

Chemical structural and thermodynamic study of anthocyanins family in viewpoint of electron transfer

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ABSTRACT

Today, most of the anthocyanins which have been discovered in nature derive from six anthocyanidin aglycones result of flavylum backbone with different glycosylations and acylations including Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin. In this work, it has been investigated the information available concerning the electronic structure, physicochemical properties and the biological activity of six anthocyanins including Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin with different amounts in nature associating in fruits and vegetables related to health promoting effects toward a perceptible understanding of their stability and color. The various anthocyanins absorb the light and are generators for produced colors of the red, blue and purple in vegetables and fruits. In the present work, Infrared quantum chemical of modeling method and the Monte Carlo simulation were employed to predict the activity of anthocyanins indicating stabilization of their color due to their electronic structure using theoretical methods. So, the spin density and partial charges have been accomplished by fitting the electrostatic potential to the fixed charge of O⁺₁₇, O⁺₁₇, O⁺, O⁺₁₆, O⁺₇ and O⁺₇ cations in Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin. Then, Monte Carlo simulation unravel the logic agreement results through calculation of the relation confidants in the electrophilic structures; R²_{petunidin} = 0.9208, R²_{malvidin} = 0.9206, R²_{delphinidin} = 0.8964, R²_{peonidin} = 0.891, R²_{pelargonidin} = 0.8496, and R²_{cyanidin} = 0.8237. Anthocyanins adequately reproduce the vibrational spectra, pointing to this theoretical technique as a promising approach for predicting the spectroscopic properties of normal modes and atomic orbital of electron population.

Keywords: anthocyanins; color and stability; MC; quantum chemistry; IR; natural product; electrophilic structure.

1. INTRODUCTION

Anthocyanins including Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin which are polar and soluble in water with a large membrane bound vesicle in a cell's cytoplasm can be appeared in different colors like red, purple, blue or black [1-4].

Anthocyanins are a part of principal molecules as flavonoids synthesized via the phenylpropanoid pathway which exist in roots, stems, leaves, flowers, and fruits. Besides, it cannot be ignored that there is no conclusive evidence that anthocyanins have the special effects on human biology or diseases [5-7].

Several years ago, the investigation on plants and foods containing antioxidant properties has been begun which has introduced the multiple data exhibiting their effects in the reduction of risk of chronic diseases in people [8-10].

The chemical compounds in vegetables and fruits that deal with the health benefits illustrating several antioxidants such as vitamins C and E, carotenoids and flavonoids and their properties including molecular weight, dimensional conformation, biochemical and physical parameters of these molecules let them interact with various targets in many live organisms [11,12].

The large intake of nutrition full of anthocyanins based on human consumption inhibits potential health beneficial impacts on different diseases of cancer, neurological diseases, Alzheimer disease, obesity, inflammation and diabetes [13].

Anthocyanins are the large class of polyphenolic structures as flavonoids that are formed by plants as part of their secondary metabolism. Based on their chemical properties, flavonoids are

divided into various subclasses which share a common carbon basis named flavylum ion chain with different rings [14].

Glycosylated anthocyanidins that are jointed in the structure of anthocyanins have the highest popular type of pigments in plants. Naturally, we can find various anthocyanins because of complex glycosylation models over some aglycones. Statistically, among twenty-five aglycones indicated in vegetables and fruits, only cyanidin, delphinidin, malvidin, pelargonidin, peonidin, and Petunidin have the large amounts [15-17].

Anthocyanins are excessively colored at low pH through the eight conjugated double bonds indicating a positive charge of the structure that show the variety of color because of the different replacements in B ring of the principal chain (blue with hydroxyl replacements and red with methoxyl groups) [18-21].

These replacements impact the physicochemical properties of anthocyanins with changing their size and polarity and solubility in water toward a large range of structures in nature [22].

Many kinds of anthocyanins have been introduced as natural products such as Cyanidin, Pelargonidin (12%), Peonidin(12%), Delphinidin(12%), Malvidin(7%) and Petunidin(7%) which are different in the chemical nature of the sugars and other residues binded to one of six basic anthocyanidin cation chromophores [23,24].

It is really intriguing how the plants organize the structure or how the chemistry of the anthocyanins generates a wide range of colors mostly in the visible spectrum [25].

Besides, for approving the color and stability of anthocyanins through the chemical characteristics and other photochemical

properties, several new anthocyanin-inspired dyes and pigments have been synthesized for use in cosmetics or foods with favorable colors and stability compared to the color and stability of natural anthocyanins [26-28].

The researches have illustrated that the color of natural anthocyanins is sensitive to pH of the medium (activity in pH= 4-5 as the weak acids). About the pH= 3, the changing of the color causes the colored anthocyanin cation, AH^+ , is converted into colorless or near-colorless products [29].

2. MATERIALS AND METHODS

Normal mode calculation is the study of harmonic potential wells by analytic means which include the simultaneous motion of all atoms during the vibration leading to a natural description of molecular vibrations. Therefore, they are good candidates for representation of the molecular Hamiltonian. Since a transformation between different sets of coordinates is possible, the anharmonic terms can be calculated in one representation, and then be transformed into another one [30,31].

The theoretical calculations were done at different steps of theory to investigate the more accurate equilibrium geometrical parameters and IR spectral data for each determined structure. It is supposed that the polarization functions into the basis set used in the calculation always lead us to the considerable improvements on the obtained results in theory.

The Simulation exhibits the methods which produce a popular sample of a system at a specific temperature using calculating most of the properties through the partition function [32].

Monte Carlo, MC, force fields used in simulating physical and mathematical systems are computational algorithm classes based on repeated occasional samples to computing their consequences. MC method is a statistical sampling technique which discovers a number of scientific questions. Computation of random or pseudo-random numbers causes the accuracy of calculation particularly for unfeasible or impossible to estimate an exact data with a

3. RESULTS

In this investigation, the plant pigments of six anthocyanins including Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin have been calculated using theoretical methods to evaluate the effects of these anthocyanins in natural products.

As it has been shown, a vibrational calculation with its own eigenvector for finding thermodynamic values of anthocyanins including ΔG , ΔH , $\ln K$. Electronic Energy and Core-Core Interaction have been calculated (Table 1 and Fig. 1).

The electronic energy including the core-core repulsion has been calculated by Gaussian09 [26], in analogy with ab initio methods, the total relative energy (as seen in table 1) to a situation where the nuclei (with their core electrons) and the valence electrons have been infinitely separated.

The variety between these subclasses arises of double bonds and carbonyl groups in the C ring. Therefore, the values have exhibited that Malvidin has the lowest optimized energy and the

In this work, a solid theoretical perceiving of the relationship between the structure and IR spectroscopy has been run on the natural plant pigments which have magnificent concepts for their applying; safe dyes or coloring agents in pharmaceutical products and foods while high stability and lightfastness of the color are significant factors. Therefore, it has been compared the structural properties of six principal anthocyanins by quantum chemical methodologies as the computational design and the simulated class to stimulate the physicochemical properties toward approving their stability and color changing.

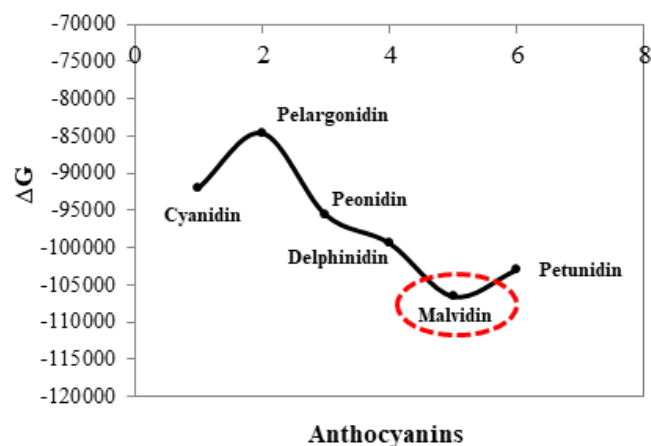
deterministic algorithm [33]. It doesn't always need random numbers to apply deterministic, pseudo-random sequences, making it easy to test and re-run simulations [34].

In MC methods, a sequence of points in the phase space is produced from an initial geometry by adding a random "kick" to the coordinates of a randomly chosen atom or molecule. The new configuration is approved if the energy decreases and with a probability of $e^{-\Delta E/kT}$ if the energy increases. Based on the metropolis procedure, the configurations in the ensemble obey a Boltzmann distribution, and the possibility of approving higher energy configurations allows MC methods to increase and escape from a local minimum [35,36].

MC simulations are widely applied in biology, chemistry, physics, and engineering for identifying the structural and thermal properties of complex systems at the atomic level.

MC simulations need only the ability to evaluate the energy of the system which may be advantageous if calculating the first derivative is unavailable or time-consuming. Moreover, since only a single particle is moved in each step, only the energy changes associated with this move should be calculated, not the total energy for the whole system. A disadvantage of MC methods is the lack of the time dimension and atomic velocities, and they are therefore not suitable for studying time-dependent phenomena or properties depending on momentum [37,38].

most stabilized compound compared to some other anthocyanins (Fig. 1).



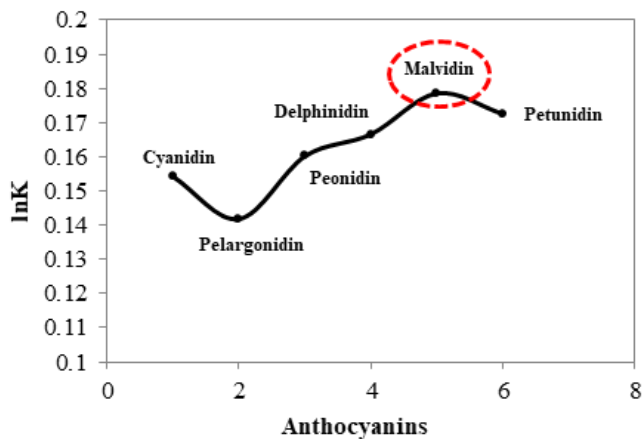


Figure 1. Calculated thermodynamic properties of anthocyanins; Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin in natural products.

Obviously, the IR theoretical method has been done on Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin for discovering how they do their duties as the anthocyanins via different active parts of OH, O⁺ and O-CH₃ cation on the structures (Fig. 2).

The vibrational spectral data obtained from IR spectra have assigned the modes based on the results of the theoretical calculations as intensity and frequency curves using HyperChem8 [27]. The fundamental vibrational modes were characterized depending on their stability of anthocyanins. It has been investigated the high frequency of normal modes of these structures through variant positions of each molecular basis (Fig.2). Then, in Fig.3, several intensities and frequencies with identified symmetry have been considered for unraveling the stable geometry of the group of anthocyanins (Fig. 3).

Although, a quantitative description of a potential well requires a more careful approximation, it has been explained the chosen frequencies of the density of states rather well. So, in this work, it has been illustrated the main results of the frequencies and intensities of active modes on the anthocyanins of Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin (relation coefficient, $R^2 = 0.9604$) [28]. The normal modes of these structures can usually be associated with a certain kind of motion of the molecule (Fig. 3).

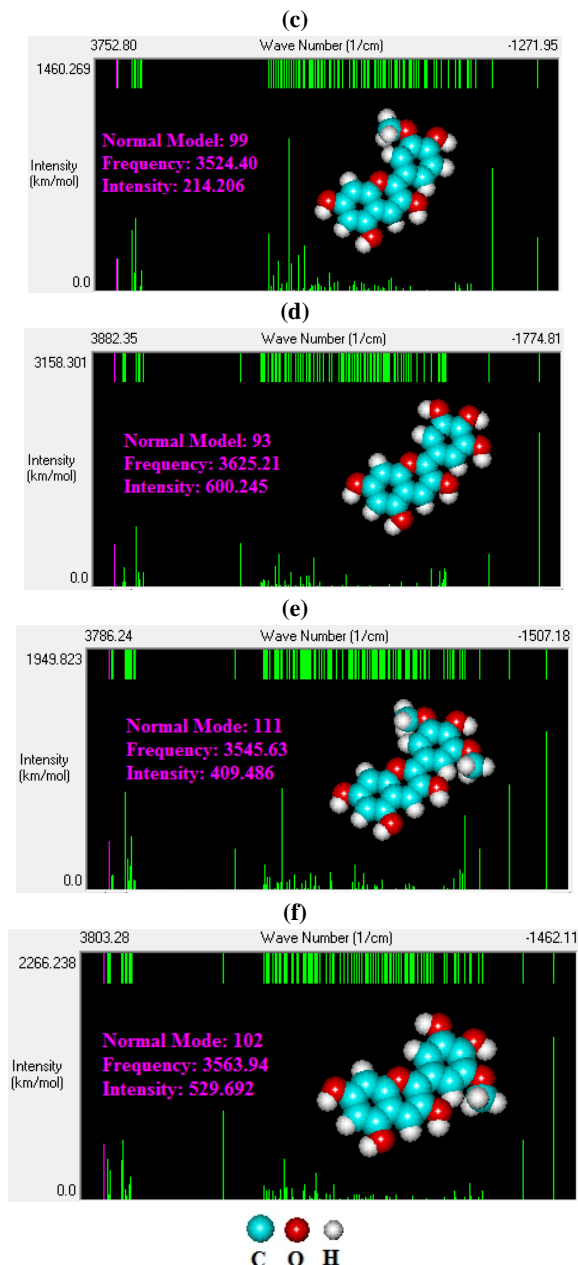
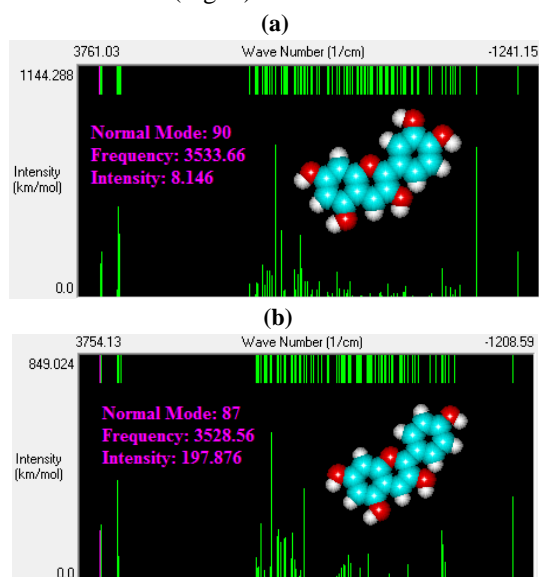


Figure 2. IR spectra of anthocyanins ; (a) Cyanidin (b) Pelargonidin (c) Peonidin (d) Delphinidin (e) Malvidin and (f) Petunidin.

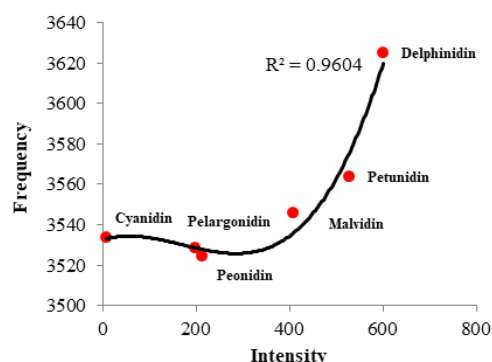


Figure 3. The changes of Frequency via Intensity of anthocyanins ; (a) Cyanidin (b) Pelargonidin (c) Peonidin (d) Delphinidin (e) Malvidin and (f) Petunidin .

Therefore, low-frequency modes are to a very good approximation with low-energy modes, and vice versa. It should also be considered that at the high frequency, quantum impacts become significant to a stabilized structure. However, the transformation

to normal mode coordinates remains valid in a quantum description; so, only the dynamic interpretation must be adapted.

Moreover, the spin density and partial charges have been obtained by fitting the electrostatic potential to a fixed charge of O^{+17} , O^{+17} , O^{+7} , O^{+16} , O^{+7} and O^{+7} cations in Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin, respectively (Tables 2 and 3, Figs 4 and 5).

In Fig. 5, it has been measured the fluctuation of atomic charge of O^{+17} , O^{+17} , O^{+7} , O^{+16} , O^{+7} and O^{+7} cations as the electrophilic groups of Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin which leads us to find the reason for the activity and the stability of these structures in the natural products.

Then, Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin have been led to a description of Monte Carlo simulation by potential energy in 300K energy via time scale (0-100). Optimal values are close to 0.5. Varying the step size can have a large effect on the acceptance ratio. The MC Options dialog box permits us to set up the MC simulation parameters toward to the good agreement data through the calculation of the relation confidents for these compounds ; $R^2_{\text{petunidin}} = 0.9208$, $R^2_{\text{malvidin}} = 0.9206$, $R^2_{\text{delphinidin}} = 0.8964$, $R^2_{\text{peonidin}} = 0.891$, $R^2_{\text{pelargonidin}} = 0.8496$, and $R^2_{\text{cyanidin}} = 0.8237$ (Fig.6).

Basically, for calculating the desired thermodynamic averages, it is necessary to have some methods available for computation the potential energy by MC simulation, in the form of a function representing the potential interaction in the molecular mechanics or in the form of direct quantum-mechanical calculations.

Also, it should be noted that constraining potentials have been used at finite temperature, 27°C introducing a constraining potential which enables one to define the groups of anthocyanins. Since the constraining potential is artificial, the dependence of calculated thermodynamic properties on the form and the radius of the constraining potential must be investigated on a case-by-case basis (Fig.6).

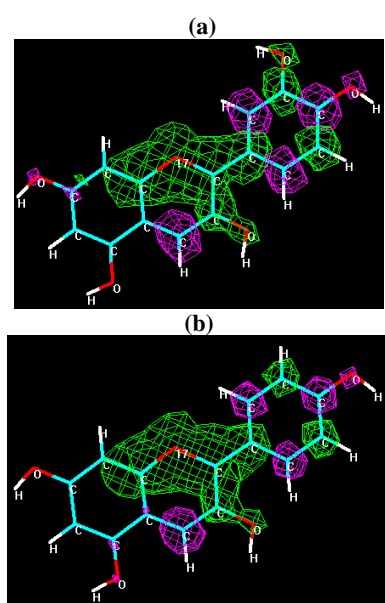


Figure 4. The 3D Isosurface schematics of calculated total spin density for different atoms in anthocyanins; (a) Cyanidin (O^{+17}) (b) Pelargonidin (O^{+17}) (c) Peonidin (O^{+7}) (d) Delphinidin (O^{+16}) (e) Malvidin (O^{+7}) and (f) Petunidin (O^{+7}).

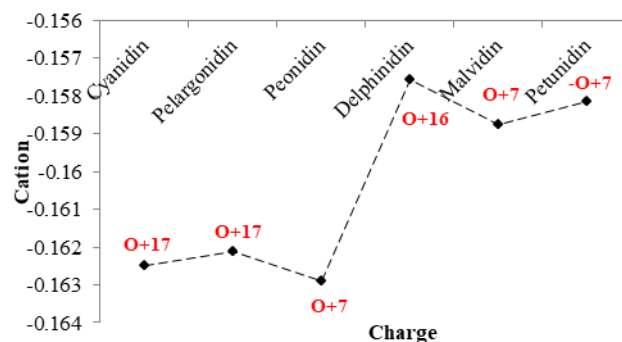


Figure 5. The charge of O^{+} for different anthocyanins of Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin.

The results of Figs.5 and 6 suggest that the different data observed in Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin are predominantly related to the situation of active sites of Oxygen atoms in these structures which transfer the electronic charge the molecules.

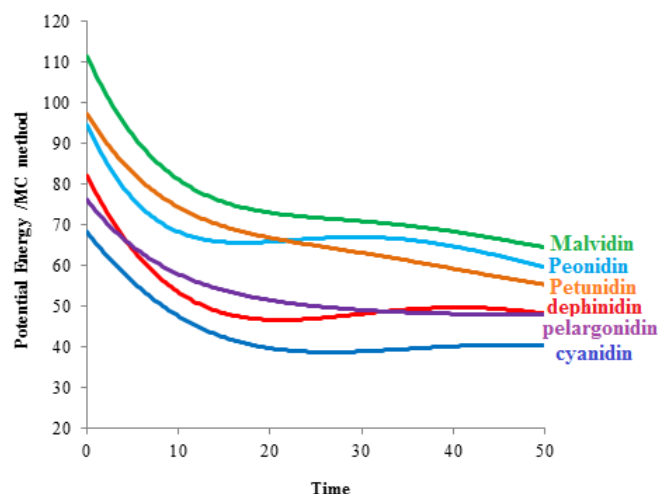


Figure 6. Calculated graphs of potential energy (kcal/mol) via time by Monte Carlo method for Malvidin, Peonidin, Petunidin, Delphinidin, Pelargonidin, and Cyanidin.

Table 1. Thermodynamic properties of anthocyanins; Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin in natural products.

structure	ΔG (kcal/mol)	ΔH (kcal/mol)	$E_{\text{electronic}}$ (kcal/mol)	$E_{\text{core-core}}$ (kcal/mol)	$\ln K \times 10^{-5}$
Cyanidin	-92005.7731	-91.5532	-549835.6326	457829.8594	1.5419
Pelargonidin	-84616.9430	-51.8641	-500729.9901	416113.0472	1.4181
Peonidin	-95578.4989	-77.4408	-598278.6702	502700.1713	1.6018
Delphinidin	-99397.6653	-134.3043	-601993.5164	502595.8511	1.6657
Malvidin	-106542.6173	-105.5801	-705068.6325	598526.0152	1.7855
Petunidin	-102969.9147	-119.7155	-653178.1861	550208.2713	1.7256

Table 2. The charge of O^+ cation for different anthocyanins of Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin.

Cation	Charge	dipole moment (Debye)	
Cyanidin (O^+_{17})	-0.162506		5.494
Pelargonidin (O^+_{17})	-0.162107		4.714
Peonidin (O^+_7)	-0.162914		5.177
Delphinidin (O^+_{16})	-0.157577		6.682
Malvidin (O^+_7)	-0.158748		6.600
Petunidin (O^+_7)	-0.158159	6.898	

Table 3. Atomic Orbital Electron Populations of O^+ cation for different anthocyanins of Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin.

Anthocyanins	Alpha Orbitals				
	cation	S	Px	Py	Pz
Cyanidin	O^+_{17}	0.995494	0.845595	0.626975	0.833037
Pelargonidin	O^+_{17}	0.995501	0.846009	0.626257	0.833287
Peonidin	O^+_7	0.995521	0.846257	0.626209	0.832799
Delphinidin	O^+_{16}	0.995436	0.844615	0.627893	0.831231
Malvidin	O^+_7	0.995470	0.845518	0.626741	0.830039
Petunidin	O^+_7	0.995444	0.844780	0.627773	0.831227

4. CONCLUSIONS

The modeling and simulation of anthocyanins including Cyanidin, Pelargonidin, Peonidin, Delphinidin, Malvidin and Petunidin show that the stabilization energy and geometry have been affected by the infrared theoretical method through the evaluation of the thermodynamic properties and the electronic structural of indicated compounds; then the Monte Carlo force

field achieving the best results for the potential energy vs. the time scale. The calculations have demonstrated that such extrapolation schemes significantly overestimate the anthocyanins by active sites of electrophilic molecules, Oxygen bonds, which are the most active points at the indicated structures toward a wide range of health promoting researches.

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