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Computational insight into the antioxidant mechanisms of major catechins found in cocoa: DFT study

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Among diverse classes of antioxidants, polyphenolic compounds exhibit important chain-breaking properties to quench reactive radical species which are generated during the oxidative processes of both commercial and biological products. Antioxidants as external supplements are used to maintain the concentration of free radicals as low as possible and to avoid oxidative stress. They are profoundly utilized in the food manufacturing to preserve the quality of the ready-to-eat foods and to improve the shelf life. Among the polyphenolic food products, cocoa is rich in catechins. The three major catechins available in cocoa are (+)-epicatechin, (-)-catechin and dimeric procyanidin. Computational studies of density functional theory (DFT) have been accomplished to explore the antioxidant potential of these catechin molecules. Reaction enthalpy values related to three key mechanisms of basic antioxidant pathways; [1] hydrogen atom transfer (HAT), [2] single-electron transfer - proton transfer (SET-PT), and [3] subsequent proton loss-electron transfer (SPLET) were computationally investigated using B3LYP/ 6-311++G (d, p) and M062X/ 6-311++G (d, p) level of theory. The aqueous phase studies were carried out under the IEFPCM solvation model. The hardness, softness, electronegativity and electrophilicity of antioxidants were computed using HOMO-LUMO energy calculations. According to these computational investigations, it was revealed that the HAT mechanism has demonstrated the lowest set of enthalpies compared to other two reaction mechanisms (SET-PT and SPLET). It was positively obvious that dimeric procyanidin possessed the lowest set of average enthalpies as showing the highest antioxidant potential with compared to the other two catechins. Based on average enthalpies, antioxidant potential of catechins found in cocoa can be placed in the following order of ascending: (-)-epicatechin < (+)-catechin < dimeric procyanidin. Energies of molecular orbitals ($E_{HOMO-LUMO}$) present in these three natural catechins exhibited that dimeric procyanidin molecule has possessed the highest radical scavenging capability as further verifying the "trend of antioxidant potential" observed under the thermodynamic parameters (BDEs, IPs, PDEs, PAs and ETEs) previously computed. It can be concluded that modification of the chemical structure of dimeric procyanidin provides insight into the design of structurally novel, potent antioxidants which will be more economical and beneficial in pharmaceutical industry.

Keywords: Antioxidant, Catechins, DFT study