Comparison Study of the Stab ility and Properties of Vibrational Spectra For Some Flavonols Compounds by Quantum Mechanical Calculations

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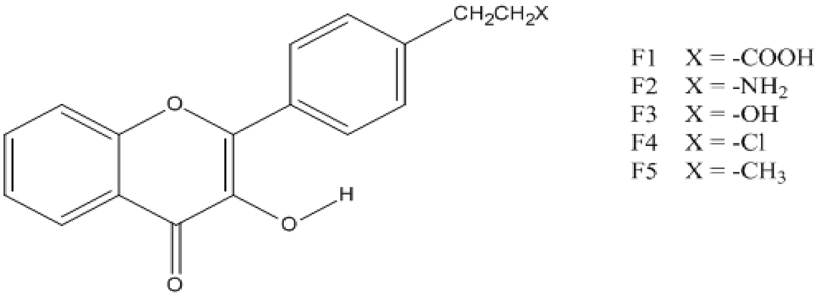
Absetract

Flavonoles compounds which have chemical structures[$C_{18}H_{14}O_5$(F1), $C_{17}H_{15}NO_3$(F2), $C_{17}H_{14}O_4$(F3), $C_{17}H_{13}ClO_3$(F4), and $C_{18}H_{16}O_3$(F5)] were selected in this work.



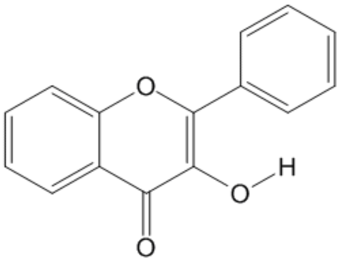
A complete and detailed study of the flavonoles compounds is performed by popular quantum mechanical methods. It includes vibrational spectra, and electronic spectra of organic molecules. Semi-empirical methods (ZINDO/1, PM3 and ZINDO/S) were carried out to evaluate heat of formation $\Delta H^{\circ}f$, binding energy ΔEb, dipole moment for all compounds. Also vibration frequencies and electronic transitions of flavonoles compounds were calculated.

Keywords: *Flavonols, Standard enthalpy of formation, Vibrational spectra, Binding energy, Dipole moment.*

Introduction

Flavonoids are polyphenolic compounds which occur ubiquitously in foods of plant origin; they are extremely important because of their health effects. It has been predicted which average intake of all flavonoids is several grams per day [1]. Flavonoids comprise a group of phenolic secondary plant metabolites that are widespread in nature. Major flavonoids are: flavans, flavanones, flavones, flavonols, flavanols, flavanonols, cetechins, anthocyanidins and isoflavones. [2]. Flavonoids comprise the largest group of phenolic pigments in fruits, vegetables and grain used by the chemical, pharmaceutical and food industries [3,4]. Identified flavonoids have anti-oxidant, anti-allergic, anti-inflammatory, antiviral, vase-protecting and anti-hepatotoxic activities [5-9].

Flavonols are a class of flavonoids which have the 3-hydroxyflavone backbone (IUPAC name: 3-hydroxy-2-phenylchromen-4-one). Their diversity stems from the different positions the phenolic -OH groups. They are distinct from flavanols (with an "a", like catechin), another class of flavonoids.



Flavonols are present in a wide variety of fruits and vegetables. In Western populations, estimated daily intake is in the range of (20–50) mg per day for flavonols. Individual intake varies depending on the type of diet consumed [10]. The detailed knowledge of flavonoles molecular structures, both from energetic and geometric viewpoints, is of great importance to gain a deeper insight into their possible therapeutic applications[11]. Computational chemistry methods are one of the most powerful tools to achieve advances in this field, They provide very valuable information at moderate economical costs, prior to time-consuming and expensive experimental or clinical studies, and allow inferring the effects of different molecular features on compounds properties[12,13]. With the rise of powerful computers, the scientific community has been able to run experiments using quantum mechanical methods to efficiently and quickly predict valuable structural and spectral data. Yet, there are numerous quantum mechanical programs and methods available to carry out these computations [14]. Therefore, the question arises as to which are the most accurate and efficient? In this study, the program of Hyperchem was used in calculation of flavonols. The semi-empirical methods in the Hyperchem package which were studied are PM3 and ZINDO/S. The semi-empirical methods make approximations to make these calculations much faster than more sophisticated methods. An example of an approximation made is the two electron model of the Hamiltonian in Schrodinger’s equation being parameterized and calculations carried out normally otherwise [15].

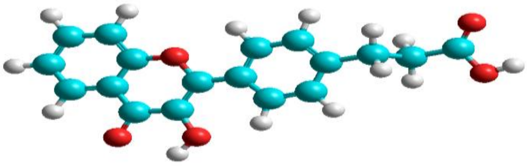
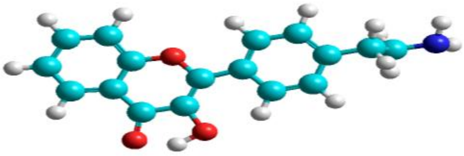
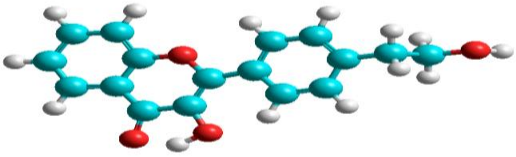
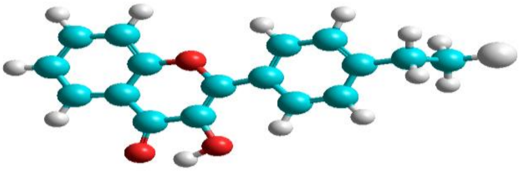
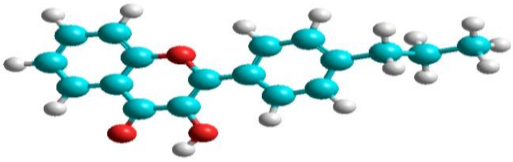
Hyperchem Experiments

As mentioned before, Hyperchem was used to test the semi-empirical and *ab initio* levels of calculation in this study. Each compound shown before was created in Hyperchem and then their geometries were optimized. These optimized geometries in the semi-empirical method of PM3 were computed for all compounds, this gave the theoretical infrared spectral data for Flavonols.

Computational Method

Molecular geometry optimization, energies, vibrational spectra and electronic spectra calculations were performed with the hyper chem.8 softwere by using semiempirical methods, the ZINDO/1 method used to calculate total energy heat of formation (ΔH˚f), binding energy (ΔE_b) and dipole moment (μ) for Flavonoles compounds in **Table 2**.

Table 1: The Chemical Structure and Molecular Weight of Flavonoles Compounds

Molecular Formula	Chemical Structure	Molecular Wight	Symbol
$C_{18}H_{14}O_5$		**310.30**	**F1**
$C_{17}H_{15}NO_3$		**281.3059**	**F2**
$C_{17}H_{14}O_4$		**282.29066**	**F3**
$C_{17}H_{13}ClO_3$		**300.736**	**F4**
$C_{18}H_{16}O_3$		**280.317**	**F5**

PM3 used for evaluating the wave number for the compounds at the optimized geometry to ensure that no imaginary frequencies were obtained confirming which it corresponds to a local minimum on the potential energy surface,**Table 3.** ZINDO/S method used to calculate electronic transitions for these compounds.

Results and Discussion

Table 2: Conformation Energetic In Kcal.mol^{-1} [Standard Enthalpy Of Formation ($\Delta H°_f$), Binding Energy (ΔE_b) and Dipole Moment (μ) (in Debye)] For Flavonols.

Compounds	**ZINDO/1**			
	Total energy	**$\Delta H°_f$**	**ΔE_b**	**μ**
F1	-132500.47	-8235.15	-12338.39	8.414
F2	-114276.96	-7895.19	-11873.53	6.327
F3	-117783.52	-7751.85	-11624.65	5.155
F4	-116163.89	-7629.98	-11420.09	6.705
F5	-112079.17	-8166.72	-12255.05	4.670

As shown in **Table 2** the binding energy and energy required for formation of the compounds arranged as follow.

$$E_b\ F4 > Eb\ F3 > Eb\ F2 > Eb\ F5 > Eb\ F1$$

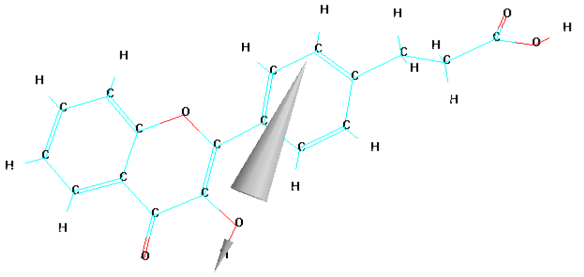
$$\Delta H°_f\ F4 > \Delta H°_f\ F3 > \Delta H°_f\ F2 > \Delta H°_f\ F5 > \Delta H°_f\ F1$$

Heat of formation of F1 compound is smallar than other compounds thus, we expected that, the formed compound is to be thermodynamically more stable.

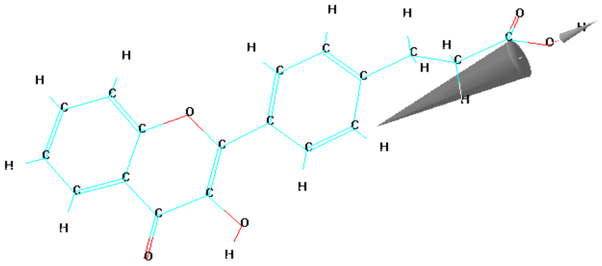
The strength of the dipole moment depends upon the difference in the electronegativity of the atoms in the molecule, therefore F1 compound has the bigger dipole moment because it contains five oxygen atom. In the second order comes F4 compound because it contains three oxygen atom and chlorine atom.

Table 3: Comparison Of Theoretical Vibrational Frequencies (Stretching in cm^{-1}) For The Active Chemical Group In Flavonols Compounds.

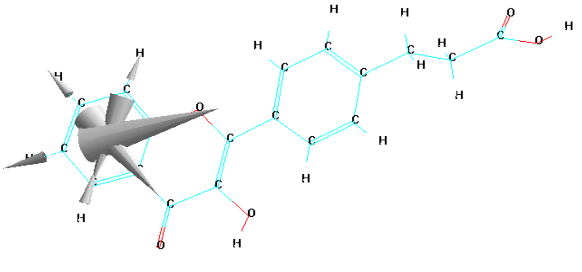
Bond Frequency	F1	F2	F3	F4	F5
ν (N-H)	–	33523.42 ,3388.23	–	–	–
ν C−H aromatic	3075.72	3075.63	3075.65	3075.93	3086.64
ν C=C aromatic	1644.07	1643.66	1643.91	1643.72	1697.62
ν C=C olefin	1841.19	1839.79	1839.85	1840.86	1833.22
ν C−H aliphatic	2955.80	2910.60	2972.04	2951.26	2993.91
ν O−H carboxylic	3855.76	–	–	–	–
ν O−H phenolic	3849.11	3849.39	3850.21-3909.71	3849.04	3833.71
ν C=O	1934.09	1933.45	1932.92	1933.15	1882.44
ν C=O carboxylic	1977.71	–	–	–	–



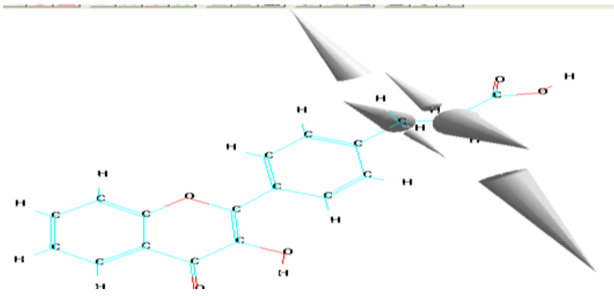
ν (O−H) phenolic 3749.11 cm^{-1}



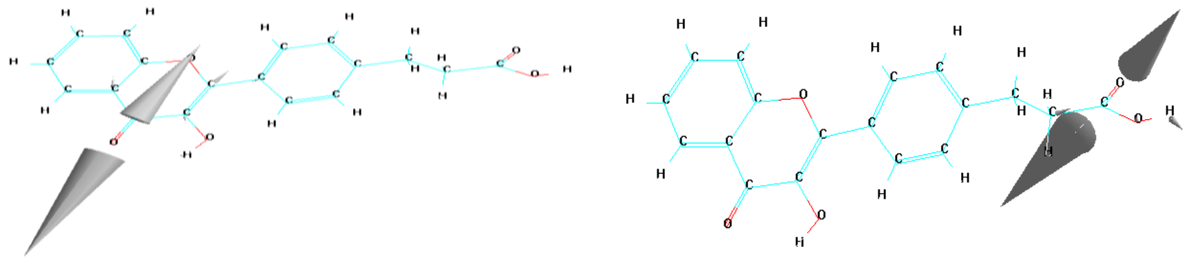
ν (O−H) carboxylic cm^{-1} 3755.76



3075.72cm^{-1} ν (C−H) aromatic

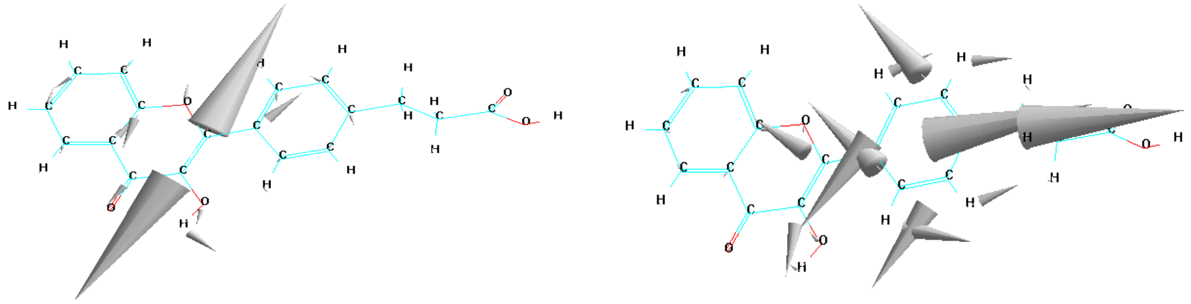


ν (C−H) aliphatic 2955.80 cm^{-1}



cm-1 ν (C=O) 1834.09

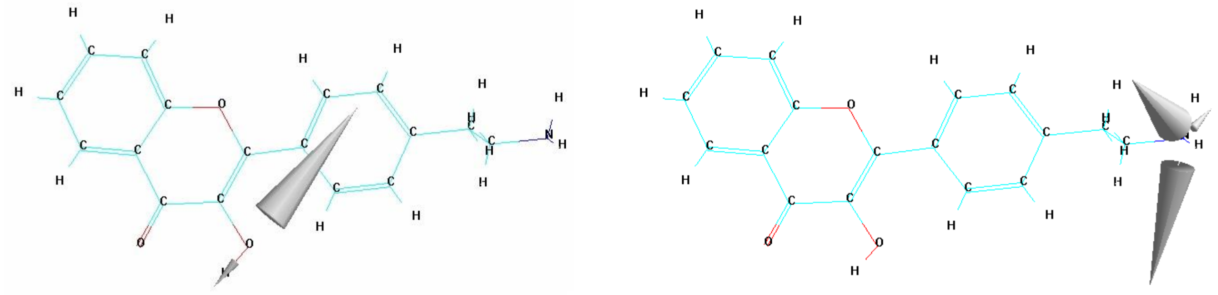
1877.71 cm-1 ν (C=O) carboxylic



1641.19 cm-1 ν (C=C) olfenic

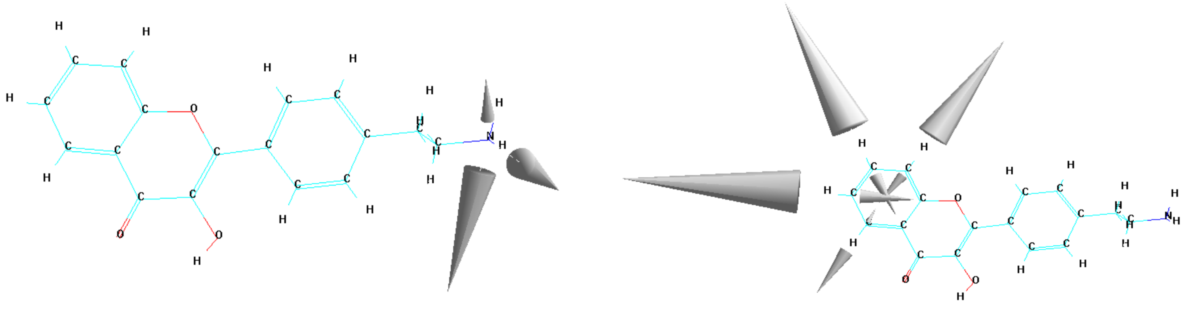
1644.07cm-1 ν (C=C) aromatic

Fig. 1: Theoretical Vibrational Modes (Stretching) For The Active Chemical Group In F1 Compound



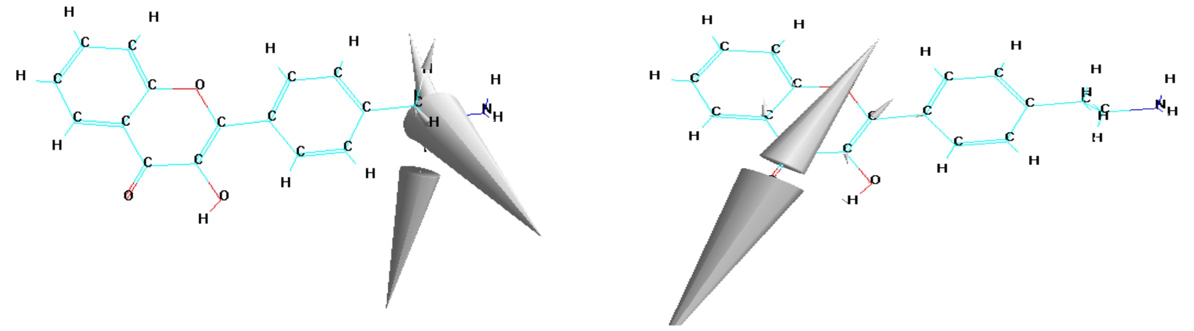
3749.39 cm^{-1} ν (O−H) phenolic

3523.42 cm^{-1} ν (N−H)

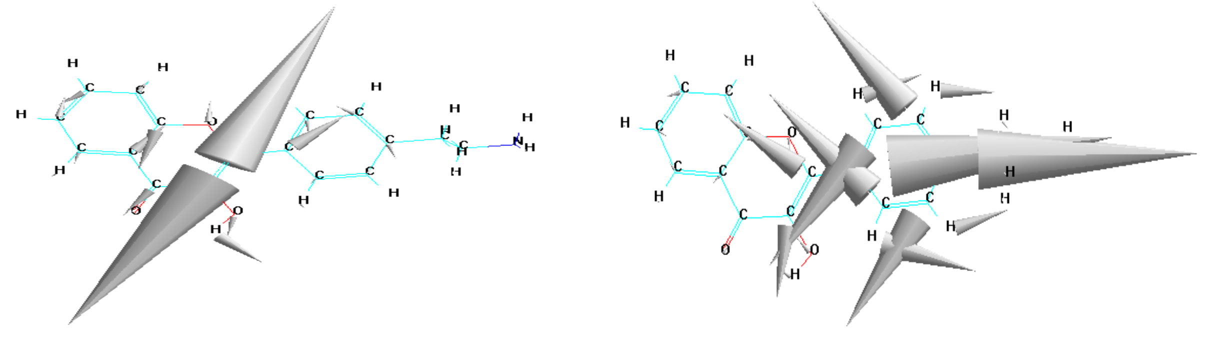


3388.23 cm^{-1} ν (N−H)

3075.63 cm^{-1} ν (C−H)

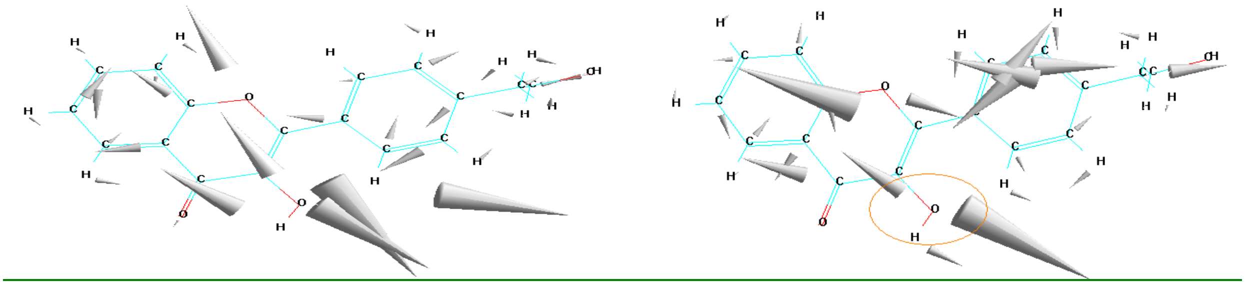


ν (C−H) aliphatic cm^{-1} 2910.60 1833.45 cm^{-1} ν (C=O)

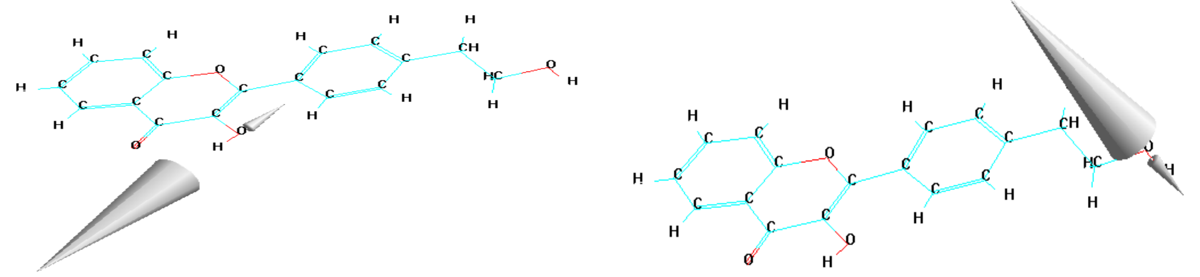


1639.79 cm^{-1} ν (C=C) 1643.66 cm^{-1} ν (C=C) aromatic

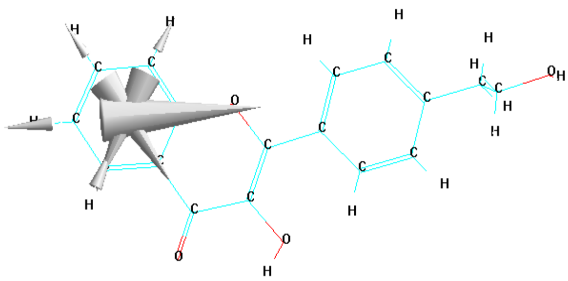
Fig. 2: Theoretical Vibrational Modes (Stretching) For The Active Chemical Group In F2 Compound



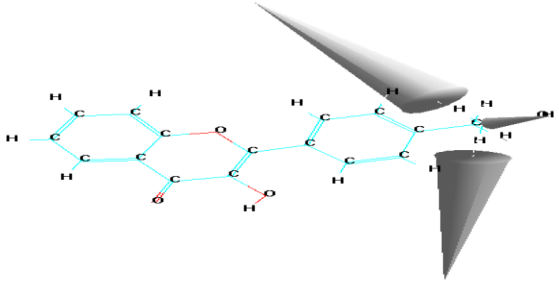
Aromatic 3075.65 cm^{-1} ν (C−H) 3809.71 cm^{-1} ν (O−H) phenolic



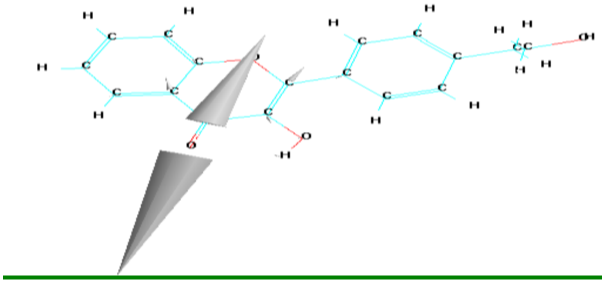
3850.21 cm^{-1} ν (O−H) 3709.71 cm^{-1} ν (O−H)



3075.65 cm^{-1} ν (C−H) aromatic



2972.04 cm^{-1} ν (C−H) aliphatic



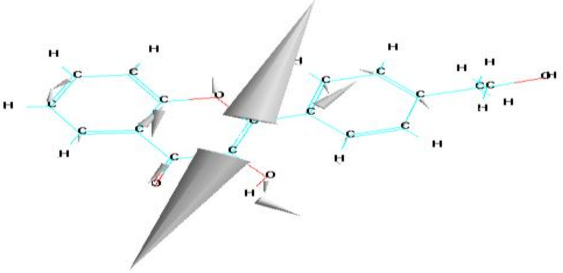
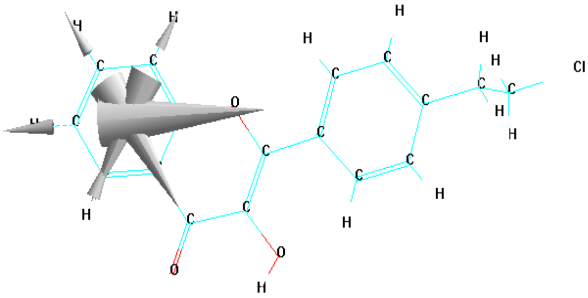
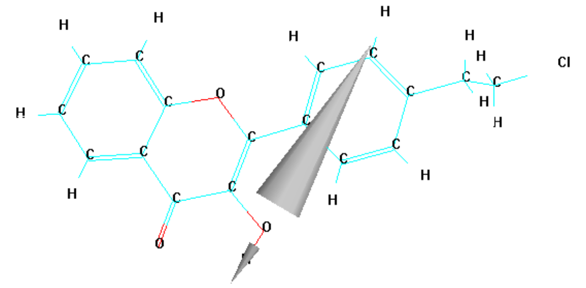


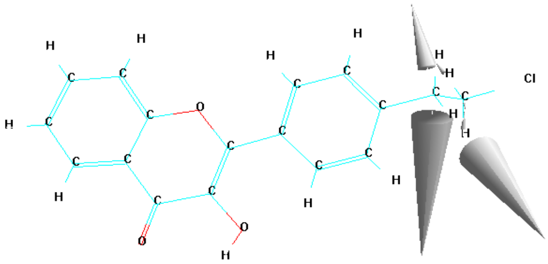
Fig. 3: Theoretical Vibrational Modes (Stretching) For The Active Chemical Group In F3 Compound



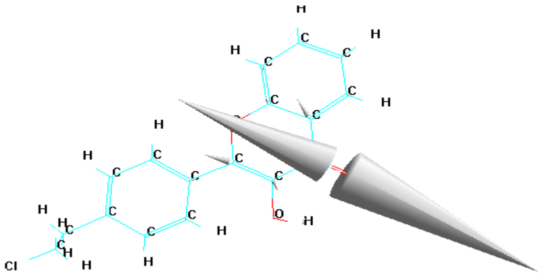
3075.93cm^{-1}ν (C−H) aromatic



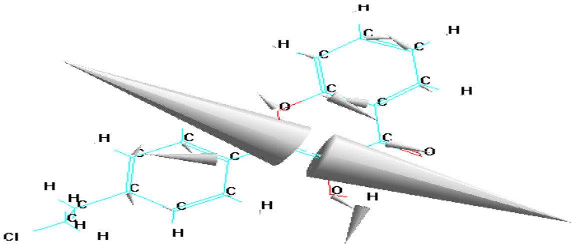
3849.04cm^{-1} ν (O−H)



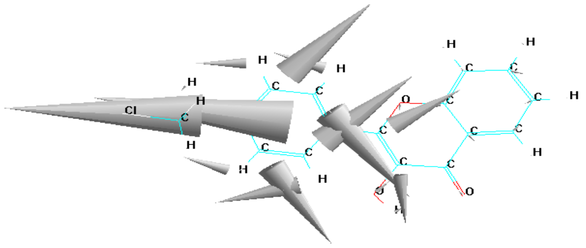
2951.26 cm^{-1}ν (C−H) aliphatic



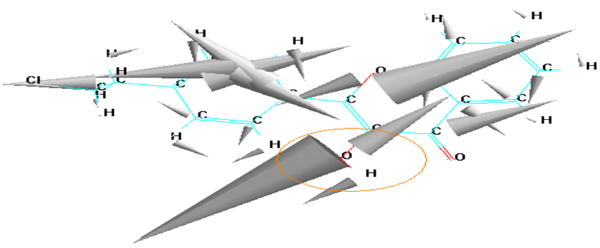
cm^{-1}ν (C=O) 1833.15



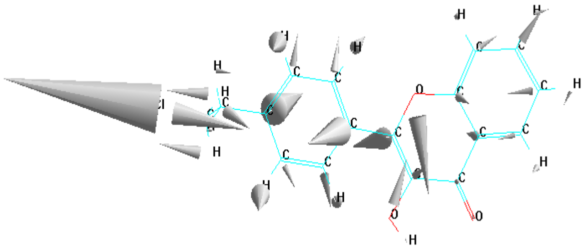
ν (C=C) 1690.86 cm^{-1}



1643.72 cm^{-1}ν (C=C) aromatic

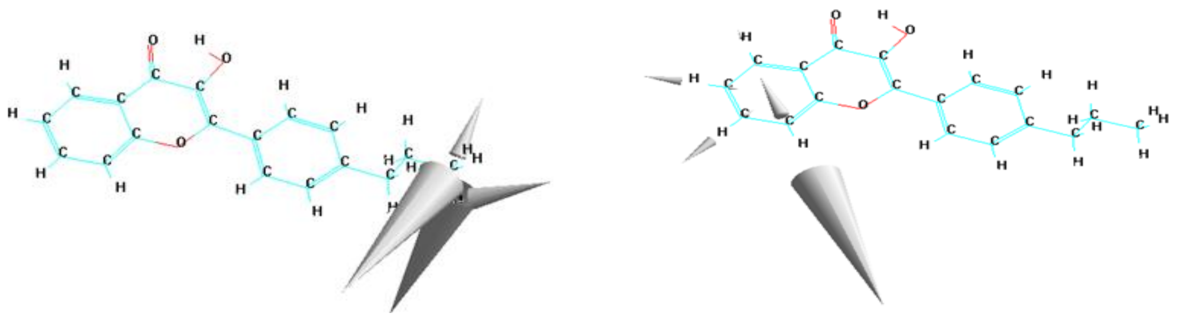


1311.97 cm^{-1} ν (C−O)

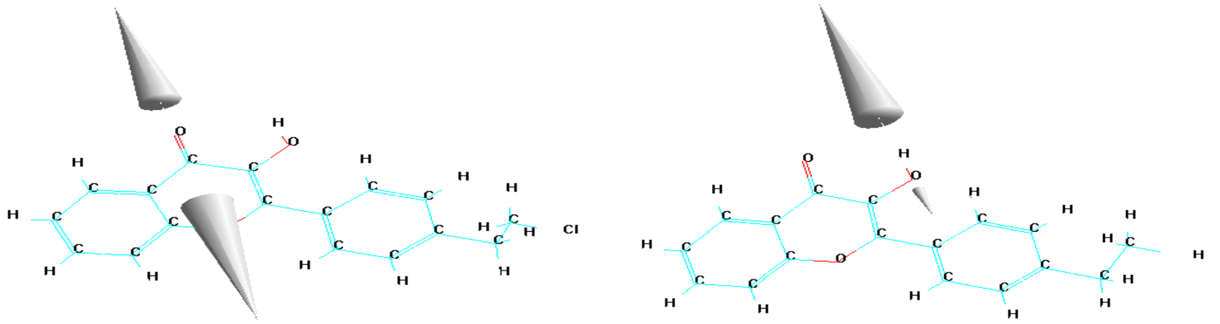


747.56 cm^{-1} ν (C−Cl)

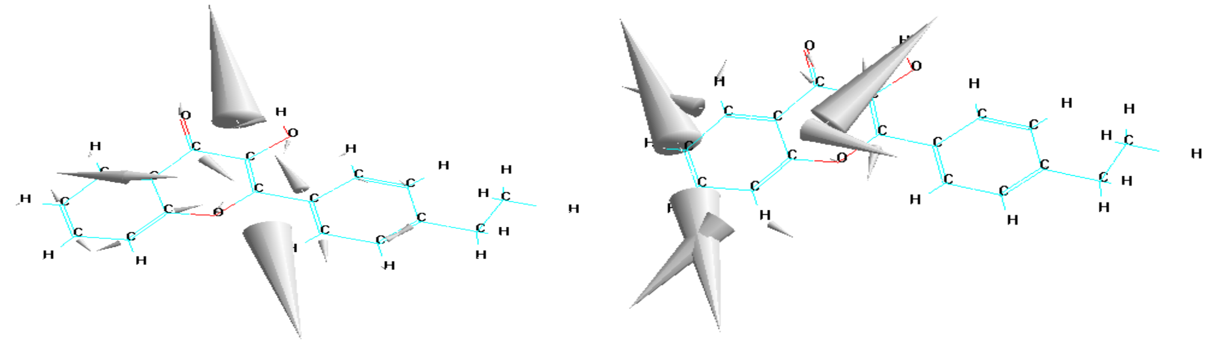
Figure 4: Theoretical vibrational modes (stretching) for the active chemical group in F4 compound



ν(C−H) aliphatic:2993.91 cm^{-1} ν(C−H) aromatic:3086.64 cm^{-}



1882.44cm^{-1} ν (C=O): ν (O−H):3170.80 cm^{-1}



ν(C=C)olefin:1833.22 cm^{-1} ν(C=C) aromatic:1697.62 cm^{-1}

Figure 5:Theoretical Vibrational Modes (Stretching) For The Active Chemical Group In F5 Compound

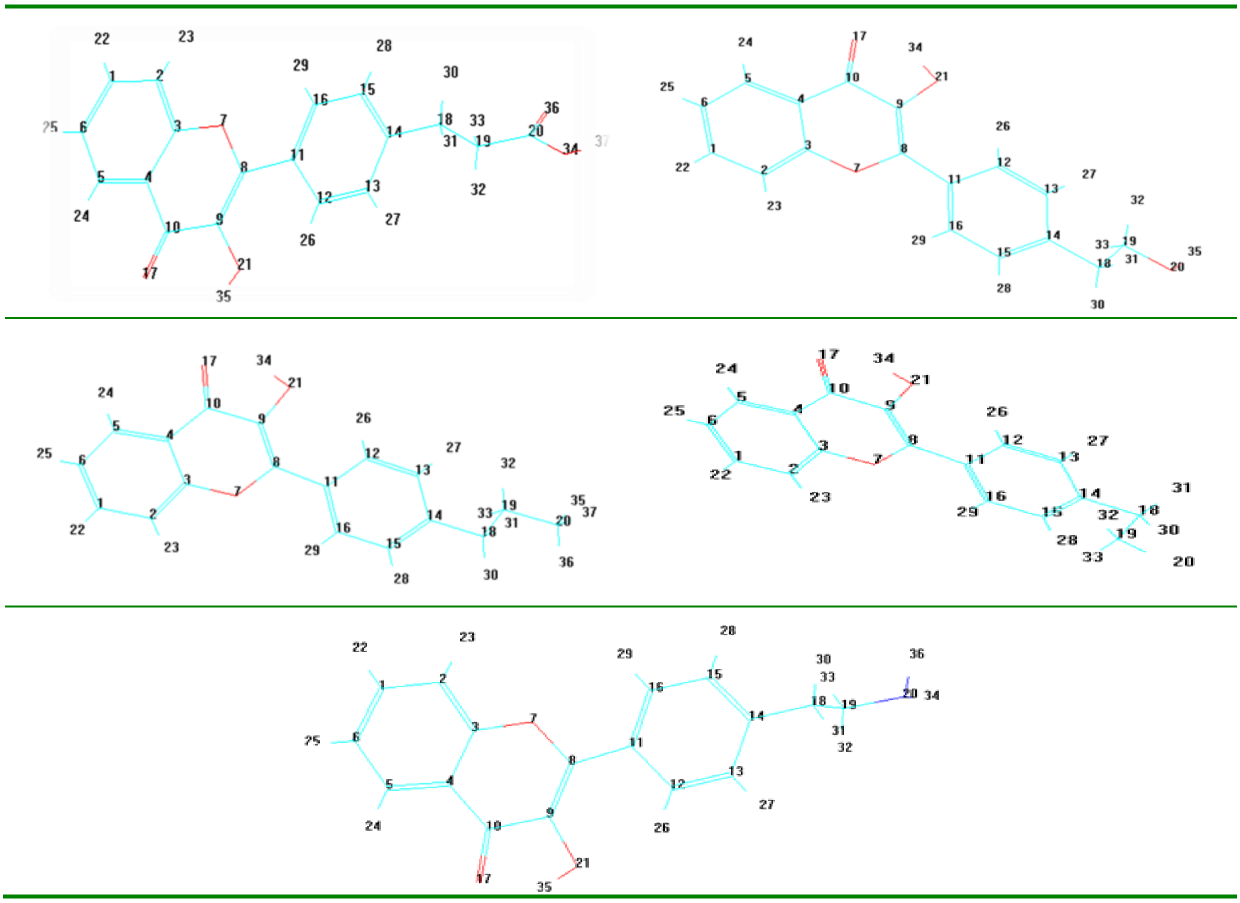
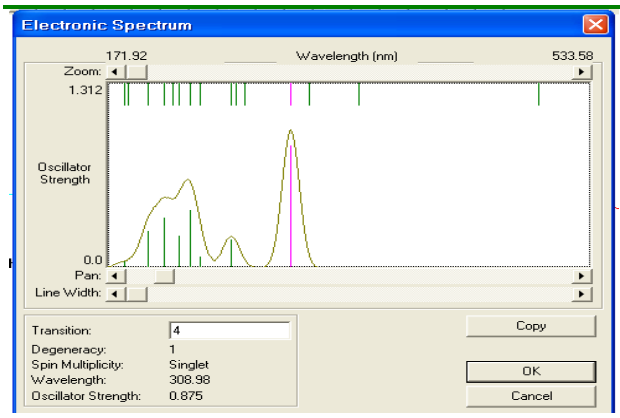


Fig. 6: Serial Number of Atoms View of Flavonols Compounds

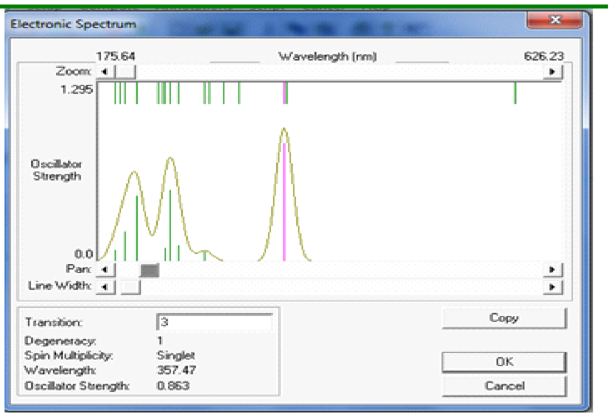
The theoretical UV-spectra of compounds were calculated by using ZINDO/S method. The serial number of atoms was plotted in the structure of compounds in order to determine the type orbitals than type of transition figure (6). Theoretical spectrum of compound F1 exhibited λ_{max} at 308.90 assigned to n→π* (O17→C10) or (O36→C20). The spectra of (F2, F4, F5) exhibited λ_{max} at 357.02,358.33 and 357.76 nm respectively, the quantum data indicate that these peaks are generated mainly from n→π* transition (O17→C10).

Table (4):-Ultra violet spectra of flavonols from ZINDO/S calculation and Experiment.

Symbols	Transition	λ_{max} (nm)
F1	**n→π***	**308.90**
F2	**n→π***	**357.47**
F3	**n→π***	**357.02**
F4	**n→ π***	**358.33**
F5	**n→ π***	**357.76**

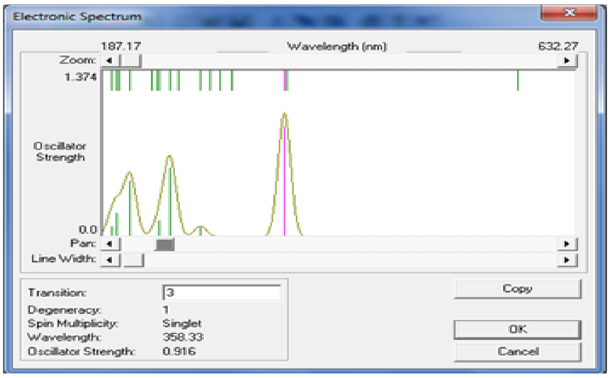


Transition: 4
Degeneracy: 1
Spin Multiplicity: Singlet
Wavelength: 308.98
Oscillator Strength: 0.875

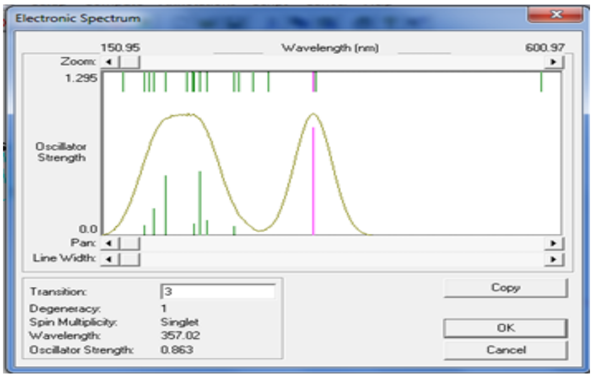


Transition: 3
Degeneracy: 1
Spin Multiplicity: Singlet
Wavelength: 357.47
Oscillator Strength: 0.863

UV spectrum of F1 λ_{max} 308.90 **UV spectrum of F2 λ_{max} 308.90 & 357.47**

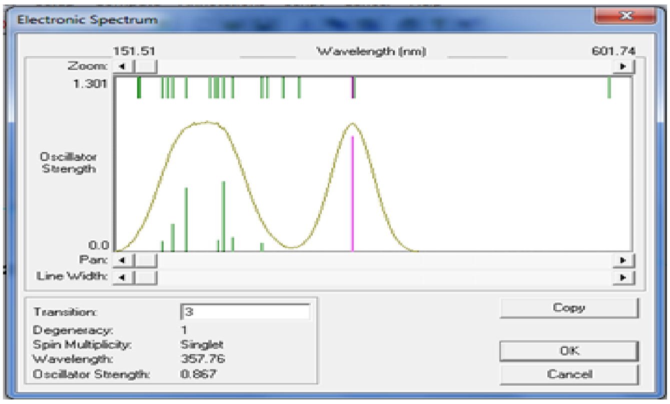


Transition: 3
Degeneracy: 1
Spin Multiplicity: Singlet
Wavelength: 358.33
Oscillator Strength: 0.916



Transition: 3
Degeneracy: 1
Spin Multiplicity: Singlet
Wavelength: 357.02
Oscillator Strength: 0.863

UV spectrum of F4 λ_{max} 308.90 **UV spectrum of F3 λ_{max} 308.90**



Transition: 3
Degeneracy: 1
Spin Multiplicity: Singlet
Wavelength: 357.76
Oscillator Strength: 0.867

UV spectrum of F5 λ_{max} 308.90 & 357.76

Fig. 7: Serial Number Of Atoms View Of Flavonols.

Conclution

The results of semiempirical methods are usually good in a qualitative sense and very useful in the comparison of data obtained for structurally related compounds. According to the data processing in this work, the calculated energies showed that F1 compound is more stable than other compounds. Theoretical vibration data were calculated and gave good results as expected, also electronic transitions of Flavonol compounds were calculated and show simple differences in λ_{max} value between them.

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