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Research Article / Araştırma Makalesi

A STUDY ON THE CHEMICAL PROPERTIES OF EUGENOL AND EUGENOL ACETATE, CLOVE ESSENTIAL OILS

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ABSTRACT

Eugenol and eugenol acetate are a clove essential oil getting from hydrodistilltion of Syzygium aromaticum's buds and leaves. It has antimicrobial, antioxidant, analgesic, anticancer activities and used for protecting foods from microorganisms , used as tradational medicine. Eugenol is eager to dissolve in blood and give reaction to radicalic forms of other moleculues. Because of that; It slows cancer cells formation by preventing the radicalic damage.
Keywords: Clove, eugenol, eugenol acetate, DFT and HF.

KARANFİL UÇUCU YAĞLARINDAN EUGENOL VE EUGENOL ASETATIN KİMYASAL ÖZELLİKLERİ ÜZERİNE BİR ÇALIŞMA

ÖZ

Eugenol va Eugenol Asetat karanfilin tomurcuk ve yapraklarından hidrolizasyon ile elde edilen esansiyel bir yağdır. Gıdaları mikroorganizmalardan korumak için geleneksel olarak kullanılan antimikrobik, antioksidan, analjezik, anti-kanser aktiviteleri vardır. Eugenol kanda çözünürlüğü olan ve diğer moleküllerin radikalik formlarına karşı reaksiyon vermeye isteklidir. Bu özelliğinden dolayı radikalik hasarları önleyerek kanser hücrelerini yavaşlatmaktadır.
Anahtar Sözcükler: Karanfil, eugenol, eugenol acetate, DFT and HF.

1. INTRODUCTION

Clove has been used as a spice for hundred years. It is also used as antibacterial, antispasmodic, antiparasitic, carminative, diarrhea and chronic gastiritis[1,2]. Its main volatile oil, eugenol has pharmacological proporties such as antimicrobial, antioxidant, anticarcinogenic, antimutagenic, antifunigant, anesthetic and analgesic effects [3-5]. Clove, giving smell and taste, is called " eugenol " as essential oil . Eugenol , clove extract , and a major portion of plant is said to be antioxidative items. In a study, clove buds isolated from the extracts and examined antioxidant properties of them by two different methods to evaluate. Result of these, the main component of the cloves for both of them is found that eugenol, and eugenol acetate [6,7].

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Clove and oregano essential oil on cotton seed oil maintained at room temperature and they show the antioxidative effect and this effect is higher than in the clove than from the others [8]. Activity of clove, sage, thyme and ginger on meat fat is dependent on the concentration of the antioxidant were detected. Among these substances, It has been determined that clove species are most effective, the ginger and thyme are the least effective [9]. In a study, ıt has been dtermined that the antioxidant activity of eugenol is due to the presence of its phenolic group at low concentration [10].

Eugenol has anti-inflammatory properties and treatment of cervical cancer [11]. When it is used for cancer cells and It decreases inracellular nonprotein thiols and it has important agent to induced apoptosis in HL60 and it is a potential chemopreventive agent against colon cancer [12,13]. It was an inhibitor of melanoma cell proliferation by getting a significant tumor growth delay [14]. Eugenol and 2-methoxyestradiol inhibited the growth of prostate cancer cells and caused apoptosis [15,16]. Eugenol showed better antioxidant activity than Geraniol, Geranial Acetate and Gingerol[17]. Antiradical activity of extract oil of eugenol in clove is so close to (2,2_diphenyl_1_picrylhydrazyl (DPPH) and more than (2,6_ditret_ _butyl _4_hydroxytoluene, (BHT) [18].

2. MATERIALS AND METHODS

The electronic structures of eugenol and eugenol acetate are commonly studied by DFT and HF, included in DFT and HF methods, containing Becke's gradient correction for exchange, and RB3LYP methods were used for quantum chemical calculations and geometry optimization. In the case of the RB3LYP functional, the non-local correlation was provided by the LYP expression, and the correction was carried out by means of the 6-31+g(d,p) functional. The thermodynamical values in blood and gas were calculated by using DFT and HF method. The correction was carried out by means of the 6-31+g(d,p) functional. These methods and fully optimized geometric structure of the compounds using this method were determined and evaluated [28].

3. RESULT AND DISCUSSION

The active compounds of Eugenol and Eugenol Acetate's moleculer structures are given in the Figure 1 and Figure 2.

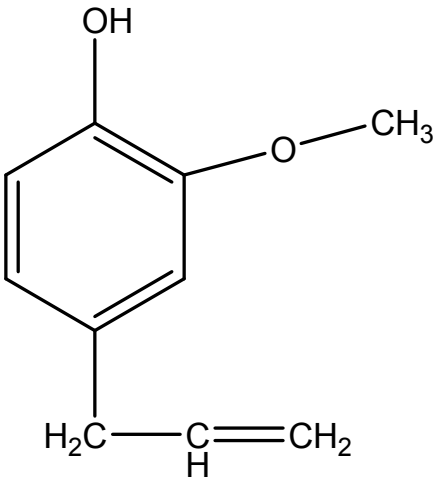

Figure 1. Moleculer Structure of Eugenol

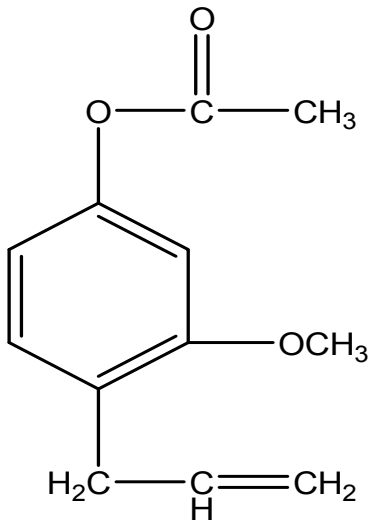

Figure 2. Moleculer Structure of Eugenol Acetate

In the table 1; The Gibbs Free Energy,HOMO,LUMO, Δ (HOMO-LUMO) and Dipol moments of Eugenol and Eugenol Acetate in blood by using DFT are given.

Table 1. The Eugenol, Eugenol Acetate values of ΔG, HOMO, LUMO, Δ (HOMO-LUMO) and Dipol Moment

DFT (In Blood)	ΔG (Hartree)	HOMO (eV)	LUMO (eV)	Δ (HOMO-LUMO) (eV)	Dipol Moment (Debye(D)
Eugenol	-538.590987	-0.00713	0.00163	-0.00876	3.9427
Eugenol Acetate	-691.224065	-0.00011	0.00419	-0.00430	3.0519

According to the molecular orbital theory; when it occurs atoms within molecules necessary bond creates atomic orbitals mixed molecule of molecular orbitals leading to formation they approach each other. These orbitals can be considered as one where there is greater probability of electrons in molecules[19]. HOMO ve LUMO enerji değerleri arasındaki boşluk molekülün kimyasal kararlılığı olarak tanımlanır [20]. When we looked the gibbs free energy of Eugenol and Eugenol Acetate in the table 1; Eugenol Acetate is higher than eugenol. So,eugenol acetate is more stable than eugenol. According to HOMO,LUMO and HOMO-LUMO differnces;Eugenol acetate behaves as acid due to the higher HOMO than eugenol. The stability of eugenol acetate is higher than eugenol because of the band gap is bigger than eugenol. Ha emphasized that flavonoids having OH groups demonstrated the strong inhibitory effect [29]. Eugenol is unstable and eager to accept electrons from radicalic forms.

In the table 2; The Gibbs Free Energy,HOMO,LUMO, Δ (HOMO-LUMO) and Dipol moments of Eugenol and Eugenol Acetate in blood by using HF are given.

Table 2. The Eugenol, Eugenol Acetate values of ΔG, HOMO, LUMO, Δ (HOMO-LUMO) and Dipol Moment

HF (In Blood)	ΔG (Hartree)	HOMO (eV)	LUMO (eV)	Δ (HOMO-LUMO) (eV)	Dipol Moment (Debye(D)
Eugenol	-535.228333	-0.30309	0.07047	-0.37356	3.9687
Eugenol Acetate	-686.985461	-0.31931	0.06920	-0.38851	3.2094

The gibbs free energy of Eugenol and Eugenol Acetate in the table 2; Eugenol Acetate is higher than eugenol. So,eugenol acetate is more stable than eugenol. According to HOMO,LUMO and HOMO-LUMO differnces; eugenol acetate behaves as acid due to the higher HOMO than eugenol. The stability of eugenol acetate is higher than eugenol because of the band gap is bigger than eugenol. Eugenol is unstable and eager to accept electrons from radicalic forms. Therefore, In blood the values of HOMO,LUMO, Δ (HOMO-LUMO) and dipol moments are parallel, close to each other by using DFT and HF.

In the table 3; The Gibbs Free Energy,HOMO,LUMO, Δ (HOMO-LUMO) and Dipol moments of Eugenol and Eugenol Acetate in gas form by using DFT are given.

Table 3. The Eugenol, Eugenol Acetate values of ΔG, HOMO, LUMO, Δ (HOMO-LUMO) and Dipol Moment

HF (Gas)	ΔG (Hartree)	HOMO (eV)	LUMO (eV)	Δ (HOMO-LUMO) (eV)	Dipol Moment (Debye(D)
Eugenol	-535.203138	-0.28835	0.14936	-0.43771	2.9244
Eugenol Acetate	-686.955181	-0.30618	0.14156	-0.44774	2.2030

When we looked the gibbs free energy of Eugenol and Eugenol Acetate in the table 3; in gas form, Eugenol Acetate is higher than eugenol. So,eugenol acetate is more stable than eugenol. According to HOMO,LUMO and HOMO-LUMO differnces; eugenol acetate behaves as an acid due to the higher HOMO than eugenol. The stability of eugenol acetate is higher than eugenol because of the band gap is bigger than eugenol. Eugenol is unstable and eager to accept electrons from radicalic forms.

In the table 4; The Gibbs Free Energy,HOMO,LUMO, Δ (HOMO-LUMO) and Dipol moments of Eugenol and Eugenol Acetate in gas form by using HF are given.

Table 4. The Eugenol, Eugenol Acetate values of ΔG, HOMO, LUMO, Δ (HOMO-LUMO) and Dipol Moment

DFT (Gas)	ΔG (Hartree)	HOMO (eV)	LUMO (eV)	Δ (HOMO-LUMO) (eV)	Dipol Moment (Debye(D)
Eugenol	-538.558470	-0.19914	0.00679	-0.20593	2.8179
Eugenol Acetate	-691.186092	-0.01463	0.00949	-0.02412	1.2318

The gibbs free energy of Eugenol and Eugenol Acetate in the table 4 in gas form; Eugenol Acetate is higher than eugenol. So,eugenol acetate is more stable than eugenol. According to HOMO,LUMO and HOMO-LUMO differnces; eugenol acetate behaves as acid due to the higher HOMO than eugenol. The stability of eugenol acetate is higher than eugenol because of the band gap is bigger than eugenol. Eugenol is unstable and eager to accept electrons from radicalic forms. Therefore, In gas form, the values of HOMO, LUMO, Δ (HOMO-LUMO) and dipol moment are parallel, close to each other by using DFT and HF.

Calculation of the polarity of the measurement of dipole moment, considering the dipole moment vector of each bond is present in the form of the resultant moment vector [21]. The solubility of eugenol is more higher than eugenol acetate in blood from the gas form by using DFT and HF. DFT and HF calculation parallel to each other. So,we can conclude that: eugenol dissolves in blood more than eugenol acetate and it is eager to react to the radicalic forms.

Ionization potential (I) is the energy to move away one e^- from the molecule in gas phase.

$I= -E_{HOMO}$

Ionization potential of Eugenol acetate in gas phase by using HF is 0.30618eV. It is higher than from the others in Table 3.

Electron affinity (A) is the enery of a molecule added one e^- .

$A= -E_{LUMO}$

Electron affinity of Eugenol acetate in blood by using DFT is 0.00419 eV. It is higher than from the others in Table 1.

Electronegativity (X) of a molecule is the power of the acception electron.

$X= I+A/2$

In Table 4; Electronegativity of Eugenol in gas form by using DFT is

0.096175 eV. It is higher than from the others. İt is the most electronegatif molecule [22].

Chemical hardness (n) is the diffuculty of mobility of electron in a molecule.

$\eta= I-A/2$

In Table 4;Chemical hardness of Eugenol in blood by using DFT is

0.096175 eV. Eugenol is the most rijid molecule [23].

Chemical softness (n) is the mobility of electron in a molecule.

$S= 1/ 2 \eta$ [24].

In Table 1; Chemical softness of Eugenol Acetate in blood by using DFT is

24.5098 eV. Eugenol Acetate is the less stable. It is the most reactive molecule in clove essential oil.

The chemical potential (Pi) defined as the negative of electronegativity (X) $Pi=-(I+A/2)$ Moreover some researches have proposed the electrophilic power of a molecule as $\omega=(Pi)^2 /2 \eta$ [25-27].

In Table1; Electrophilic power of Eugenol in gas form by using DFT is

0.00925 eV.

The mos elctrophilic of them in clove is Eugenol.

The hyrogen bonds of Eugenol and Eugenol Acetate are given in the Figure 3 and Figure 4. Hydrogen bond formations are shown on the moleculer shapes of these two molecules on the Figure 3 and 4.

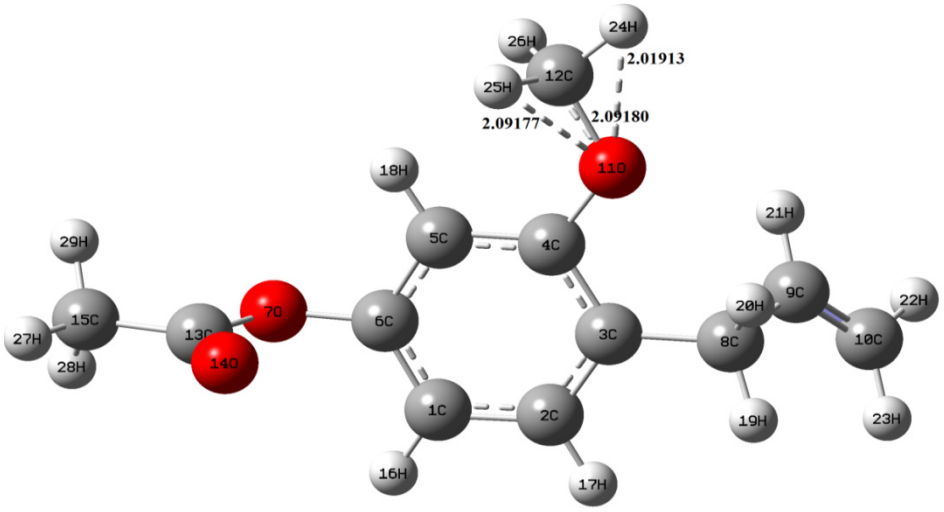

Figure 3. Hydrogen bonds of Eugenol Acetate

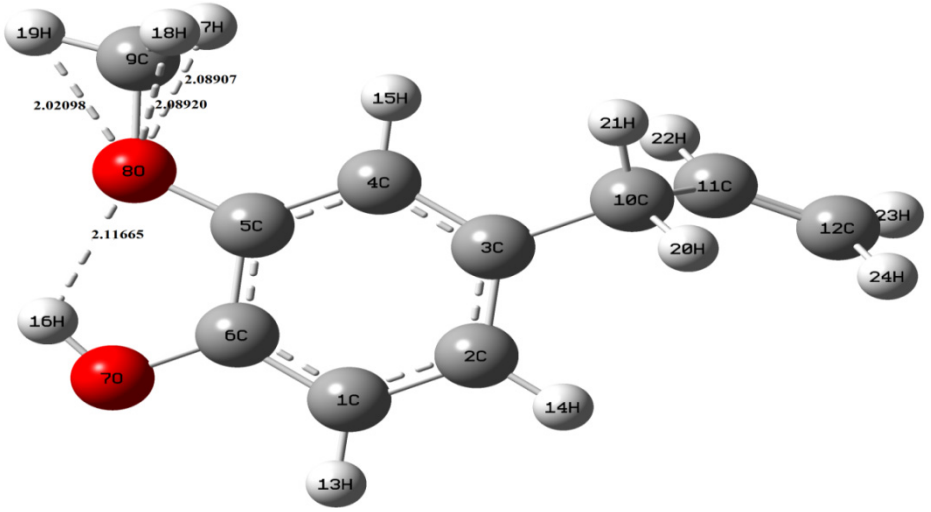

Figure 4. Hydrogen bonds of Eugenol

The diferences of gibbs free energy of Eugenol and Eugenol Acetate may be interaction of O with H atoms. The formation of H bonds between these molecules. They are shown in the Figure 3 and Figure 3.

4. CONCLUSIONS

In general,the proporties of eugenol and eugenol acetate as theoretical by using DFT and HF . The stability and solubilty of Eugenol in blood is more than eugenol acetate. Moreover, Because of the hydrogen bonds of eugenol acetate, the gibbs free energy of this molecule is higher than Eugenol. When we looked the table 1,2,3,4; We can say that all values in the gas and blood form of eugenol and eugenol acetate as the Gibbs Free Energy are parellel to each other by two methods (DFT and HF).

We can conclude that my study is accurete as theoritical by looking these values by DFT and HF.According to HOMO-LUMO differences in table 1; the difeerence between Eugenol is 0.00876 and for Eugenol Acetate is 0.00430. Eugenol is more stable than Eugenol Acetate. Eugenol has higher dipol moment than Eugenol Acetate. Therefore we can assume that; Eugenol is eager to dissolve in blood and give reaction to radicalic forms of other moleculues. Because of that; It slows cancer cells formation by preventing the radicalic damage.

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Notes

The authors declare no competing financial interest.

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