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Research Article

A non toxic natural food colorant and antioxidant 'Peonidin' as a pH indicator: A TDDFT analysis

Vijisha K. Rajan, Shameera Ahamed T.K., Hasna C.K., K. Muraleedharan*

Department of Chemistry, University of Calicut, Malappuram 673635, India

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ABSTRACT

A computational inestigation on the difference in colors of two plants 'Peony' and 'Morning glory' by the same pigment 'Peonidin' has been performed by means of absorption characteristics. Peonidin imparts purple color to the flowers in Peony and blue to that in Morning glory. TDDFT tool in Gaussian 09 software package has been employed to analyze the UV–vis spectra and has shown that in acidic media Peonidin exists in its flavylium cationic form where as in alkaline media it exists in the quinoidal base form. These two structural forms have colors red and blue respectively. TDDFT results of flavylium ion in acetic acid moves the absorption to higher wavelength and corresponds to purple color and is the color of Peony flower. One of the quinoidal bases in alkaline media gives violet-blue color to flowers in Morning glory. This is true as Peony grows in acidic soil only while Morning glory grows in alkaline soil only. The affinity towards pH values makes Peonidin to act as pH indicator besides its radical scavenging capacity. Further a good food colorant must be non toxic. The toxicological analysis has shown that Peonidin is non-irritant, non-mutagenic, non-carcinogenic and non-tumorigenic. The compound has sufficient solubility to use as a potential drug. Also the compound has a positive drug score. All these results confirm the potential druggability of Peonidin and its non toxicity.

1. Introduction

Chlorophyll, carotene, anthocyanidins, etc., imparts colors to plants. The shade in which a substance appeared is the complementary shade of the color that they have absorbed. Due to the instability of chlorophyll, its concentration decreases during summer resulting in the fading of color of leaves. Carotene absorbs blue-green light and looks like yellow. When plants have both chlorophyll and carotene, they could absorb red, blue-green and blue, and appear as green. During summer, chlorophyll decreases and carotene persists so that leaves changes their color to yellow. Unlike chlorophyll and carotene, the pigment anthocyanidins, a major class of flavonoids, are not membrane bound pigments, but dissolved in the cell sap. Their pH sensitivity makes them to use as pH indicators. At acidic pH they impart red and at basic pH they give blue or violet-blue color. In plants, in presence of light, the anthocyanidins are produced as a result of reaction between protein and sugar in the cell sap. As concentration of anthocyanidins increases, plants become bright colored. For example, apple appears red on the side where light falls and green on the other side.

Anthocyanidins are major constituents of vascular plants and are harmless water soluble natural pigments (Lu et al., 2014). This have been used as a good natural food colorant since historical times. Due to the wide range of uses there are a number of research articles available in literature about the anthocyanidins including its metal chelation (Asada et al., 2015; Horbowicz et al., 2011; Tachibana et al., 2014), antioxidant (Bueno et al., 2012; Elmastas and Aboul-enein, 2012; Guzmán et al., 2009; Mascayano et al., 2018), anticancer and antidiabetic (Castañeda-ovando et al., 2009) capacities. However the relationships of the structures of anthocyanidins with the properties that they have shown are not yet completely understood. In this scenario, a detailed structural analysis of anthocyanidins is particularly relevant.

The affinity towards pH, metal ions, temperature, concentration, light, etc., makes them unstable in the isolated state. The important feature of anthocyanidins is the presence of chromenylium/flavylium ion. Due to this, effective π-conjugation significantly enlarges in comparison to flan-3-ols. So HOMO-LUMO gap decreases than flavan-3-ols. This π-conjugation is responsible for its strong absorption around 500 nm (Castañeda-ovando et al., 2009) and thus they are brightly colored; this in turn enables them to be used as a natural food colorant. As the use of artificial colorants have been expanded to a splendid extent and become a extremely good risk to human fitness due to the fact of their toxicity so that the development of some herbal meals colorant are specially relevant in the area of food industry. Carotenoids and anthocyanidins are the broadly used herbal food colorants.

* Corresponding author.
E-mail addresses: vijirajan4@gmail.com (V.K. Rajan), kmuralika@gmail.com (K. Muraleedharan).

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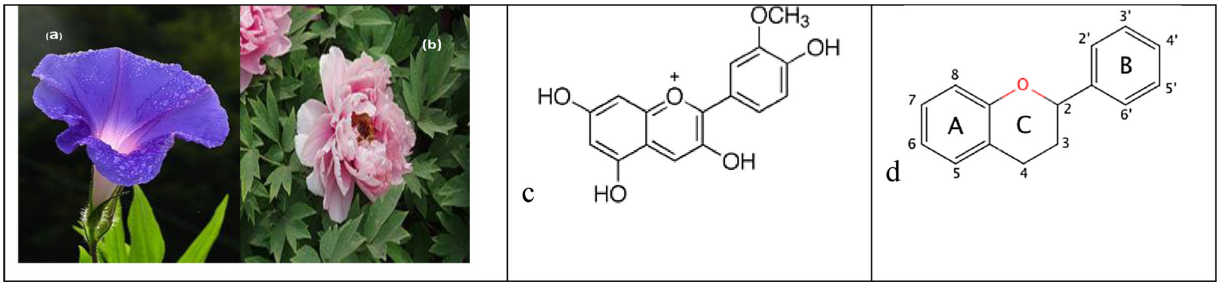

Fig. 1. (a) Morning glory, (b) Peony (c) Peonidin, (d) Flavoniod with ring names.

The basic structure of anthocyanidins consist of an aromatic ring [A] bonded to a heterocyclic ring [C] that contains an oxygen which is also bonded by a C—C bond to a third aromatic ring [B] (see Fig. 1d). They belong to polyphenolic groups containing at least one —OH group in the benzene ring (Pietta, 2000). The present work focused on the difference in the color of flowers in Peony and Morning glory even though both of them contain Peonidin as the color pigment (see Fig. 1a–c). Peonidin, the second most abundant anthocyanidin, is an O-mehtylated anthocyanidin and is considered as a primary plant pigment. The name 'Peonidin' is derived from the plant Peony as it gives purple-red hue to the flowers of Peony. It is also present in Morning glory, where it gives blue color to the flowers. It is interesting that the same pigment gives two different colors to flowers of two plants. Morning glory is found to grow in alkaline soil whereas Peony preferably grows in acidic soil. So there is a difference in pH values and which may the reason for their color change.

From literature, it has been seen that anthocyanidins could act as pH indicators (Mohd et al., 2011; Sims and Morris, 1984). It has been observed that anthocyanidins are highly sensitive to pH values of the medium in which they are present and they undergo some structural reorganization with pH values. As a result, they exhibit different colors at different pH values so that they could act as pH indicators. Peonidin exhibits different colors with respect to the pH values of the environment where the plants are lived. At low pH values (in acidic media) the flavylium cations exist and are red in color. As the pH values increase this cationic form undergo several structural deformations to form quinoidal bases and then to chalcones.

The present work uses a computational approach to analyze the color of flowers of Peony and Morning glory. There are several structural forms of anthocyanidins at different pH values and these structural forms and their UV–vis spectral characteristics are analyzed with the help of TDDFT tool in the G09 software package (Frisch et al., 2009).

2. Computational methodology

The present work has used a computational approach to the study the color change of an anthocyanidin, Peonidin in two plants namely Peony and Morning glory. The input structures are drawn by using the Gaussview-5.0 graphical user interface (Dennington et al., 2008). All the computational works have been carried out through Gaussian 09 software package with DFT-B3LYP as level of theory and 6-31 + G (d, p) as the basis set.

The Density Functional Theory (DFT) is very convenient for computational analysis because of its large accuracy and high predicting power of physical and chemical properties (Cramer, 2004; Lewars, 2004). The level of theory adopted was B3LYP, which consists of Becke's exchange functional (Becke, 1993) in conjunction with Lee-Yang –Parr correlational functional (Lee et al., 1988) and the basis set used is 6-31 + G (d, p). The computational calculations are performed both in the gas phase as well as in solvent phase. The solvent phase reactions are usually carried by using the continuum models and among the different continuum models, the IEF-PCM model have been used in this work.

The present article has focused on Peonidin and its color. The detailed structural analysis of stable isomer of Peonidin and its antioxidant capacity are not included in this article, as it is already published. The structural optimizations on the stable isomer of Peonidin have been carried out with different basis sets and different level of theory. From that a better level of theory and basis set has been selected and is DFT-B3LYP/6-31 + G (d, p) (Rajan et al., 2018). Again the TDDFT analysis has also been performed with different level of theory like DFT-B3LYP/6-31 + G (d, p), DFT-CAMB3LYP/6-31 + G (d, p), M05/TZVP and PBE0/TZVP. The results are analyzed to select the most appropriate one for the UV spectral studies of Peonidin and its different structural isomers. The structural variations with pH values could be easily explained through the TDDFT analysis.

3. Result and discussions

3.1. Structure of Peonidin

The basic structure of Peonidin is the anthocyanidin ring with extended conjugation. Generally anthocyanidins are stable at lower pH and thus have bright colors. However, Peonidin and Petunidin are found to be stable up to a pH value of 8. This enables them to be used as natural food colorant in addition to their antioxidant capacity. The optimized structure of peonidin is shown in Fig. 2.

It has been reported that the anthocyanidins change their structures according to the pH values. This results in the change in color, there by they can act as pH indicators. The different structural isomers of Peonidin at different pH value is shown in Fig. 3, the structural forms are obtained from the work of Birse, Raymond Brouillard and Jacques-Emile Dubois and Chantal Houbiers and et al. (Birse, 2007; Brouillard et al., 2003; Brouillard and Dubois, 1973; Houbiers et al., 1998). The optimized structures are shown in Fig. S1.

Here the compound 3 is in the form of flavylium cation, compounds 1, 2 and 4 are in quinoidal base form and rests are in the form of chalcones. At lower pH values, the anthocyanidins are often in their flavylium cationic form and consequently anthocyanidins are intensely colored in acidic media. As the pH value increases, there occur some structural variations and they changes their color from purple red to navy blue. Most of the anthocynidins undergo degradation when the pH values approach to 8 and beyond, due to the instability of flavylium cation. Peonidin and Petunidin are stable up to the pH 8 and are in blue color at this pH value. The existences of quinoidal bases and chalcones are highly favoured in the alkaline media. As the pH value increases, a proton losses from the flavylium cation rapidly, and form quinoidal bases, which are also colored. So in acidic media anthocyanidins prefer to exist in their flavylium cationic form where as in higher pH values they prefer to exist in the quinoidal bases and chalcone form (Bridle et al., 1994; Mohd et al., 2011). As the color of flavylium cation, quinoidal bases and chalcones are different, they show color change in accordance with the pH of the medium and this property makes anthocyanidins to use as pH indicators.