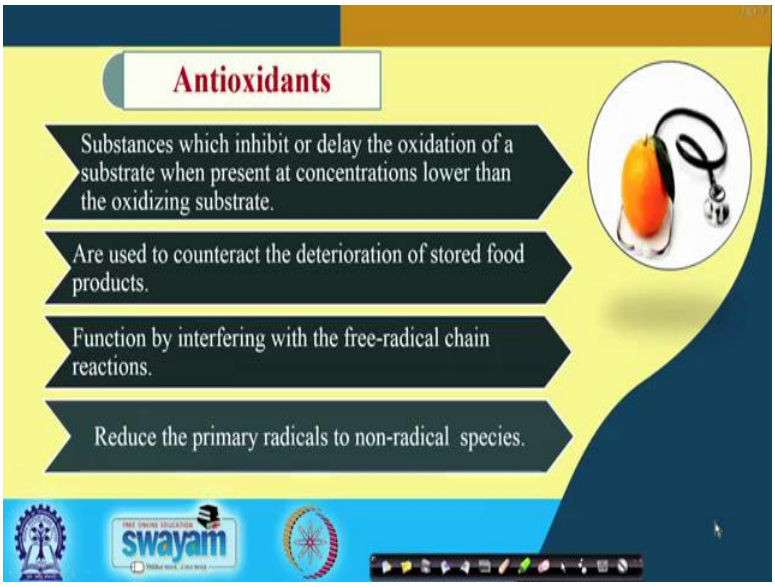
Novel Technologies for Food Processing and Shelf Life Extension

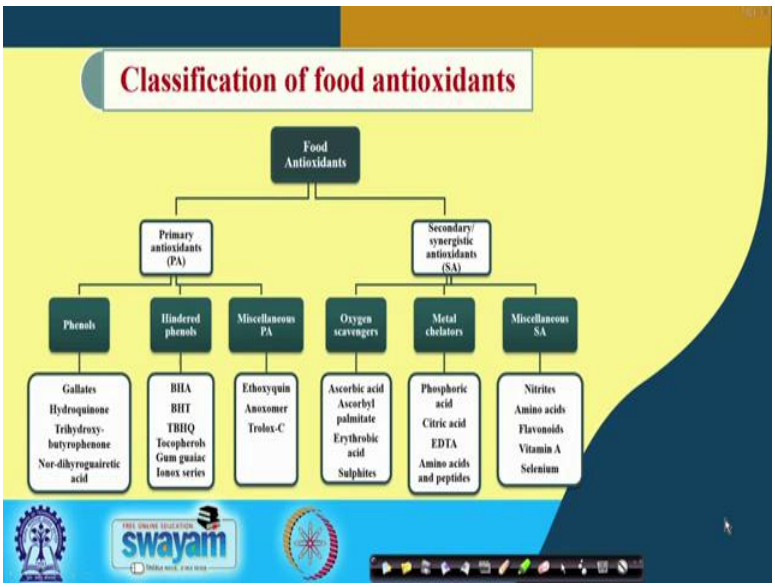
Prof. Hari Niwas Mishra
Department of Agricultural and Food Engineering
Indian Institute of Technology, Kharagpur

Lecture - 36
Natural Antioxidants

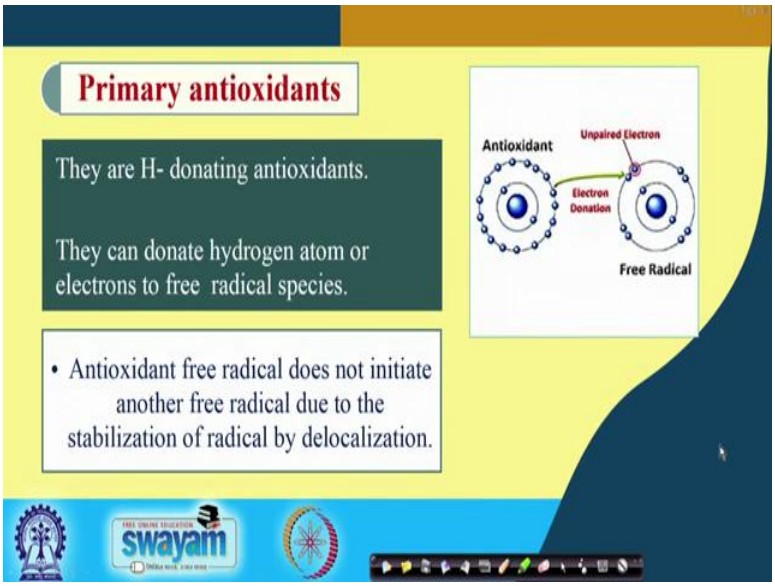
This lecture is about natural antioxidants.



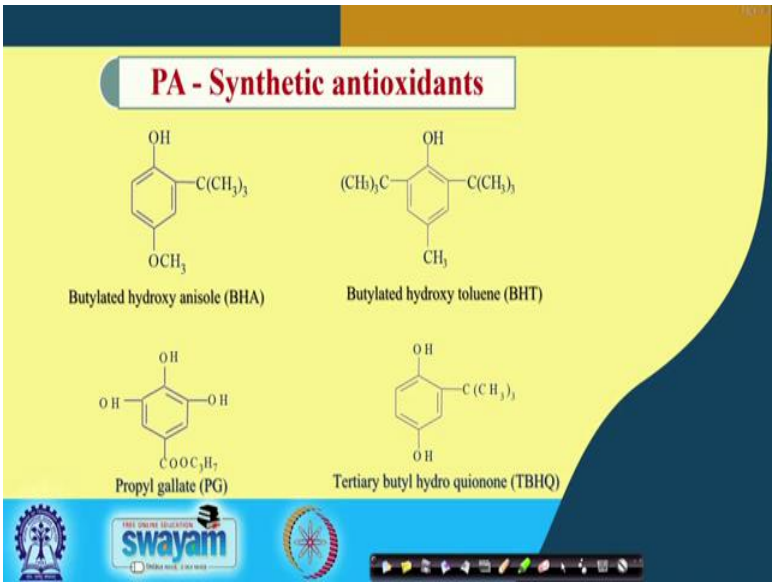
The antioxidants are substances which inhibit or delay the oxidation of a substrate when present at concentrations lower than the oxidising substrate. They are used to counteract the deterioration of stored food products; they function by interfering with the free radical chain reactions and reduce the primary radicals to non-radical species.



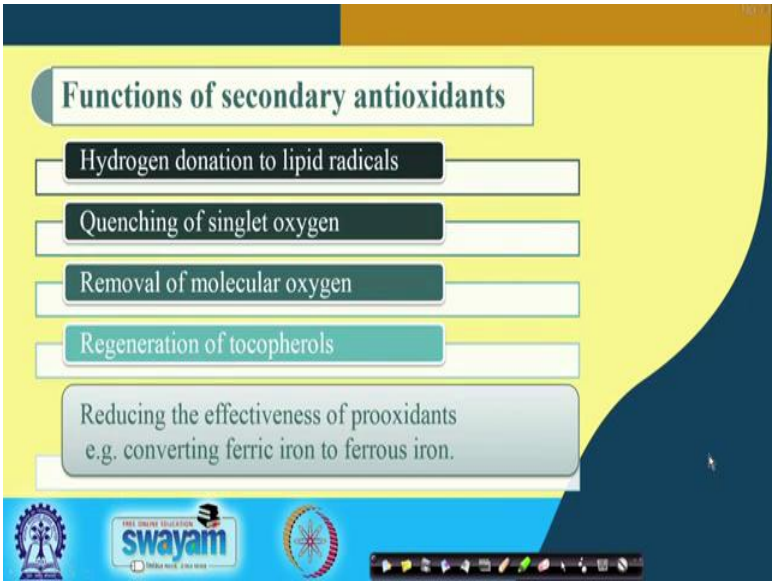
Food antioxidants are classified into two major types. They include primary antioxidants or secondary antioxidants. The primary antioxidants are generally phenols, hindered phenols or other miscellaneous compounds. The secondary or synergistic antioxidants include those which are oxygen scavengers, metal chelators and other miscellaneous compounds.



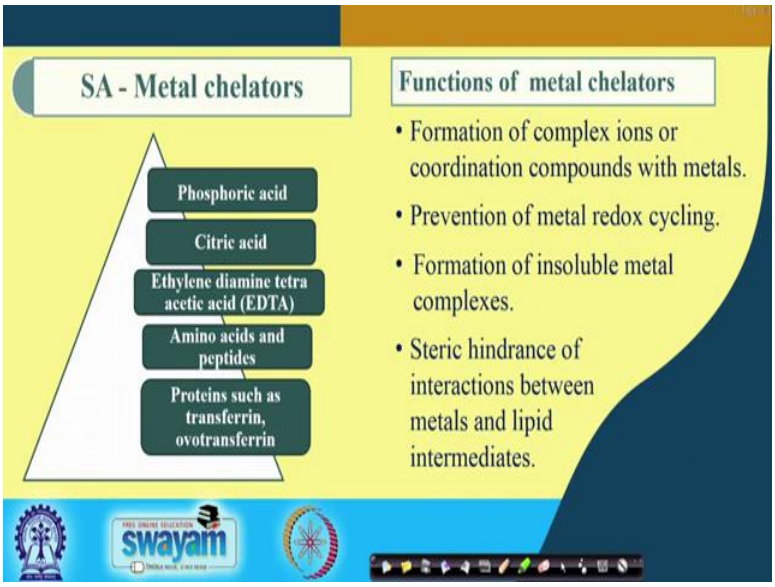
The primary antioxidants are normally hydrogen donating antioxidant as (see figure) they can donate hydrogen atom or electrons to free radical species. The antioxidant free radical does not initiate another free radical due to the stabilization of radical by delocalization.



The synthetic antioxidants which are most commonly used particularly in oils etc. to extend their shelf life or the one which is in the category of primary antioxidants include butylated hydroxy anisole, butylated hydroxy toluene, propyl gallate and tertiary butyl hydro quionone.

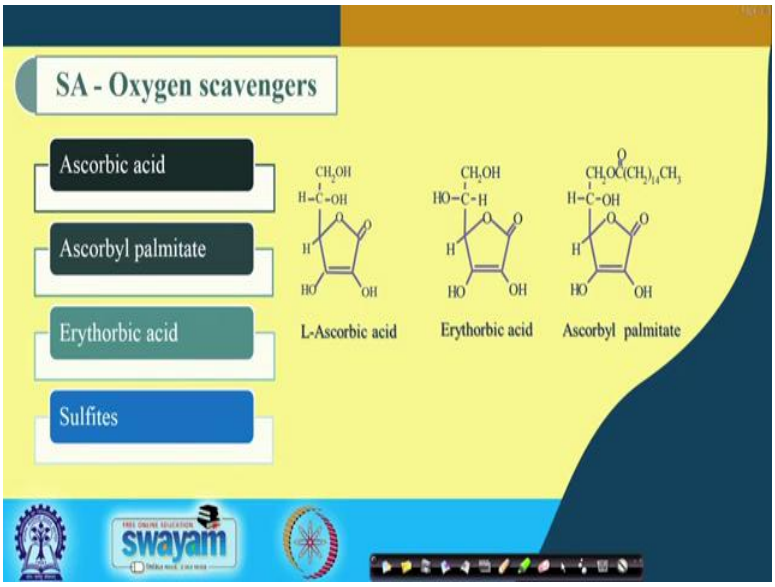


The secondary antioxidants function by hydrogen donation to lipid radicals, quenching of the singlet oxygen, removal of molecular oxygen, and regeneration of tocopherols. They function by reducing the effectiveness of pro oxidants, like for example converting ferric iron to ferrous iron forms. There are various metals and other agents which act as pro oxidants in food material.

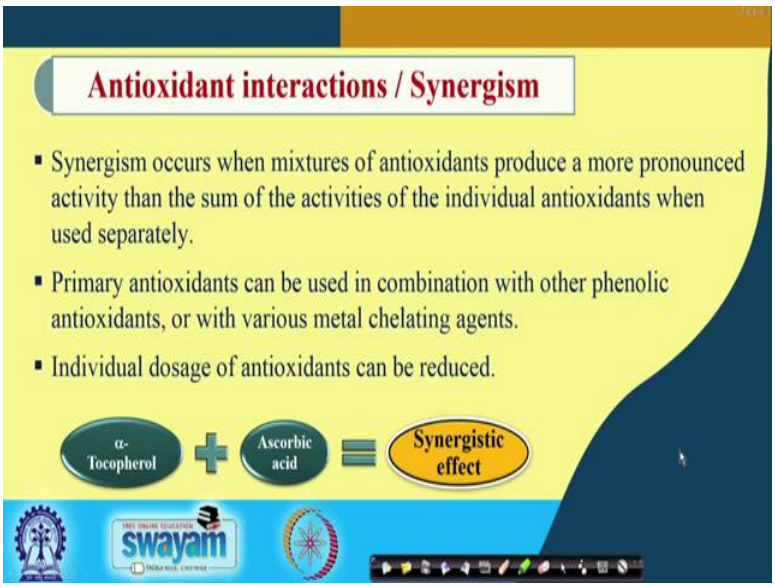


The metal chelators secondary antioxidants includes compounds like phosphoric acids, citric acid, ethylene diamine tetra acetic acid (EDTA), amino acids and peptides and proteins such as transferrin or ovotransferrin etc.

The metal chelators function by the formation of complex ions or coordination compounds with metal, prevention of metal redox cycling, formation of insoluble metal complexes. They also function by steric hindrance of interactions between the metals and lipid intermediates.



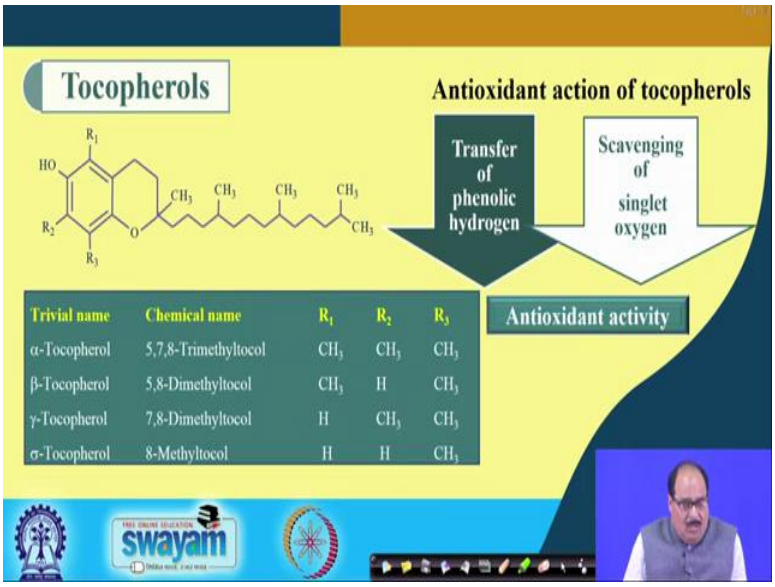
The oxygen scavengers secondary antioxidants include compounds like ascorbic acid, ascorbyl palmitate, erythorbic acid, sulphites, etc.



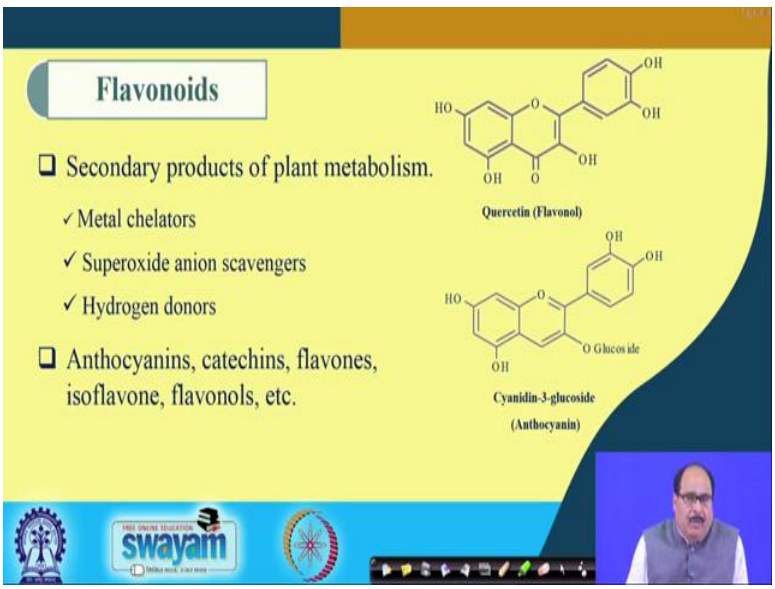
The antioxidants have synergistic properties. The interactions of different antioxidants improves the effectiveness of each other. Synergism occurs when mixtures of antioxidants produce a more pronounced activity than the sum of activities of the individual antioxidants when used separately. In fact, this synergistic behaviour helps in reducing the doses of individual antioxidants. So, it is a common practice to use mixture of antioxidants rather than one single antioxidant. These mixtures may be a mixture of primary antioxidants plus secondary antioxidants like for example α-tocopherol can be mixed with ascorbic acid.

Even the primary antioxidants like BHA and BHT we need to have 0.02% of antioxidant. For example, it is advisable to have 0.01 plus 0.01 % of two antioxidants rather than having 0.02 % concentration of one single antioxidant. So, the addition of antioxidants together provides a better effect as far as the shelf life extension and other properties are concerned.

Most of the synthetic antioxidants have one or the other problems sometimes the health concerns and other concerns like their effect on food constituents etc. So, nowadays there is a trend towards the use of natural antioxidant in place of synthetic antioxidants and majority of the natural antioxidants are generally plant extracts like tocopherols which are present in oilseeds, also known as Vitamin E. Ascorbic acid (Vitamin C) present in fruits and vegetables, β-carotene extracts of herbs and spices such as rosemary, sage, thyme, oregano, etc. are the examples of natural antioxidants. The polyphenols present in the plant extracts are the potential source of antioxidants.

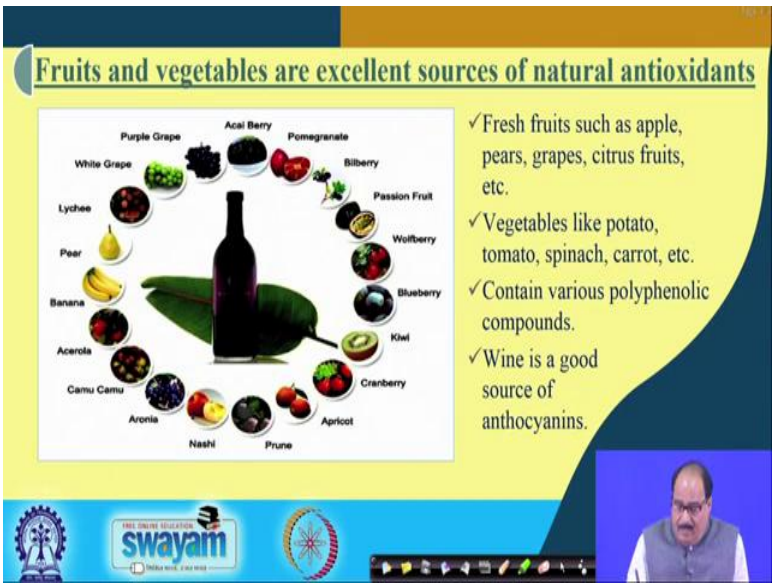


Structure of tocopherol can be seen in this figure; in the phenolic rings, there are groups R_1, R_2 and R_3. Depending upon the nature of these R_1, R_2 and R_3, which are normally methyl group and formyl group, the tocopherols are of four types. For example, when all the three 5, 7 and 8 are methyl groups, it becomes 5, 7, 8- Trimethyltocol; it is α-tocopherol. When at position 5 and 8, there are methyl group and at position 7 there is a formyl group, the resultant tocopherol becomes β-tocopherol and similarly gamma and delta tocopherols are there and all these tocopherols have good antioxidant potentials. They function by the transfer of phenolic hydrogen or by scavenging of singlet oxygen.



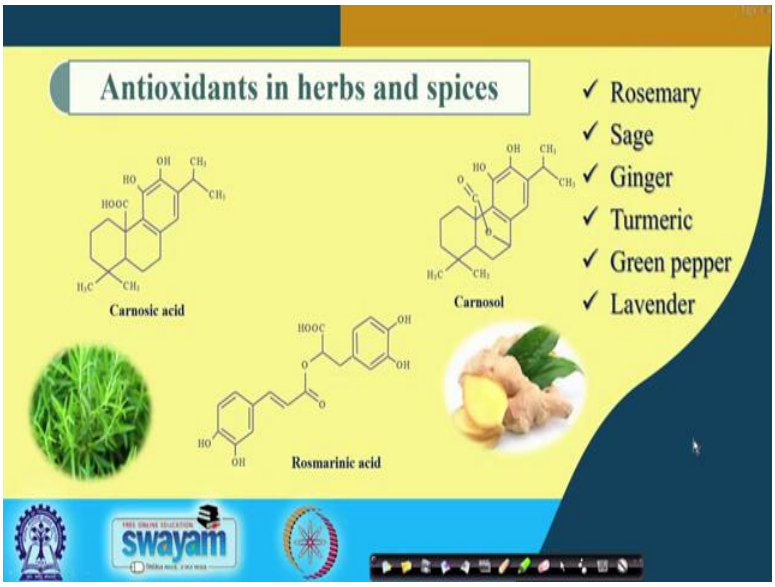
Flavonoids are the group of secondary antioxidant which are generally secondary products of plant metabolism; they are metal chelators, superoxide anion scavengers and

hydrogen donors, anthocyanins, catechins, flavones, isoflavones, flavonols etc. belong to this group of antioxidants.

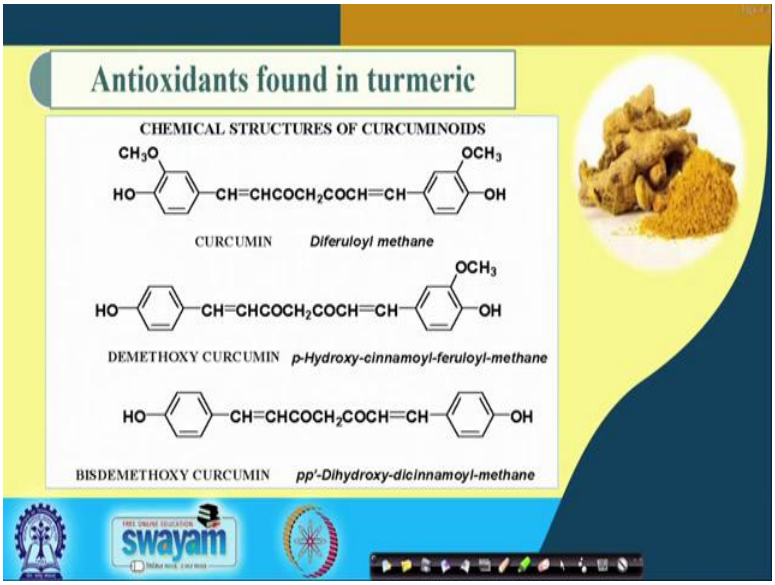


Fruits and vegetables are excellent sources of natural antioxidants. Fresh fruits like apple, pears, grapes, citrus fruits etc., vegetables like potato, tomato, spinach, carrot all these contain lot of antioxidants. The common antioxidant compound in these fruits and vegetables are phenolic compounds. Wine is a good source of anthocyanins which are good antioxidant potentials.

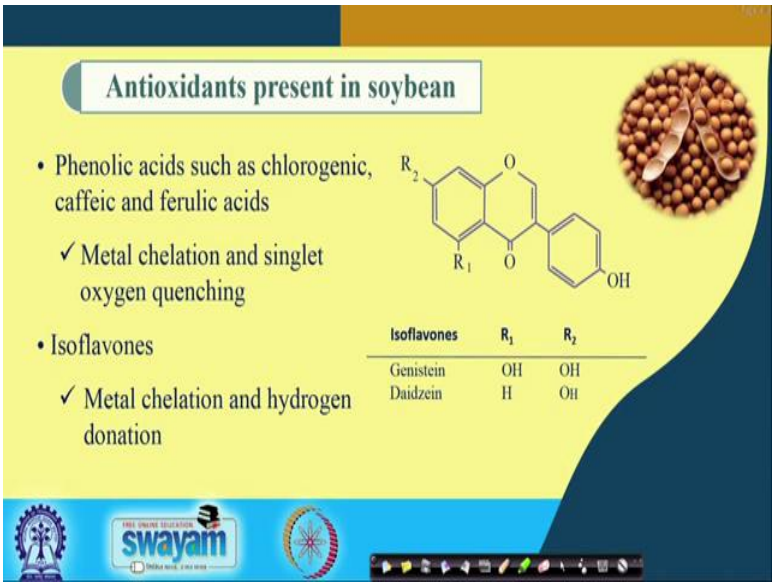
In the tea, green tea and coffee beans, the polyphenolic compounds like epicatechins, epigallocatechin, chlorogenic acids, etc. are the major antioxidant compounds.



In herbs and spices like rosemary, sage, ginger, turmeric, green pepper, lavender etc. they contain lot of polyphenolic and other compounds which have antioxidant properties. Other spices are used for their antioxidant properties from the time immemorial in different preparations. Some of the compounds with significant antioxidant potentials in these materials include carnosic acid, carnosol, rosmarinic acids and so on.



The antioxidants found in turmeric include curcumin, demethoxy curcumin, bisdemethoxy curcumin and so on.

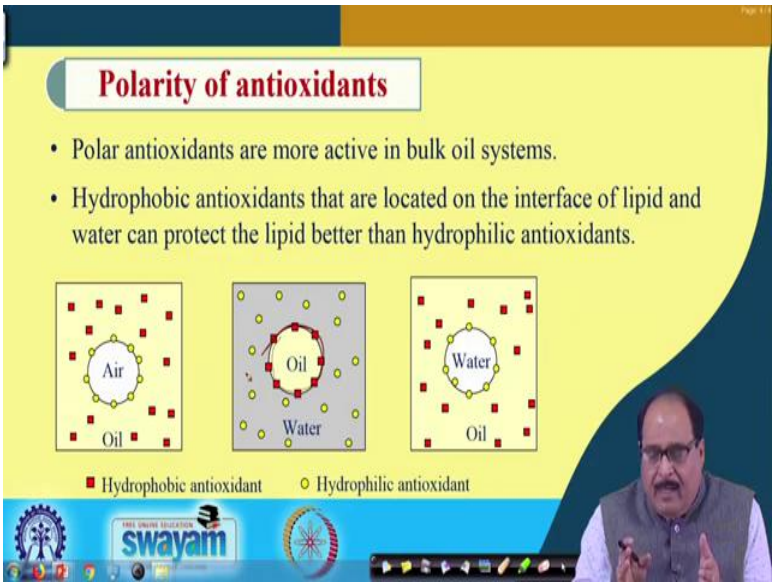


The soyabeans also contain good amount of natural antioxidants, phenolic acids like chlorogenic acid, caffeic acid and ferulic acids. They are metal chelation and single oxygen quenching. Isoflavones in soyabeans work by metal chelation as well as hydrogen donation.

The natural antioxidants are very good for use in the food materials. They are being now encouraged. However there are certain advantages and disadvantages both for the use of these natural antioxidants. The advantages include that they are readily accepted by the consumers, they are considered to be safe and in fact, no safety tests are required by regulatory agencies. The component being used as a natural antioxidant is a food or extract of the material which is being generally listed in the category of GRAS i.e.

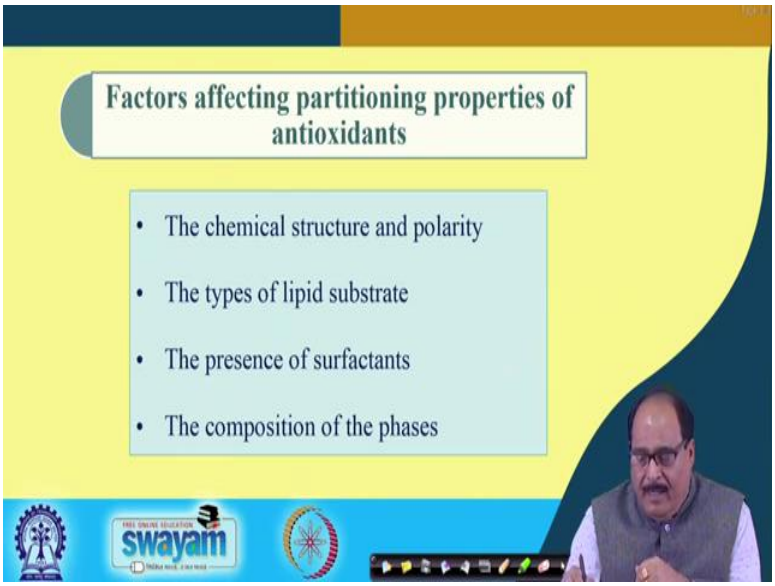
generally recognised as safe. However there are certain disadvantages. They are usually more expensive if purified, and less efficient if not purified. For example, suppose any citrus juice as a source of antioxidant is to be used, its antioxidant potential may be little less, but if the ascorbic acid is extracted from the juice using standard procedures and protocols, then its antioxidant potential can be increased. But the extraction methodologies will add to the cost of them. Its activity may vary depending upon the differences in the concentration of the materials used. The safety of the product often becomes a concern.

Other disadvantages may include that at the concentration in which the unpurified form of extract might be required to give the desired antioxidant effect, it may impart undesirable colour, aftertaste or off flavour in the product. So, that becomes another major limitation of the use of unpurified form of natural antioxidant or the plant extract directly in the food material as a source of antioxidant.

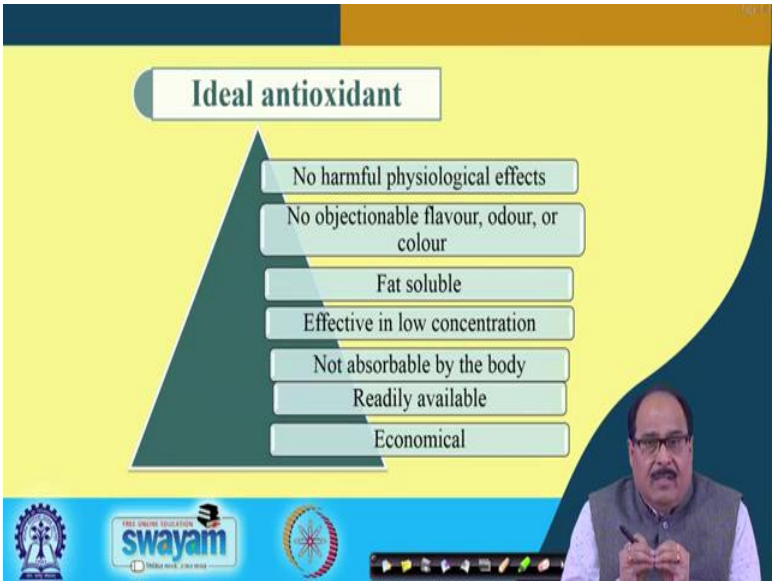


Another important factor for consideration in the antioxidant is its polarity. In fact, the polar antioxidants are more active in bulk oil system than those of the non polar antioxidants. If the hydrophobic antioxidants are located on the interface of the oil and water (see the middle picture), then they are more effective, they can protect the lipid better than the hydrophilic antioxidants. Here in the first picture, the air is inside and oil and the hydrophilic antioxidant are present in the interface of the air and oil.

In the 3rd picture hydrophilic antioxidant is present in interfere of the water and oil. So, the one in the middle is more effective as the hydrophobic antioxidant is present at the interface of the oil and water.



The partitioning properties or antioxidant potential of these compounds depends on the various factors and those include the chemical structure of the compound and its polarity, the types of the lipid substrate, the presence of surfactants and the composition of the phases i.e. water, air, oil and other phases.



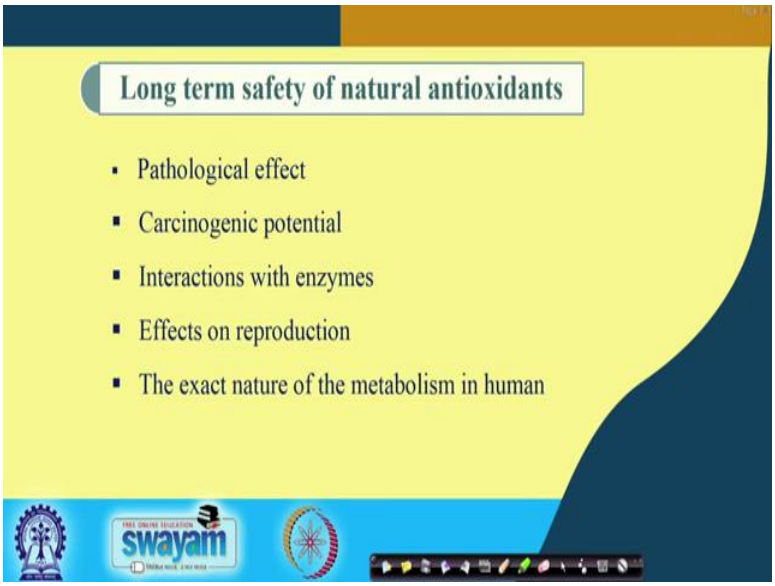
An ideal antioxidant should have no harmful physiological effect. It should have no objectionable flavour, colour or odour. It should be fat soluble, so that it can easily dissolve or mix with those oils to provide better antioxidant properties. And more

importantly the antioxidant should be effective in low concentrations. They should not be absorbed by the body, they should be readily available and economical to use.

As far as the natural antioxidants are concerned, it is better if they are used in the form of their juice or their extracts, however it should be properly optimised, standardised, so that at the level of concentration required to give the desired antioxidant effect it should not impart any undesirable property to the material or affect the sensory attributes and other functional characteristics of the component.

These natural antioxidants have a lot of potential. They can be used for shelf life extensions of food materials. In our laboratory, extraction of antioxidants from rosemary and turmeric have been done. The rosemary extracts were used in different concentrations for studying their effect on the shelf life extension of sunflower oil. The experiments were done to check the oxidative stability of the sunflower oil or similar oil which has more PUFA content whether improved by addition of rosemary extracts or such other natural antioxidants. The study indicated that addition of these extracts improve the oxidative stability of sunflower oil. It resulted in the shelf life extension, and it improved frying properties of the oil. The products which were fried in such oil for example, potato chips fried in the oils, sesame oil or sunflower oil containing rosemary extracts, they exhibited better stability during the storage. Similarly, the natural colours and antioxidant extracted from turmeric like curcumin and base curcumis, they were added into the oil. It was observed from experiments that the curcumin not only extended the shelf life of the oil, but it also added to the colour of the oil.

The products fried in such oils were found to be attractive golden brown in colour and were liked by the sensory finalists. So, these natural antioxidants extended the shelf life of oil, and improved the oxidative stability of the products fried in this oil.



Before these natural antioxidants are used by the industry, there are certain issues which need to be studied and checked whether the regular use or long term use of natural antioxidant is having any pathological effect on the consumers. The carcinogenic potential, the interactions with the enzymes etc., these natural antioxidants might have with the food enzyme or with the body enzymes etc., the type of effects likely to have on reproduction process are also the factors. Even the exact nature of the mechanism in which these natural antioxidants get metabolized in the food as well as in the human system. It has been seen that its long term use will depend upon more and more information on these issues but ultimately it can be said that these natural antioxidants have a very great potential for being used in the food products, particularly those products which are likely to be spoiled by oxidation processes or auto oxidation processes.

These food grade natural antioxidants can be effectively used to improve their oxidative stability and their shelf life without having any adverse effects on the sensory and other characteristics.