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Letter to Editor: Antioxidant Action of Phenols under Heavy Metal Stress

Dinesh Kumar

Department of Chemistry, Aligarh Muslim University, Aligarh, Uttar Pradesh: 202002

The conception of antioxidant action of phenolic compounds is not novel. There have been many reports of induced accumulation of phenolic compounds and peroxidase activity in plants treated with high concentrations of metals.[1]

Antioxidant action of phenolic compounds is due to their high tendency to chelate metals. Phenolics possess hydroxyl and carboxyl groups, able to bind particularly iron and copper. The roots of many plants exposed to heavy metals exude high levels of phenolics. They may inactivate iron ions by chelating and additionally suppressing the superoxide-driven Fenton reaction, which is believed to be the most important source of ROS. Tannin-rich plants such as tea, which are tolerant to Mn excess, are protected by the direct chelatation of Mn. Direct chelation, or binding to polyphenols, was observed with methanol extracts of rhizome polyphenols from Nympheae for Cr, Pb and Hg. According to Morgan et al. this general chelating ability of phenolic compounds is probably related to the high nucleophilic character of the aromatic rings rather than to specific chelating groups within the molecule.

There is another mechanism underlying their antioxidant ability. Metal ions decompose lipid hydroperoxide (LOOH) by the hemolytic cleavage of the O-O bond and give lipid alkoxyl radicals, which initiate free radical chain oxidation. Phenolic antioxidants inhibit lipid peroxidation by trapping the lipid alkoxyl radical. This activity depends on the structure of the

molecules, and the number and position of the hydroxyl group in the molecules.[2]

Arora et al. show that phenolics (especially flavonoids) are able to alter peroxidation kinetics by modifying the lipid packing order. They stabilize membranes by decreasing membrane fluidity (in a concentration-dependent manner) and hinder the diffusion of free radicals and restrict peroxidative reaction.[3]

According to Verstraeten et al., in addition to known protein-binding capacity of flavanols and procyanidins, they can interact with membrane phospholipids through hydrogen bonding to the polar head groups of phospholipids. As a consequence, these compounds can be accumulated at the membranes' surface, both outside and inside the cells. Through this kind of interaction, as they suggest, selected flavonoids help maintain membranes' integrity by preventing the access of deleterious molecules to the hydrophobic region of the bilayer, including those that can affect membrane rheology and those that induce oxidative damage to the membrane components.

On the other hand, in vitro studies have shown that Flavonoids can directly scavenge molecular species of active oxygen: ·O2 - - superoxide, H2O2 -hydrogen peroxide, .OH -hydroxyl radical, 1O2 -singlet oxygen or peroxyl radical. Their antioxidant action resides mainly in their ability to donate electrons or hydrogen atoms. Polyphenols posess ideal structural chemistry for this activity and have been shown to be more effective in vitro than vitamins E and C on molar basis.[1]

As described by Bors et al. there are three structural features that are important determinants for the antioxidant potential of flavonoids:

a) the orto 3',4'-dihydroxy structure in the B ring (e.g. in catechin, quercetin);

b) the 2,3-double bond in conjunction with the 4-oxo group in the C ring (which allows conjunction between the A and B ring, or electron delocalization;

c) the presence of a 3- OH group in C ring and a 5-OH group in the A ring.

Among them the 3-OH group is the most significant determinant of electron-donating activity. The glycosilated flavonoids lose

their activity in comparison with aglycones. The hydrogen peroxide-dependent oxidation of flavonols has been observed in situ in epidermal strips of leaves of Vicia faba, Tradescantia virginiana and in mesophyll cells of V. faba.

Plants contain two major types of peroxidases, which can be divided into two groups: peroxidases (AP X) which use ASC as the preferential electron donor and others, which use phenolics. AP X is mainly localized in chloroplasts, cytosol and peroxisomes and its function is to scavenge the H2O2 which is formed in these organelles. In these compartments, ascorbate is oxidized to the MDA (monodehydroascorbate) radical by AP X to detoxify H2O2. MDA is a radical with a short lifetime that, if not rapidly reduced disproportionates to ascorbate and DHA (dehydroascorbic acid) which is reduced to ascorbate by (GSH)-dependent glutathione reductase (DHAR). MDA radical can be reduced to ascorbate by non-enzymatic reaction of ferrodoxin (Fd) or by NAD(P)-dependent enzymatic reaction of MDAR (monodehydroascorbate reductase). Some works indicate that high concentrations of heavy metals can inhibit action of AP X.[5]

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