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Studies on the UV filtering and radical scavenging capacity of the bitter masking flavanone Eriodictyol

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ABSTRACT

A computational analysis of UV filtering and radical scavenging capacity of a flavanone, Eriodictyol has been performed under DFT-B3LYP/6–31 + G (d, p). Eriodictyol is nontoxic and nonirritant bitter masker commonly used in the wine industry. It has been reported that the flavanones were widely acceptable for photoprotection due to its potential UV filtering and radical scavenging capacity. This study provides theoretical evidence that the eriodictyol has an absorbance in the UV-A and UV-B region of the electromagnetic spectrum and therefore can be used as a potential UV filter in sunscreen lotions and other cosmetic products. The major transitions in the UV–Visible spectrum of Eriodictyol are between HOMO and HOMO-1 with LUMO level and are well explained by NBO-NLMO tool in G09 software. In addition to this, Eriodictyol is a potent antioxidant than that of the most commonly studied Quercetin. The most active site in the compound is 3′ position and is confirmed by NPA, NBO and pKa value analysis. The lowest energy conformer of Eriodictyol contains a Hydrogen bond between carbonyl oxygen (O2) and H30. This is confirmed by the highest value of interaction energy between lone pairs of O2 and σ* of O3– H30. Both the two lone pairs of O2 interacts with the σ* of O3-H30. This decreases the bond order of 5 −OH and at the same time it restricts the hydrogen transfer from this position to form a radical. Similarly, the lone pair of O5 (3′ position) interacts with H33 resulting in the low bond order value and consequently less favorable for radical formation. These results indicate that the BDE values follow the order 3′ < 4′ < 7 < 5. Thus the title compound can be used for photo protection due to its potential UV filtering and radical scavenging capacity.

1. Introduction

Our eyes are sensitive only to the visible region (400–700 nm) in the electromagnetic spectrum and are unable to see the radiations outside this region in the solar spectrum. Ultraviolet (UV) radiations have a shorter wavelength than the visible light. There are 3 types of UV radiations which are UV-A (315–400 nm), UV-B (280–315 nm) and UV-C (100–280 nm). When sunlight falls to earth, all the UV-C and 90% UV-B radiations are absorbed by ozone, oxygen, water vapor and carbon dioxide. So the UV light reaching on earth comprised mainly of UV-A and a little UV-B. The UV-B is responsible for the delayed tanning and burning and it cannot penetrate deep into the skin while UV-A is having a long wavelength, can penetrate into the skin and is responsible for the immediate tanning, wrinkling, and aging of the skin. Both UV-B and UV-A promote the development of skin cancer. So these dangerous UV radiations must be filtered from sunlight by what is called UV filters otherwise we have to suffer a lot of skin disorders like aging, tanning, burning, cancer, erythema, suppression of immune system, eye damage, etc.

The sunscreen lotions contain potential ingredients for both photoprotection and UV filtering. It has been observed that polyphenols like flavonoids present in these UV sunscreens can act as potential UV filters in addition to their radical scavenging capacity [1]. They contain conjugated pi-electron system and therefore can excite an electron from the ground state to the excited state by absorbing radiations in the UV region of the solar spectrum. The radical scavenging activity makes flavonoids to be the good candidates for photo-protection [2].

It is well known that the flavonoids are potent for their radical

Abbreviations: ROS, Reactive Oxygen Species; RNS, Reactive Nitrogen Species; DFT, Density Functional Theory; HAT, Hydrogen Atom Transfer; SPLET, Sequential Proton Loss Electron Transfer; BDE, Bond Dissociation Energy; IEF-PCM, Integral Equation Formalism Polar Continuum Models; SCRF, Self-Consistent Reaction Field; FMO, Frontier Molecular Orbital; HOMO, Highest Molecular Orbital; LUMO, Lowest Unoccupied Orbital; VIP, Vertical Ionization Potential; VEA, Vertical Electron Affinity; NBO, Natural Bond Orbital; NAO, Natural Atomic Orbitals; NHO, Natural Hybrid Orbitals; SET, Single electron transfer; AIP, Adiabatic Ionization Potential; SETPT, Single-Electron Transfer followed by Proton Transfer; PDE, Proton Dissociation Enthalpy; PA, Proton affinity; ETE, Electron Transfer Enthalpy; NPA, Natural Population Analysis; CASSCF, Complete Active Space Self-Consistent Field

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Table 5
Atomic charges of atoms in Eriodictyol by NPA.

Atom No	Charge	Atom no	Charge
O 1	−0.53237	C 18	0.3606
O 2	−0.59947	C 19	0.2499
O 3 (Position 5)	−0.68783	C 20	−0.26798
O 4 (Position 7)	−0.67743	C 21	0.27819
O 5 (Position 3′)	−0.72679	H 22	0.24962
O 6 (Position 4′)	−0.69265	H 23	0.27674
C 7	0.07115	H 24	0.28547
C 8	−0.56031	H 25	0.25652
C 9	−0.07603	H 26	0.24619
C 10	−0.30247	H 27	0.27621
C 11	0.5191	H 28	0.25948
C 12	0.36582	H 29	0.26269
C 13	0.39906	H 30	0.5218
C 14	−0.28925	H 31	0.49576
C 15	−0.23946	H 32	0.50495
C 16	−0.34997	H 33	0.50996
C 17	−0.38721		

Table 6
Bond orders of OH bonds in Eriodictyol.

Bond	Bond order
5 —OH	0.6158
7 —OH	0.7408
3′ —OH	0.7308
4′ —OH	0.7166

values of —OH groups in ring B are lower than that of ring A. To confirm this, atomic charge analysis has been performed. Position with highest atomic charge is most susceptible to radical attack and stable radicals of antioxidant are formed at this position. The charges of different atoms in Eriodictyol through Natural Population Analysis (NPA) are given in Table 5.

The highest charge has been seen at O5 (position 3′) and is the most active site in Eriodictyol. This is clear from the BDE values also. The second lowest BDE is at position 4′and is having higher charge next to position 3′. Again, the charge at position 5 is greater than that at position 7, but the BDE values are in the reverse order. The presence of carbonyl group and the hydrogen bond formation in position 5 makes the oxygen atom at this position more negative than that at position 7. However, the hydrogen bond restricts the Hydrogen abstraction at position 5 so that the BDE value increases. So the BDE values follow the order 3′ < 4′ < 7 < 5.

In order to confirm the order of radical formation as discussed above, we have computed the bond orders of all the four —OH groups and are given in Table 6 since NBO analysis is a unique tool in computational chemistry to predict the bond orders in a molecule. Looking at Table 6, the lowest bond order is seen for position 5 which indicates that this bond is weak enough to break faster than the remaining. This is in contradiction with the results in Section 3.3. Again the second lowest bond order is seen at 4′ position. So by bond order values, the order of easiness for radical formation is 5 > 4′ > 3′ > 7.

In order to find out the correct order, we have analyzed the donor-acceptor interactions in Eriodictyol (see Table 1 in *Data in Brief*). The lowest energy conformer of Eriodictyol contains a Hydrogen bond between carbonyl oxygen (O2) and H30. This is confirmed by the highest value of interaction energy between lone pairs of O2 and σ* of O3-H30. Both the two lone pairs of O2 interacts with the σ* of O3-H30. This decreases the bond order of 5 —OH and at the same time it restricts the hydrogen transfer from this position to form radical. Similarly, the lone pair of O5 (3′ position) interacts with H33 resulting in the low bond order value and consequently less favorable for radical formation. Taking account of all these factors the correct order for radical formation is 3′ < 4′ < 7 < 5 which is in agreement with the results in Section 3.3.

4. Conclusion

In summary, a computational analysis of the UV filtering and radical scavenging capacity of a flavanone, Eriodictyol has been performed under DFT-B3LYP/6-31 + G (d, p). As Eriodictyol is nontoxic and nonirritant in nature and has an absorbance in the UV-A & UV-B region of electromagnetic spectrum, it can be used as a potential UV filter in sunscreen lotions and other cosmetic products. In addition to this, the compound has the potential antioxidant capacity and is found to be higher than that of Quercetin. The most active site in the compound is 3′ position and is confirmed by NPA charge, NBO and pKa value analysis. The BDE values follow the order 3′ < 4′ < 7 < 5. The major transitions in the UV–Visible spectrum of Eriodictyol are between HOMO and HOMO-1 with LUMO level. They are analyzed and well explained by NBO-NLMO tool in G09. Thus the title compound can be used for photoprotection due to its potential UV filtering and radical scavenging capacity.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jphotobiol.2018.06.017.

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