (0.1505 Å according to B3LYP method). The data obtained are consistent with the calculated values of Fukui functions [6], according to which the regions near the  $C_\beta$  atom are most suitable for the electrophilic attack in compound **I**, and the regions around the hydroxyl groups both in the aromatic ring and in the aliphatic chain are most suitable for the nucleophilic attack. It was also revealed that the regions near the  $C_\beta$  atom are suitable for free-radical attack.

**Table 2:** The values of charges on atoms according to Mulliken in structural units of lignin calculated by the methods <sup>A</sup>RHF/6-311(d,p) and <sup>B</sup>B3LYP/6-311(d,p)

Atom	<b>I</b>		<b>II</b>		<b>III</b>	
	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP
$C_1$	0.244	0.156	0.230	0.155	0.232	0.152
$C_2$	-0.100	-0.091	-0.092	-0.090	0.236	0.121
$C_3$	-0.087	-0.077	-0.089	-0.067	-0.100	-0.068
$C_4$	-0.074	-0.069	-0.069	-0.075	-0.047	-0.066
$C_5$	-0.073	-0.071	-0.143	-0.109	-0.087	-0.089
$C_6$	-0.139	-0.125	0.251	0.149	0.210	0.174
$C_7$	-0.092	-0.090	-0.081	-0.079	-0.094	-0.079
$C_8$	-0.168	-0.152	-0.216	-0.205	-0.192	-0.194
$C_9$	0.118	-0.009	0.137	0.016	0.137	0.015
$C_{13}$	-	-	-0.023	-0.125	-0.001	-0.123
$C_{15}$	-	-	-	-	-0.006	-0.115
$O_{10}$	-0.469	-0.397	-0.475	-0.401	-0.470	-0.401
$O_{11}$	-0.451	-0.359	-0.460	-0.356	-0.464	-0.362
$O_{12}$	-	-	-0.520	-0.406	-0.525	-0.411
$O_{14}$	-	-	-	-	-0.488	-0.364

The Mulliken charge distribution on the carbon atoms in the aromatic ring which form the molecule **II** is such that the maximum positive charge is concentrated on the  $C_1$  atom (0.155), and the maximum negative charge is on  $C_5$  atom. In the aliphatic chain, the maximum and the only positive charge is concentrated on the  $C_\gamma$  atom (0.016), and the maximum negative charge is on the  $C_\beta$  atom (-0.205). The reactivity of the hydroxyl group is probably related to the high electronegativity of oxygen atoms. The calculated data are also consistent with the calculated values of the Fukui functions [6] where a high reactivity of the hydroxyl group at the aromatic ring with respect to nucleophilic reagents is reported.

The chemical structure features of compound **III** are reflected in its electronic structure. In the aromatic ring, the maximum positive charge is concentrated on the  $C_6$  atom (0.174), and the maximum negative charge is on the  $C_5$  atom (-0.089). In the aliphatic chain, the maximum positive charge is concentrated on the  $C_\gamma$  atom (0.015), and the maximum negative charge is on the carbon atom  $C_\beta$  (-0.194). Thus, the most suitable region for nucleophilic attack is the region around the hydroxyl group in the aliphatic chain.

Given that there are differences in the charge distribution of the studied molecules, a number of significant analogies can also be noted. The lone-pair electrons of oxygen atom of the hydroxy group can be overlapped by the  $\pi$ -electron cloud of the aromatic ring which can lead to the formation of high electron density at the positions. It has been established that at positions 3, 4, 5 a negative charge is concentrated on all carbon atoms. The oxygen atom in the methoxy groups concentrates the maximum negative charge on itself which leads to the appearance of deficit of electron density on the atoms  $C_2$  (**II**),  $C_6$  (**II**, **III**).

All three studied model alcohol molecules have a double bond aliphatic fragment attached to aromatic ring. Thus, a center with increased electron density appears on the carbon atom  $C_\beta$  (**I** = -0.152, **II** = -0.205, **III** = -0.194) which is consistent with the calculations of [6]. All negative charges of carbon atoms in the aromatic ring are compensated by



positive charges on hydrogen atoms, and positive charges are compensated by negative charges of oxygen atoms of hydroxy and methoxy groups.

It was also studied that for all the studied model structures, a significant positive charge is concentrated on the carbon atoms of the methoxy groups, which determines the  $\delta^+$  position and indicates a deficit in electron density.

Table 3 presents the calculation of the main energy characteristics of model compounds. The calculated data of the minimum energy of compound **II** are consistent with the calculated value by the MNDO method [5] which amounted to -12319.279 eV.

The studied compounds, as can be seen from Table 3 (according to the B3LYP method) are electrophiles. The boundary molecular orbital (LUMO of electrophile) is separated from other molecular orbitals by the energy gap of more than 1 eV. The calculated difference of the boundary orbitals shows that the most unstable compound is compound **II** which concentrates the minimum value of ionization potential.

**Table 3:** The values of the main energy characteristics of the structural units of lignin calculated by the <sup>A</sup>RHF/6-311(d,p) and <sup>B</sup>B3LYP/6-311(d,p) methods

Method of calculating	I		II		III	
	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP
HOMO [eV]	-8.120	-5.889	-7.959	-5.692	-8.251	-5.738
LUMO [eV]	3.267	-0.791	3.134	-0.871	3.139	-1.033
$\eta$ [eV]	5.694	2.549	5.546	2.410	5.695	2.353
S [eV]	0.088	0.196	0.090	0.207	0.088	0.212
$E_{\min}$ [eV]	-13509.059	-13592.780	-16608.781	-16710.057	-19708.190	-19826.993

## Conclusion

Based on quantum chemical calculations, it was found that the electronic structure of lignin is determined primarily by the charge distribution in its structural phenylpropane unit.

Based on the foregoing and studies, it follows that the considered methods RHF/6-311 (d, p) and B3LYP/6-311 (d, p) allow us to describe the geometric and electronic characteristics of model structural units of lignin.

Using the methods of quantum chemistry, the structural units of lignin were optimized, and the geometric, electronic, and energy characteristics of the molecules under study were calculated. Based on the results of these values, the series of reactivity of carbon and oxygen atoms of the studied molecules in electrophilic-nucleophilic reactions are arranged. For coumaric alcohol (**I**), the only carbon atom  $C_1$  has a positive charge, in the series of atoms with negative charges, the reactivity is  $C_8 > C_6 > C_2 > C_7 > C_3 > C_5 > C_4 > C_9$  and  $O_{10} > O_{11}$ ; for coniferyl alcohol (**II**), respectively  $C_1 > C_6 > C_9$  and  $C_8 > C_{13} > C_5 > C_2 > C_7 > C_4 > C_3$  and  $O_{12} > O_{10} > O_{11}$ ; for synapyl alcohol (**III**),  $C_1 > C_6 > C_2 > C_9$  and  $C_8 > C_{13} > C_{15} > C_5 > C_7 > C_3 > C_4$  and  $O_{12} > O_{10} > O_{14} > O_{11}$ .

The presence of phenolic hydroxyl leads to high electron density compound at positions 3, 4, 5. The highest positive charge in all compounds is localized on the carbon atom  $C_1$  conjugated to the hydroxyl group which leads to reactivity with nucleophilic reagents. The largest negative charge in all compounds is localized on the  $C_\beta$  ( $C_8$ ) atom. A positive charge is concentrated on the carbon atoms in the methoxy groups of synapyl alcohol at positions 2 and 6 of the benzene ring, indicating the possibility of nucleophilic substitution reactions. The results obtained are consistent with the method for evaluation of reactivity using the Fukui functions.

## References

- [1]. Alekhina M., Ershova O., Ebert A., Heikkinen S. and Sixta H. (2015). Softwood kraft lignin for value-added applications: Fractionation and structural characterization. *Ind. Crops Prod.*, 66: 220–228.
- [2]. Li C., Zhao X., Wang A., Huber G.W. and Zhang T. (2015). Catalytic Transformation of Lignin for the Production of Chemicals and Fuels. *Chem. Rev.*, 115: 11559–11624.
- [3]. Heiter, C., Dimmel, D.R. & Schmidt, J.A. (2010). *Lignin and Lignans. Advances in Chemistry*, CRC Press, New York, 636.



- [4]. Shevchenko S.M. (1994). Theoretical approaches to lignin chemistry. *Croatica chemical acta.*, 67 (1): 95-124.
- [5]. Elder T.J. and Worley S.D. (1984). The application of molecular orbital calculations to wood chemistry. *Wood Sci. Technol.*, 18: 307-315.
- [6]. Martinez C., Rivera J.L., Herrera R., Rico J.L., Flores N., Rutiaga J.G. and Lopez P. (2008). Evaluation of the chemical reactivity in ligninprecursors using the Fukui function. *J. Mol Model.*, 14: 77–81.
- [7]. KolchinaG.Yu., Movsum-zade N.Ch., BakhtinaA.Yu. and Movsumzade E.M. (2016). Overview of the main achievements of mankind in quantum chemistry. *Oil & gas chemistry*, 1: 51-60.
- [8]. KolchinaG.Yu., Movsum-zade N.Ch., BakhtinaA.Yu. and Movsumzade E.M. (2015). Origin and chronology of the stages development quantum chemistry. *History and pedagogy of natural science*, 4: 34-43.
- [9]. Alex A. Granovsky, Firefly version 7.1.G, <http://classic.chem.msu.su/gran/firefly/index.html>.
- [10]. Schmidt M.W., Baldrige K.K., Boatz J.A., Elbert S.T., Gordon M.S., Jensen J.H., Koseki S., Matsunaga N., Nguyen K.A., Su S., Windus T.L., Dupuis M. and Montgomery J.A. (1993). General Atomic and Molecular Electronic Structure System. *Comput. Chem. Eng.*, 14: 1347-1363.
- [11]. Yang W. and Mortier W. (1986). The use of global and local molecular parameters for the analysis of the gas-phase basicity of amines. *J. Amer. Chem. Soc.*, 108: 5708-5711.
- [12]. Cioslowski J., Martinov M. and Mixon S.T. (1993). Atomic Fukui indexes from the topological theory of atoms in molecules applied to Hartree-Fock and correlated electron densities. *J. Phys. Chem.*, 97: 10948-10951.
- [13]. Lee C., Yang W. and Parr R. (1988). Local softness and chemical reactivity in the molecules CO, SCN- and H<sub>2</sub>CO. *J. Mol. Struct. (Theochem)*, 163: 305-313.

