

## Ferns: Repository of Antioxidant Moieties in Plant Groups

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### Abstract

In the geological time scale it is the Silurian to lower Devonian the origin of the vascular plant with its gradual plan with its gradual diversity as well as development started. Among those species, Pteridophytes is the first cryptogam where the vascular bundle is experienced with lignifications, however, in a scanty manner. Therefore, lignin may be supposedly the initial residue for complex secondary metabolites. Inquest for other secondary metabolites the fern species vis-à-vis other Pteridophytes are a rich source on antioxidation. The chemical diversity of secondary metabolites more focused to antioxidation potential is based on availability of polyphenolics its variants, insertion or substitutions of different functional groups ionization potential, ligand formation, bulk and adducts conjugate formation and other intramolecular mutation. However, the actual behavior for measurement of antioxidation is diverse according to standard methods and its modification concern. This article may be literature support for diversity and abundance of secondary metabolites with special reference to antioxidation capacity from fern and allied species.

**Keywords:** Antioxidation; Reactive Oxygen Species; Polyphenolics; Fern

### Introduction

Antioxidation is a set of biochemical reactions that essentially causes a transfer of electron ( $e^-$ ) to the most oxidized species of biomolecules. These reactions are essentially important when there is an increasing disorder of reactive oxygen species (ROS) with its biosynthesis than lysis [1]. Therefore, from the point of oxidative damages of plant tissues antioxidation is most important. This is also fused when a plant tissue faces oxidative stress for their induction for different antioxidants as well as antioxidative pathways. This is mostly due to the negative effect of ROS with free radicals on plant itself and other living organisms.

The in-depth studies to screen analysis of effective compounds are needed later; the antioxidants are the severe of other organisms from their oxidative degenerations exercise throughout the scientific domain. The natural antioxidants mostly from natural products have fewer side effects on consumers. From the plants it is almost the secondary metabolites, however, especially phenol derivatives are played most principle constituents for antioxidants. Antioxidants may be unique with its abundance in chemical diversities, chemical structures, conjugation with other residues, the frequent formation of hydrogen bonds, metal ion chelation properties; affinity to different solvents, nucleophilic reactions to reduced the oxygen species, high redox potentialities, involvement in a web of enzymatic cascades, etc.

It is not only the ROS but also the reactive nitrogen species (RNS) which are also targeted by these antioxidants to have balance between generation or accumulation and its lysis through biological system. So, this has been an interesting module in deciphering the free radical action, its hydrolysis by antioxidants and collectively the quenching properties of any plant species regardless of taxonomic hierarchy. In a dual manner antioxidants may serve the protective role in inhibition of ROS synthesis within the tissues as well as scavenging of those after excess accumulation and also sequestering through chelate complexion with ligands binding metals, photosensitizing

quenching mechanisms. Overall total antioxidants categorically may be useful in distinct domain of natural and synthetic compounds. In comparison to natural synthetics have a deviatory structure with distinct side effects and another alternative of chemical properties [2]. From the plant natural source it is the polyphenolic residues altered with one or few hydroxyl (OH<sup>-</sup>) groups in the nucleus of the compound. Typically, this structure denotes the phenolics with their major classes' phenolic acids and flavonoid conjugate exclusively cumaric acid (hydroxybenzoic acid and hydroxylated cinnamic acid for example).

### **Pteridophytes: A non flowering groups with more complex secondary metabolites**

The pteridophytic species with its origin and evolution in geological time scale within a transition period of lower Devonian. A significant turnover of lower temperature to gradually increasing higher temperatures, anoxygenic to oxygenic environment might constitute a situation more prone of oxidative nature. The tolerance and sustenance of those species on that environment ought to be successful in antioxidation strategy. Another criterion which would be vulnerable for plant growth and development was the photorespiration.

A gradual increase in oxygen (O<sub>2</sub>) along with elevated temperature and irradiation most of the plants became susceptible to photorespiration oxidation excluding the C<sub>4</sub> species [3]. Pteridophytes vis-à-vis the fern, still represented with few or non-significant C<sub>4</sub> species are able to withstand the photooxidative exposure. Therefore, the antioxidation mechanism inherent in nature has been obviously in exercise within fern species to support tolerance to oxidative stress. The more insensitivity of pathogenic invasion of pteridophytes might be a clue for its possible cellular system with more antioxidative substances particularly, those are secondary metabolites in nature. Apart from antioxidants secondary form, deposit of array of bioactive substances is mostly anti-microbial in nature. The most culture antioxidant properties as reported from few fern species are *Pteridium*, *Dryopteris*, *Lycopodium*, *Osmunda*, *Adiantum*, *Polypodium*, *Anthyrium*, *Pteris* etc [4]. Typically, the family represented by Osmundaceae, Dryopteridaceae are exhibited with versatile antioxidant residues along with common vitamin-C. This is the reason the health care business with regards to ageing and chronic disorder the activity of fern products are more preferred. It would be imperative to justify these properties of fern with regards to the chemical constituents structure and nature of the biometabolites, there possible mode of action and probable regulation of their biosynthesis would be imperative to justify. This mini review would be an approach for discussion for antioxidation activities of biomolecules with attention of factors regulation on these activities.

It is predominantly the quenching of ROS by the polyphenolic compounds of their antioxidation mechanisms. The key is the neutralization of ROS from its antioxidation activity to transfer electrons from antioxidants or in the form of (H<sup>+</sup> + e<sup>-</sup>) to the ROS [5]. Phenolics and polyphenolics exercise four major reactions to achieve their potential of antioxidation. Of those, predominating is the proton bound e<sup>-</sup> transfer. This reaction is facilitated by a direct transfer of hydrogen to the ROS or free radical. The reaction is a reduced radical species along with oxidized e<sup>-</sup> donor residues [6]. In most of the cases the unsaturated nucleus of benzoic acid and derivatives are the most important for these reactions. Mostly cinnamic acid and flavonoids include exercising to these reactions. In another reaction that is coupled with e<sup>-</sup> and proton transfer is based on migration of e<sup>-</sup> from phenolic residues to the free radical to scavenge. In these reactions the antioxidants behave as cation radical where there is a conversion of deprotonated species and H<sup>+</sup> is transferred to free radical (R<sup>•</sup>) [7]. Antioxidation capacity for polyphenolics is expected to exercise with their thermodynamic properties as well as the phenolic radical synthesise in reaction medium. Concentration of anion and radical cations are also bothered to follow up on the reaction. Therefore, these parameters are well met with the cellular constituents and bio residues in plant extracts [8].

For the non-flowering or cryptogam species the plant extract shown with more ionization properties in a particular solvent and its own molecular property. The property of salvation of the plant extract and consequently its stabilization with anion are more important [9]. Basics in chemical constituents for the antioxidants are found in ferns. Out of those of phenolics it is the attached OH<sup>-</sup> groups that offer the reactivity, as for example hydroxylation in cinnamic acid as termed caffeic acid is exhibited more potent than cinnamic acid. p-Coumaric acid having one OH<sup>-</sup> group in the aromatic nucleus is intermediately in activity [10]. Moreover, the position of the OH<sup>-</sup> group in *o*, *m* and *p* is another criterion for activity escalation. It is the phenolics and derivatives which have the capacity to snatch e<sup>-</sup> by the carboxylic

acid (COOH<sup>-</sup>) in benzene nucleus that offers strong antioxidant deficiency. It has also antagonistic effects against hydrogen donating properties of hydroxylated benzoic acid [11]. It is also reported that the COOH<sup>-</sup> group is less potential in e<sup>-</sup> acceptance when any OH<sup>-</sup> group is not adjacent to it. This is the basis that 3, 5-hydroxy benzoic acid is more antioxidizing when OH<sup>-</sup> is attached at 2, 5 in nucleus. Any introduction of methionine residues either at phenolics ring or COOH<sup>-</sup> also diminishes the e<sup>-</sup> withdrawing capacity by COOH<sup>-</sup> group [12]. The unsaturation on extended side chain as -COOH-CH-COOH- found in cinnamic acid than in benzoic acid is high where only COOH<sup>-</sup> groups extend the e<sup>-</sup> withdraw capacity. This is also traced from caffeic acid than protocatechuic acid and ferulic acid. It is the presence of double bond to delocalize the e<sup>-</sup> that causes a transient radical formation by the phenolics residues during ROS scavenging [13].

On the other hand in many fern species the presence of alkyl ester is a feature, however, that may not contribute any enhancement of antioxidizing property. This is read in case of tri-hydroxy benzoic acid that is esterified with quinic acid that may reduce the antioxidizing property. For example, chlorogenic acid is not any significant property in ROS neutralization as compared to caffeic acid. The unsaturated nucleus as presented in different ring in flavonoids sometimes became a key factor for antioxidation activity. Thus, as in catechol the ring-B interfaces the phenols with methoxy (-OCH<sub>3</sub>) group. Still, monophenolic B-ring shows the variation in properties. So, the ring-B could be more efficient from its unsaturation donate e<sup>-</sup> to catechol. Any substitution in ring-B maybe with OH<sup>-</sup> also influences the activity. This is more cited in myricetin which exceeds improved antioxidation over sequestering. Again, the number of OH<sup>-</sup> group, if it is single in B-nucleus also affects the same. Still, increase in OH<sup>-</sup> group in ring-B of flavonoids is not necessarily marked any significant activity [14]. The properties of antioxidants with their information are of dimer. It has well been accepted for that nucleus that unsaturated aromatic ring and projected OH<sup>-</sup> groups at various positions are the key for antioxidation activity [15]. This has well been established in use of conventional analysis with 3-ethylbenzothiazoline-6-sulfonic acid. The position of OH<sup>-</sup> group in *o*, *m*, and *p* positions was determined. The other established analytical methods the different polyphenolics are shown with different antioxidizing potentials according to their position of OH groups. As for e.g. Trolox equivalent antioxidant capacity (TEAC) recorded a better antioxidant capacity for resorcinol than other phenol like catechol and hydroquinone. The formation of adduct through covalent bondings, phenolic compounds and ABTS<sup>+</sup> is a standard method for analysis of several plant polyphenolics [16].

The adducts have enough capacity to be distinguished typical ultraviolet (UV) spectrum within 260 - 360 nm that gives the characteristics of unknown phenolic compounds. The formation of dimer with ABTS<sup>+</sup> in the process of neutralization is done by monohydroxy phenol. Sometimes in ferulic acid, a common hydroxy phenol in pteridophytes when forms dimer with ABTS<sup>+</sup> cation is displayed with improved antioxidation than alone. This has been displayed with a correlation with reduced DPPH [17]. An inverse relationship of potential with the donation of an e<sup>-</sup> to the free radical is an index also for better performance of polyphenolics. The secondary OH<sup>-</sup> groups are the major responsible for such a value and when it is lower may also indicate a good antioxidant. Here also a multiple OH<sup>-</sup> insertion to the aromatic nucleus may be conjugate the compounds with data of electrochemical reducing potential. Position of the OH<sup>-</sup> groups in *o* position and the oxidation of phenol is converted into quinone. The later may lower the electrochemical potential [18]. Substitution of -OCH<sub>3</sub> group replacing OH<sup>-</sup> can also changes the potential values with more positiveness as cited in ferulic and caffeic acid [19]. This has equally been stated for oxidation of other polyphenolics like flavonoids where methoxy substitution is more common.

### Influencing factor for regulation of antioxidation

From the earlier discussion this is quite obvious the substituting groups are the major determinations for antioxidizing capacities. However, some other factors like concentration and choice of metal, H<sup>+</sup> ion concentration, system temperature, solubility of antioxidants may influence the antioxidizing capacity [20]. As for example polyphenolics in ferns records a decreasing order or antioxidation with increasing metal concentration in DPPH and ABTS<sup>+</sup> assay. In acidic pH the DPPH and ABTS<sup>+</sup> are nonsignificant which may be due to disassociation of phenolics and its counter acts to the ion from ABTS<sup>+</sup> to be reduced.

For the β-carotene for its bleaching assay if a solution with lower pH values it may cause an increase in reductions of the phenolics compounds. This is understood as an inhibition of radical which is facilitate by inhibition of peroxy radicals which is intricated by increas-

ing  $H^+$  concentration. Peroxy radicals are the product when molecular oxygen atom forms double bonded fatty acid [21]. As opposed to  $H^+$  few alkali metal ions can also induce the formation of peroxy radical. This is the cause such a solution if added with  $\beta$ -carotene the antioxidation activity comes down. Surprisingly if water is used as solvent it can induced the antioxidizing activity of polyphenolics. Few polyphenolics like flavonoids which induced peroxy radicals are more promising in aqueous system in DPPH and ABTS<sup>+</sup> assay. In aqueous environment the dissolution of solvent cluster is responsible too for transfer of  $H^+$ ,  $e^-$  in a neutralization reaction.

### Plant polyphenol is with special activity with relation to antioxidation

It is cited in a plethora of literature about the scavenging of free radicals by polyphenolics, however, less is known for the accessories and ancillaries of their roles. In fact, polyphenolics may have their dual role in tissue either directly used or antioxidation or/and its pro-antioxidants activity by play. The pro-antioxidants with the use of common flavonoids like quercetin, caffeic acid, catechin, myricetin etc. are behaved as antioxidants [22]. This is more accurate when plants are exposed to abiotic stress or edaphic factor i.e. high concentration of ions, alkaline pH, an abundance of heavy or transition metals, polyphenolics would be behaving as pro-antioxidants.

With special reference to the formation of easily changeable radicals and access for redox formation with the transition cation the activity is enhanced. Hydroxyl radical can subtracts  $e^-$  from oxygen may form superoxide  $O_2^{\cdot-}$ ,  $\frac{1}{2} O_2$  and oxygen in triplet state. All these are quite able to form turnery complexes with nucleotides. Transition metal ion flavonoids are more complex moieties with semiquinone in nature. Cellular ionic concentration as well as pH would be more influencing for such an activity. Under acidic pH the reducing redox carrying metals exhibited with their maximum solubility are also characterized for confirm binding with the radicals and these together induce the pro-antioxidation reactions.

### Capacity of sequestering the free radical through metal ion chelation

Polyphenolics has another unique activity with not only neutralized ROS/free radical but can able to minimize the epoxidation. This process is more preferred in post-harvest technology with inhibits the deterioration of fruits and also the food products by a microorganism. In the ripening of the fruits particularly, through the post-harvest storage, the pulp tissues undergo auto-oxidation, therefore, changes insolubilization of complex polysaccharide into soluble sugar [23]. The later undergoes a readymade substrate for the bacterial decomposition of the fruits. The oxidation is a rapid process when the tissue relives a significant amount of redox ions. These can abstract hydrogen from the unsaturated moiety and thereby enhances free radical formation [24].

Redox ion is involved in a special types of reactions, the Fenton reaction which is chain wise conversion of hydrogen peroxide as well as  $OH^-$  the polyphenolics compounds when corresponds the slower of oxidation process that would be resulted from the formation of chelate with those metals as well as transfer of electrons to the metal ions. The chelation ability is also increased according to *o*, *m*, *p* position of the substitution of nucleus. This is the reason different phenolics like protocatechuic acids, gallic acids chlorogenic acid, caffeic acids show their corresponding ability of chelate formation according to the presence of  $OH^-$  groups in different positions of nucleus [25]. Within the cellular environment the better solubility of flavonoids is laid on chelation formation with iron (Fe) and copper (Cu) is determined [26]. Another parameter of antioxidation, the reducing power of copper is directly dependent of no substituent ( $OH^-$  groups) [27]. This is typified in some polyphenolics residues but non-flavonoids nature where, the  $Fe^{2+}$  is oxidized to  $Fe^{3+}$  instead of copper.

## Conclusion

From the above-said discussion, it is clear that the natural products for antioxidation purposes are diverged both in their types, origin and activities from fern vis-à-vis plant. A vast array of antioxidants, phenolics as well as polyphenolics are more important with their natural occurrence noncontaminants and improved at least equally enough as compared to synthetic chemical residues.

With special reference to aromatic antioxidants the chemical configuration particularly, insertion of  $OH^-$  groups in the aromatic nu-

cleus is the most important. Besides direct antioxidation the other chemical properties like chelation of redox metals, pro-antioxidants, formations of adducts were other points of interest. Moreover, it is the intramolecular coordination with sharing of hydrogen bonds between the OH groups of the phenolics and phenoxy radicals. Rest of other influencing factors, presence of other redox metal and their concentration, H<sup>+</sup> may bother the antioxidation reactions.

Therefore, either to screen any biometabolites against oxidative stress, these chemicals characteristic of antioxidants and their paraphernalia to induce the process would be the screening indices either to select biometabolites from fern species or even to desire a drug for the concern purposes.

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