10.Week: ANTIOXIDANTS

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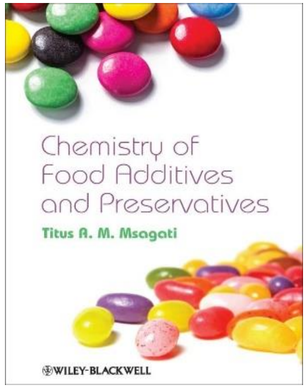
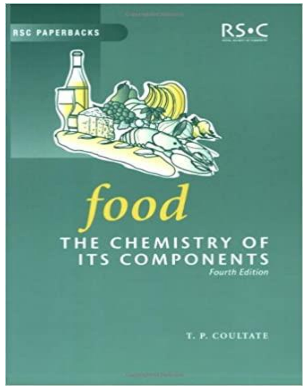
1. 

2. 

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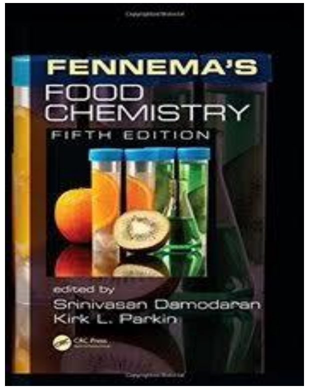
4. 

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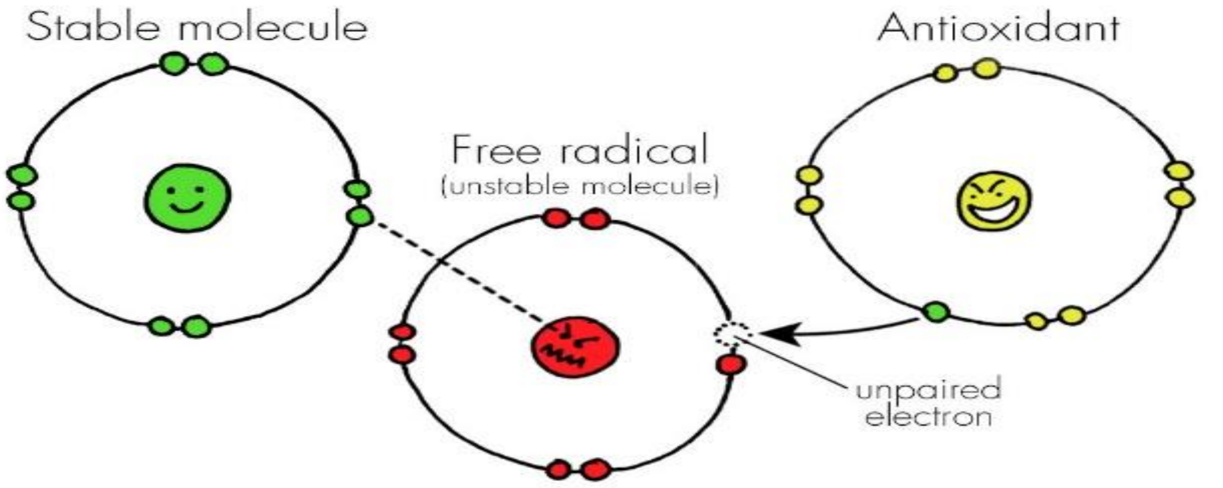
ANTIOXIDANTS

Oxidation is a real problem for food products. Oxidation reactions happen when chemicals in the food are exposed to oxygen in the air. Oxidation of food is a destructive process, causing loss of nutritional value and changes in chemical composition. Oxidation of fats and oils leads to rancidity and, in fruits such as apples, it can result in the formation of compounds which discolour the fruit. Oxidation can damage cancer-causing DNA and convert polyunsaturated fatty acids into forms that contribute to heart attacks and strokes. **Antioxidants are added to food to slow the rate of oxidation and, if used properly, they can extend the shelf life of the food in which they have been used.**

CHEMISTRY OF FREE RADICALS AND ANTIOXIDANTS

From the viewpoint of chemistry, free radicals refer to any molecule with an odd unpaired electron in its outer electronic shell, a configuration responsible for the highly reactive nature of such species.



Source: https://www.haleo.co.uk/the-body/antioxidants/

The presence of such highly reactive free radicals in biological systems is directly linked to the oxidative damage that results in severe physiological problems. The free radical species that are of concern in living systems include the reactive oxygen species (ROS), superoxide radicals (SOR), hydroxyl radicals and the reactive nitrogen species (RNS).

The oxygen-containing reactive species are the most commonly occurring free radicals in living medium and are therefore of greatest concern. The oxidative damage caused by these free radicals can be prevented by using antioxidants which include **enzymatic antioxidant systems** such as ***catalase***, ***glutathione peroxidase*** and ***superoxide dismutase*** (SOD) as well as non-enzymatic antioxidants. In nature, the generation of free radicals which cause oxidative stress and that of antioxidants or radical scavengers is carefully controlled such that there is always a balance between the two.

Examples of **non-enzymatic antioxidants** include ***vitamin C*** (ascorbic acid) which is a sugar acid, ***vitamin E*** (α-tocopherol) and ***β-carotene***, ***bilirubin***, ***propyl gallate*** (PG, a condensation ester product of gallic acid and propanol), ***uric acid***, ***tertiary butylhydroquinone*** (t-BHQ), ***butylated hydroxyanisole*** (BHA), ***ubiquinone*** and ***macromolecules which include ceruloplasmin, albumin and ferritin***. Generally, mixtures of different antioxidants provide better protection against attack by free radicals rather than individual antioxidants.

The formation of ROS (Reactive Oxygen Species) in living systems

Under normal conditions, oxygen is vital in metabolic reactions which are necessary for life. Due to its high reactive nature however, oxygen also causes severe damage to living systems due to the generation of reactive oxygen species.

Examples of reactive species produced as a result of these metabolic reactions include:

* superoxide anion (O_2^-)
* hydrogen peroxide (H_2O_2)
* hypochlorous acid
* hydroxyl radical (·OH)

The hydroxyl radicals are known to be unstable; they react spontaneously with other biological molecules in a living medium, causing destructive reactions in foodstuffs and serious physiological damage to consumers.

Negative effects of oxidants in food processes and to food consumers

The oxidation process brings about destructive reactions in food items that lead to off-flavour and loss of colour and texture due to the degradation of carbohydrate, protein, vitamins, sterols and lipid peroxidation.

The consequences to consumers include damage to nucleic acids, cellular membrane lipids and other cellular organelles, carcinogenesis, mental illnesses and disorders, lung diseases, diabetes, atherosclerosis, autoimmune diseases, aging and heart diseases.

Antioxidants as food additives are used to delay the onset of or slow the pace at which lipid oxidation reactions in food processing proceed. Most of the **synthetic antioxidants** contain a phenolic functionality with various ring substitutions (monohydroxy or polyhydroxy phenolic compounds) such as ***butylated hydroxytoluene*** (BHT), ***butylated hydroxyanisole*** (BHA), ***tertiary butylhydroquinone*** (t-BHQ), ***propylene glycol*** (PG), ***gossypol*** and ***tocopherol***. These compounds make powerful antioxidants to protect foodstuffs against oxidative deterioration of the food ingredients. The main chemical attribute that makes them suitable as antioxidants is their low activation energy property, which enables them to donate hydrogen easily and thus put on hold or lower the kinetics of lipid oxidation mechanisms in food systems.

For safety purposes and adherence to quality control standards, the use of any synthetic antioxidant preparation in food processes is expected to meet the following criteria:

* effective at low concentrations
* without any unpleasant odour, flavour or colour
* heat stable
* non-volatile
* must have excellent carrythrough characteristics

Natural antioxidants of plant origin

In addition to chemical or synthetic antioxidants, there are also a number of antioxidants that exist naturally in plants and many other herbal materials. A number of antioxidants that exist naturally in plants and many other herbal materials:

* β-carotene and xanthophyll
* flavonoid compounds
* ascorbic acid (vitamin C)
* Proanthocyanidin and bioflavonoids
* tannins, catechins and other polyphenol antioxidants
* vitamin E (tocopherols and tocotrienols)
* isoflavones
* phenolic acids and phenylpropanoid antioxidants

Phenolic non-flavonoid antioxidant compounds from natural sources

Polyphenolic non-flavonoid antioxidant compounds include resveratrol and gallic acid which are abundant in plants such as tea, grapes (red wine) and a variety of other fruits.

Phenolic flavonoid antioxidant compounds from natural sources

Antioxidants with flavonoid functionality are low-molecular weight polyphenolics which occur in a variety of vegetables and fruits. Apart from functioning as antioxidants, various flavonoids also have anti-inflammatory, anti-allergic, anticancer and anti-hemorrhagic properties. The antioxidant properties of flavonoids are responsible for the protective effect of wine and vegetable-rich diets against coronary heart disease. The majority of phenolic flavonoids extracted from natural sources (for example, gallic acid, trans-resveratrol, quercetin and rutin; have demonstrated potential beneficial effects on human health in many ways.

Acidic functional groups responsible for antioxidant activity

The antioxidant activity of certain food plants are due to various functional groups associated with some organic acids such as ***vanillic***, ***ferulic*** and ***p-coumaric acids***, found mainly in whole grains. Other acids found in barley grains such as ***salicylic***, ***p-hydroxybenzoic***, ***protocatechuic***, ***syringic*** and ***sinapic acids*** have functional groups that confer antioxidant activity. Generally, corn wheat and barley contain syringic acid, sinapic acid, protocatechuic acid, p-hydroxybenzoic acid, vanillic acid, ferulic acid, salicylic acid and p-coumaric acid as molecules containing antioxidant functional groups.

Action Mechanisms of Antioxidants

There are a number of possible mechanisms for antioxidant action and these include:

(1) ***quenching mechanism***, which occurs when the radical is in an excited triplet state which makes the antioxidant behave as a quenching agent

(2) ***direct hydrogen transfer mechanism*** which takes place if the radical is in a doublet state, enabling the direct transfer of the hydrogen atom to the radical

(3) ***charge transfer*** for doublet radical which yields a closed-shell anion and a radical antioxidant cation; and

(4) ***bond-breaking mechanisms***, as in the case for vitamin E.

FACTORS AFFECTING ANTIOXIDANT ACTIVITY

There are a number of physical factors that influence the activity of the antioxidant:

Temperature

Temperature catalyses the acceleration of the initiation reactions, which results in a decrease in the activity of the already-available or introduced antioxidants. Because of this, the variations in the temperature normally influence the manner in which some oxidants work; note that these variations are not the same for all antioxidants.

Activation energy and redox potential

Different antioxidants will have different activation energies as well as oxidation-reduction potentials. These properties mean that antioxidants have a varying ability to donate an electron easily.

Stability

Antioxidants have a varying degree of optimal performance with respect to pH. When the antioxidant is in a high-pH medium, it will undergo deprotonation. Its radical scavenging capacity will be enhanced since it will have the ability to donate an electron much easier.

HOW SAFE ARE FOOD ANTIOXIDANTS?

Due to the possible health hazards of some of the residues of antioxidants used in foods, there are a number of guidelines that have been set by international authorities such as the European Union with regard to the use of food supplements. It has been legislated that the total concentration of permitted antioxidants incorporated singly or in a mixture should be below 200 parts per million by weight when measured in fats. Adherence to the legislation is monitored and a number of methods including:

* electrochemical detection * spectrophotometric * fluorometric
*capillary electrophoresis *liquid chromatography
*gas chromatography *chromatographic methods hyphenated to mass spectrometric detection have been reported.